Syntheses and spectroscopic studies of new cobalt(I) complexes

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"The first principle is that you
must not fool yourself –
and you are the easiest
person to fool"

Richard Feynman
1965 Nobel Prizewinner
Physics

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SYNOPSIS

The new Co(I) complexes $[Me_3SnCo(CO)_3L]$ (L = PPh_3, $P(OPh)_3$, $AsPh_3$) are prepared by reductively cleaving the dimers $[Co(CO)_3L]_2$ on a sodium amalgam, followed by the addition of $Me_3SnC\ell$. A synthetic procedure is developed to prepare and purify these compounds on a large scale. A previous report that $[Co(CO)_3AsPh_3]_2$ cannot be reductively cleaved without decomposition is proved wrong. The new products prove sufficiently stable to enable them to be studied by ir, nmr (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{119}Sn\{^1H\}$) and mass spectroscopy.

The compounds $[Me_3SnCo(CO)_3L]$ (L = PPh_3, $P(OPh)_3$, $AsPh_3$) are shown to be non–susceptible towards nucleophilic substitution. Attempted displacement of a carbonyl ligand by an isocyanide ligand (using an excess of the latter) after treatment with the labilising agent Me_3NO, leads to a variety of products of which only the major one can be identified as *trans*–$[Co(CNR)_3L_2][PF_6]$ (R = t–Bu, Ph, 2,6–dimethylphenyl; L = PPh_3, $P(OPh)_3$, $AsPh_3$). Except for the case where R = t–Bu, L = PPh_3, the products are extremely unstable oils and cannot be characterised properly.

The new Co(I) bis(phosphine) complexes are prepared by reacting dppm (bis(diphenylphosphino)methane) and dppe (bis(diphenylphosphino)ethane) with $[(\pi\text{–}RC_3H_4)Co(CO)_3]$ (R = H, Me). The reaction with dppm leads to the isolation of $[(\pi\text{–}RC_3H_4)Co(CO)_2(\eta^1\text{–}dppm)]$ (R = H, Me) which are the first examples of Co(I) complexes with a monodentate dppm ligand. These extremely air–sensitive compounds are moderately stable and do not decompose below –20°C in the solid state. The reaction with dppe results in the formation of the bridged dimers $[(\pi\text{–}RC_3H_4)Co(CO)_2]_2(\mu\text{–}dppe)$ (R = H, Me) which are stable at room temperature. The dppm as well as the dppe compounds are studied with ir and nmr (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy and prove not to be fluxional.

SAMEVATTING

Die nuwe Co(I) komplekse [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) word berei by wyse van die reduktiewe klowing van die dimere [$Co(CO)_3L$]$_2$ met 'n natrium amalgaam, gevolg deur toevoeging van $Me_3SnC\ell$. 'n Sintetiese prosedure om hierdie verbindings op groot skaal te berei en te suiwer, word ontwikkel. 'n Vorige beriggewing dat [$Co(CO)_3AsPh_3$]$_2$ nie reduktief gekloof kan word sonder dat ontbinding plaasvind nie, word verkeerd bewys. Die nuwe produkte is stabiel en word m.b.v. ir–, kmr– (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{119}Sn\{^1H\}$) en massaspektroskopie bestudeer.

Daar word aangetoon dat die verbindings [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) nie ontvanklik is t.o.v. nukleofiliese substitusie nie. Die gepoogde vervanging van 'n karbonielligand met 'n isosianiedligand (deur gebruikmaking van 'n oormaat van lg.) na behandeling met die labiliseermiddel Me_3NO, lei tot 'n verskeidenheid produkte, waarvan slegs die hoofproduk as *trans*–[$Co(CNR)_3L_2$][PF_6] (R = t–Bu, Ph, 2,6–dimetielfeniel; L = PPh_3, $P(OPh)_3$, $AsPh_3$) geïdentifiseer kan word. Behalwe vir die geval waar L = PPh_3, R = t–Bu, is die produkte uitermatig onstabiele olies en kan hulle nie behoorlik gekarakteriseer word nie.

Die nuwe Co(I) bis(fosfien)komplekse word berei deur dppm (bis(difenielfosfino)metaan) en dppe (bis(difenielfosfino)etaan) met [(π–RC_3H_4)$Co(CO)_3$] (R = H, Me) te reageer. Die reaksie van dppm lei tot die isolering van [(π–RC_3H_4)$Co(CO)_2$(η^1–dppm)] (R = H,Me) wat die eerste voorbeelde van Co(I) komplekse met 'n monodentate dppm ligand is. Hierdie uiters lugsensitiewe verbindings is matig stabiel en ontbind nie onderkant –20°C in die vaste toestand nie. Die reaksie met dppe het die dimere [(π–RC_3H_4)$Co(CO)_2$]$_2$(μ–dppe) (R = H, Me) wat by kamertemperatuur stabiel is, tot gevolg. Sowel die dppm as die dppe verbindings word m.b.v. ir– en

kmr–spektroskopie (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) bestudeer en blyk nie fluksioneel te wees in oplossing nie.

ABBREVIATIONS

M	a transition metal
L	a ligand
dwm	decomposes without melting
THF	tetrahydrofuran
ir	infrared
ν	wavenumber in cm^{-1}
η^n	the superscript indicates the number of coordinated carbons
μ	indicates a bridged ligand
CNR	an isocyanide ligand
dppm	bis(diphenylphosphino)methane
dppe	bis(diphenylphosphino)ethane
nmr	nuclear magnetic resonance
nqm	nuclear quadrupole moment
J	coupling constant in Hz
ppm	parts per million
s	singlet
d	doublet
t	triplet
q	quartet

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CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION AND AIM.

Although cobalt compounds have been used for colouring glass for at least 4000 years, the metal was first isolated in a very impure form by the Swedish chemist Georg Brandt in 1735. In 1780 T.O. Bergman showed this to be a new element which was named cobalt.

In 1910 Ludwig Mond and coworkers synthesized the first organocobalt compound, octacarbonyl dicobalt, $[Co_2(CO)_8]$ [1]. In the period up to the end of World War II little progress was made in the synthesis of new organocobalt compounds and from about 1927 onwards, the chemistry of $[Co_2(CO)_8]$ and its derivatives was mainly developed by Walter Hieber and his group, initially at the University of Heidelberg and later at the Technische Hochschule in München [2].

The investigation of the organometallic chemistry of cobalt has often lagged behind that of other transition metals such as iron or chromium. More recently, the discovery of new types of rhodium or iridium complexes has often led chemists to wonder whether the less stable cobalt analogues could be synthesized.

Cobalt has a valence shell electron configuration of $3d^7 4s^2$. As it has an odd number of electrons, cobalt occurs in an odd–numbered oxidation state (–I, +I, +III) in the majority of compounds. Cobalt(O) or cobalt(II) compounds are either paramagnetic or polynuclear with metal–metal bonds. $[Co_2(CO)_8]$ is commonly used as starting material in the preparation of low oxidation state (O or I) cobalt compounds with the preparation of monomers requiring cleavage thereof. Low oxidation state organocobalt compounds are often extremely unstable, showing a tendency to decompose upon exposure to moisture, oxygen or heat.

Currently, a few groups are working towards the synthesis of new organocobalt compounds; notably those of Galamb in Hungary (alkyl and acyl cobalt carbonyls) [3], Wakatsuki in Japan (cobalt metallacycles) [4] and Werner in the Federal Republic of Germany (basic Co(I) complexes) [5].

However, owing to the infrequent and invariant nature of current publications, there seems at present to be no major aspect of organocobalt chemistry receiving particular attention. This leaves scope for a systematic study particularly of low oxidation state cobalt compounds.

The aim of the work presented in this thesis was thus to attempt the synthesis of new cobalt(I) complexes with the additional requirement that they are sufficiently stable to enable a spectroscopic study to be conducted. This was to be achieved by the efficacious employment of the stabilizing / destabilizing influences of different ligands. The new compounds could then spectroscopically be compared with existing ones. For this purpose it was decided to concentrate on complexes of the type $[XCo(CO)_3L]$ (where X is any electrophilic ligand and L a neutral donor–type ligand). The stability of the product could then be manipulated by varying X and L.

The study culminates in the preparation of several new cobalt(I) complexes which are suitable for spectroscopic study. The unique role of high–resolution nmr spectroscopy in the study of these relatively unstable compounds is demonstrated throughout.

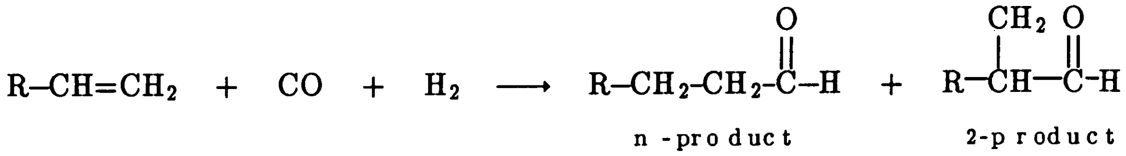
1.2 THE INDUSTRIAL IMPORTANCE OF COBALT.

Although South Africa is not an important producer of cobalt, some is produced as a byproduct from the mining of nickel and copper.(The world's largest producer is Zaire.)

Cobalt's most strategic application is as a constituent of the super–alloys which have the strength, corrosion resistance and reliability to function at elevated temperatures e.g. in high speed gas turbines.

Roughly 15% of all cobalt is used for catalytic purposes in industrial chemical processes [6]. Organocobalt compounds notably play an important role in processes which involve the catalytic incorporation of carbon monoxide into organic compounds [7]. However, organorhodium compounds have recently been found to be successful catalytic substitutes in some of the industrial processes employing cobalt catalysts [8]. In the following paragraphs an example is given and a brief comparison made between cobalt and rhodium.

One of the major industrial applications of homogeneous catalyst systems involves the addition of formaldehyde (H–CHO) (hence "hydroformylation") across the double bond of an alkene, resulting in an aldehyde containing one more carbon atom than the alkene substrate:



$$R{-}CH{=}CH_2 + CO + H_2 \longrightarrow \underset{\text{n-product}}{R{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}H} + \underset{\text{2-product}}{R{-}\overset{CH_2}{\overset{|}{C}}H{-}\overset{O}{\overset{\|}{C}}{-}H}$$

Commonly, propene is used to produce n–butanal, of which some 2.7 million tonnes is produced annually in the Western world [9]. 2–butanal, which is also produced, has considerably fewer end uses and therefore a much lower commercial value. The ratio 1–butanal:2–butanal is thus highly important in industrial hydroformylation processes.

Three types of homogeneous transition–metal complexes are presently used in hydroformylation processes:

i) cobalt carbonyl systems;
ii) phosphine–modified cobalt carbonyl systems;
iii) phosphine–modified rhodium carbonyl systems.

Under the reaction conditions $[Co_2(CO)_8]$ is converted to $[HCo(CO)_4]$, which loses a CO ligand to give the four–coordinate 16 electron species $HCo(CO)_3$, which is the active catalytic species:

$$[Co_2(CO)_8] \xrightarrow{H_2} 2[HCo(CO)_4] \underset{-CO}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_3 + CO$$

However, as $[HCo(CO)_4]$ is an extremely unstable species in solution, a minimum partial pressure of CO (200 atm at $200^{o}C$) is required for stabilization. Below this metallic cobalt will precipitate [10, 11].

When one or two of the carbonyl ligands are replaced by phosphines [12], the stability of the cobalt complex is increased, resulting in a more stable hydride catalyst which requires a lower CO / H_2 pressure (5 – 10 atm):

$$[Co_2(CO)_6L_2] + H_2 \rightleftharpoons 2HCo(CO)_3L$$

$$(L = PPh_3, PEtPh_2, PEt_2Ph)$$

Introduction of the phosphine ligands also results in a marked change in the ratio of products obtained [10, 11], this ratio largely depending on the electronic and steric properties of the particular phosphine. Unfortunately, together with the increase in stability there is a concurrent decrease in catalyst activity.

Several tertiary phosphine rhodium complexes have been used as industrial catalysts [10]. These, in particular [$HRh(CO)(PPh_3)_3$], are considerably more active (approx. 1000 times more) under milder reaction conditions than their cobalt counterparts. The rhodium catalysts also show higher selectivity, better yields and improved stability. For the sake of comparison, some reaction conditions and yields obtained with the different types of catalysts are shown in table 1.1.

TABLE 1.1 **Operating data for cobalt and rhodium hydroformylation processes.**[a]

	Unmodified cobalt	Ligand modified cobalt	Ligand modified rhodium
Temperature (^0C)	140 – 180	160 – 200	80 – 120
Pressure (atm)	250 – 350	50 – 100	15 – 25
% metal / olefin	0.1 – 1.0	0.5 – 1.0	10^{-2} – 10^{-3}
Product ratio (normal : branched)	3 – 4:1	6 – 8:1	10 – 14:1
Yield (aldehydes %)	± 80	–	± 96
Yield (alcohols %)	± 10	± 80	–

a) Taken from reference 10.

Although most industrial processes still make use of cobalt–based catalysts, some companies have introduced rhodium.

From a chemical point of view rhodium catalysts certainly have more advantages, but from a financial point of view, although lower plant capital cost and energy requirements sometimes outweigh the high catalyst investment [13], the following points should be kept in mind:

i) Rhodium is much more expensive than cobalt, the former presently trading at $1215 / ounce troy as opposed to $7.50 / pound for cobalt (closing prices on the London Stock Exchange on Friday 16 Dec. 1988).

ii) The price of cobalt has not varied much over the years, whereas rhodium prices are sometimes volatile, having risen above $1400 in 1987. As is the case with gold, rhodium is increasingly viewed as an investment opportunity which could lead to even higher price volatility.

iii) Rhodium is much less abundant than cobalt. The total world production (1981) amounted to roughly 13 tonnes compared to 30 000 tonnes of cobalt [6].

Apart from hydroformylation there are several other industrial processes which depend on cobalt catalysts [7]. While the above example serves to emphasize the significance of these catalysts in industrial organic synthesis, it should be kept in mind that most of these compounds were initially synthesized as mere academic curiosities.

By making use of the electronic and steric properties of ligands, it is possible to design a catalyst for a specific purpose.

The continuing investigation of the organometallic chemistry of cobalt is thus of great importance and remains an exciting challenge.

CHAPTER 2

REVIEW OF REACTIONS AND SPECTROSCOPIC METHODS.

2.1 INTRODUCTION.

The reactions of $[Co_2(CO)_8]$ have been studied extensively and are well documented [14 – 17]. A summary of some reactions of $[Co_2(CO)_8]$ and its derivatives is presented in this chapter.

Further, a short discussion of some spectroscopic techniques employed in the study of organometallic compounds, is presented.

2.2 SOME REACTIONS OF $[Co_2(CO)_8]$ AND ITS DERIVATIVES.

The reactions of $[Co_2(CO)_8]$ mainly fall into one of the following three classes:

i) Substitution reactions: $[Co_2(CO)_8]$ reacts with tertiary phosphines, phosphites or arsines in non–polar solvents or at high temperatures in polar solvents to give complexes of the type $[Co(CO)_3L]_2$:

$$[Co_2(CO)_8] \quad + \quad 2L \quad \longrightarrow \quad [Co(CO)_3L]_2 \quad + \quad 2CO$$

ii) Disproportionation reactions: $[Co_2(CO)_8]$ reacts with bases such as tertiary phosphines (in polar solvents) and isocyanides (in non–polar solvents) under mild conditions to give complexes of the type $[Co(CO)_3(PR_3)_2][Co(CO)_4]$ and $[Co(CNR)_5][Co(CO)_4]$ respectively. The disproportionation product decomposes upon heating to form the dimer $[Co(CO)_3L]_2$.

iii) Reduction reactions: $[Co_2(CO)_8]$ and its derivatives $[Co(CO)_3L]_2$ can be cleaved reductively to give the respective monomers:

$$[Co(CO)_3L]_2 \quad + \quad 2Na \quad \longrightarrow \quad 2Na[Co(CO)_3L]$$

The anions obtained in this way can be treated with any suitable electrophilic reagent. A few examples are given below:

* acidification leads to the hydrides $[HCo(CO)_3L]$ [18];
* addition of RX gives the alkyl derivatives $[RCo(CO)_3L]$ [18, 19];
* treatment with X_2 (X = Cl, Br, I) under mild conditions leads to $[XCo(CO)_3L]$ [19].
* reaction with an acyl followed by substitution gives the acyl derivatives [19]:

$$RCOX \quad + \quad [Co(CO)_3L]^- \quad \longrightarrow \quad [(ROC)Co(CO)_3L] \quad + \quad X^-$$

* addition of a metal salt leads to the formation of covalent compounds of the type $[R_3M'Co(CO)_3L]$ [20].

All of these constitute important routes to monomeric cobalt(I) compounds, but it is mainly the second and the last reaction types which receive attention in this work.

2.3 SPECTROSCOPY.

Several spectroscopic techniques are at the disposition of an organometallic chemist. Of these, ir, nmr and electronic spectroscopy are particularly suitable for studying the fragile compounds often encountered, while mass spectroscopy is less valuable owing to its destructive nature. Apart from these, X–ray diffraction studies have proven invaluable, but the poor stability of some compounds in solution does not always permit growth of a suitable crystal.

2.3.1 **Infrared spectroscopy** [21, 22].

Metal complexes containing carbonyl ligands show intense bands in what is known as the "carbonyl region" (2200 cm^{-1} – 1600 cm^{-1}) of the infrared spectrum. As these vibrations are highly sensitive to the environment, their energies, number and relative intensities contain important information on the geometry and the distribution of electron density in the compound.

<u>Frequency of a CO band</u>: The frequency of a band often permits distinction between bridged and terminal carbonyl ligands, but caution should be exercised if other ligands with a variety of donor and π–acceptor properties are present. The carbonyl stretching frequencies can also be used to calculate the force field or "stiffness" of an M–CO bond. In order to carry out such a calculation, it is necessary to make various approximations regarding the interactions between chemically non–equivalent CO–groups [22]. Organometallic chemists find it convenient to make use of the "Cotton–Kraihanzel" set of approximations, which enable rapid calculation of approximate force constants without having to use

elaborate computer programs [23, 24]. These approximate parameters suffice for the purpose of qualitative comparison and can be related to the bonding properties of the ligands.

Number of CO bands: The number of bands in the carbonyl region contain information on the geometry of the $M(CO)_x$ moiety. The number of bands can be predicted after the necessary symmetry operations are carried out. A comparison between the predicted and the observed number of bands often enables a particular structure to be selected. Care should, however, be taken as bands are sometimes weak or superimposed.

2.3.2 Nuclear magnetic resonance spectroscopy

Organometallic compounds contain a variety of nuclei with magnetic moments, each of which makes a contribution to the vast amount of information contained in every nmr spectrum. A summary of the properties of some of these nuclei is given in table 2.1.

TABLE 2.1 Some properties of nuclei with magnetic moments.

Nucleus	Spin(I)	Natural abundance(%)	Sensitivity
^{13}C	$^1/_2$	1.11	0.00018
^{59}Co	$^7/_2$	100.00	0.28
^{1}H	$^1/_2$	99.98	1.000
^{14}N	1	99.64	0.001
^{31}P	$^1/_2$	100.00	0.066
^{117}Sn	$^1/_2$	7.61	0.003
^{119}Sn	$^1/_2$	8.58	0.004

Attempts to obtain well–resolved nmr spectra of organocobalt compounds can be thwarted by i) paramagnetism of the complex and ii) the nuclear quadrupole moment of the cobalt nucleus. Organocobalt complexes become paramagnetic when the metal is in the +II or O oxidation state where the cobalt atom has 7 and 9 d–electrons respectively. Whereas it is impossible to obtain an nmr spectrum of a paramagnetic compound due to extensive broadening of the peaks, the quadrupole moment of a nucleus does not have such a marked effect.

2.4.2.1 ^{1}H nmr.

^{1}H nmr does not have the same value for an organometallic chemist than it does for an organic chemist. Although it is interesting to compare the spectrum of the coordinated ligand with that of the uncoordinated ligand, the protons are often too far removed from the metal centre to show any meaningful change in chemical shift or $^{n}J(HH)$ coupling constants. The ^{1}H spectrum is therefore often used as supportive evidence for information obtained from the ^{13}C or ^{31}P nmr spectrum – also, the change in $^{n}J(HX)$, where X is a heteroatom directly attached to the metal, offers interesting information.

Some large organic ligands can result in complicated spectra due to second–order phenomena (when the magnitude of the coupling constant exceeds the difference in chemical shift) necessitating the use of special routines. Sometimes it is possible to choose "nmr–friendly" ligands.

2.4.2.2 ^{13}C nmr.

^{13}C nmr spectroscopy is an extremely valuable technique not only for studying the structure of an organometallic compound but also the electronic properties of a ligand. This is because many ligands are coordinated to the metal centre via a carbon atom which thereby is subjected to a large change in environment.

Chemical shifts: ^{13}C has a total chemical shift range of about 600 ppm which is much wider than the range for protons (50 ppm). ^{13}C nmr spectra are normally recorded with the aid of broad–band noise–modulated proton decoupling and owing to ^{13}C – ^{13}C spin–spin coupling not being observed, spectra are usually not complicated.

Peak intensities: The relative intensities of the peaks can be used advantageously. The intensity of a ^{13}C resonance depends in a critical manner on the ratio of the pulse repetition time t_p to the spin–lattice relaxation time T: t_p / T. This can be explained as follows: when nuclei absorb radiation they make transitions to their upper spin states. This is schematically illustrated in fig. 2.1.

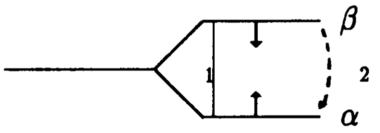


FIGURE 2.1 The spin energy levels for a ^{13}C nucleus in a magnetic field.

Irradiation at the resonating frequency of a particular nucleus results in a transition from $\alpha \longrightarrow \beta$ (path 1). Excess energy is shed by a radiationless relaxation ($\beta \longrightarrow \alpha$) (path 2).

Dissipation of the excess energy then occurs by way of various relaxation mechanisms of which spin–lattice relaxation is the most important [26, 27]. However, different carbon nuclei do not relax at the same rate, with relaxation times falling anywhere in the range 1 ms to 1000 s. Proton–bearing carbons in particular relax much faster than their quaternary analogues. In the event of the delay between applied pulses being shorter than the time needed for a particular nucleus to return to its original state, such a nucleus is never properly "measured" and its peak intensity remains small or it can even go undetected. This is a common problem with carbonyl ligands and the sp carbon of an isocyanide ligand.

Another phenomenon which has an appreciable influence on the peak intensities, is the nuclear Overhauser enhancement (NOE) effect which has been defined as "the total intensity of a ^{13}C peak upon irradiation of the proton resonances" [28]. NOE is therefore a result of the broad–band decoupling of the protons. The full theoretical enhancement is not exhibited by all peaks; some peaks experience a threefold increase in intensity while others experience none.

The relative intensity of a ^{13}C resonance line is thus roughly related to the number of protons in the vicinity of the carbon nucleus.

There are a number of ways in which enhancement of low–intensity peaks may be accomplished:

i) The concentration of the compound (in effect the number of ^{13}C atoms) can be increased. (This is often impractical owing to low solubility.)

ii) The total accumulation time can be increased.(The disadvantage of this is the tendency of organometallic compounds to decompose upon prolonged dissolution.)

iii) The delay between pulses can be increased.

iv) The pulse flip–angle can be adjusted ($< 45^0$ for slowly relaxing nuclei).

In the case of (iii) and (iv) care should be taken as the peaks of some nuclei could be suppressed under certain conditions. Differences in relaxation times sometimes render it necessary to record more than one spectrum using different settings.

The heteronuclear spin–spin coupling of ^{13}C nuclei with other nearby nuclei (e.g. ^{1}H, ^{31}P or ^{14}N) results in the splitting of the carbon signals. The multiplicity, together with the magnitude of $^{n}J(CX)$ can be used as an additional assigning aid.

2.4.2.3 ^{31}P nmr.

^{31}P nmr is mainly used to detect and study tertiary phosphine or phosphite ligands. As these ligands coordinate through the phosphorus atom, the ^{31}P nucleus is submitted to a large change in environment with a concomitant change in chemical shift. This shift can be upfield or downfield depending on the electronic properties of the ligand in question as well as those of the other ligands. ^{31}P chemical shifts show a marked dependence on the electronegativity of the heteroatom directly attached to the phosphorus [30].

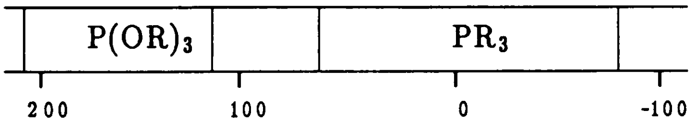


FIGURE 2.2 Chemical shift ranges for tertiary phosphines and phosphites.

The presence of more than one ^{31}P nucleus in a complex results in ^{31}P—^{31}P coupling which in turn contains information on the geometry of the molecule.

2.4.2.4 ^{119}Sn nmr.

^{119}Sn nmr has found extensive use in the study of organotin compounds. Several reviews have appeared [33]. In contrast, compounds containing, apart from tin, a transition metal have received less attention. Tin is often used as a ligand in the form of R_nSnCl_{4-n} (R = Me, Ph) [34].

^{119}Sn has a total chemical shift range of approximately 700 ppm. As with ^{31}P, the tin nucleus is extremely sensitive to its environment and the chemical shift also depends on the oxidation state of the tin atom. $J(^{119}SnX)$ coupling constants can either be obtained directly from $^{119}Sn\{^1H\}$ nmr spectra or indirectly by observing the satellites on the spectrum of the X–nucleus. In general, the electronic properties of R in R_nSnCl_{4-n} correlate fairly well with the $\delta(^{119}Sn)$ chemical shifts: the ^{119}Sn shielding decreases with an increase in the electron acceptor properties of R. Also, $^2J(^{119}Sn^1H)$ has been found to be related to the degree of inductive electron withdrawal from tin by its substituents; $^1J(^{119}Sn^{13}C)$ values have shown similar trends [34, 35].

2.3.3 Mass spectroscopy.

Mass spectroscopy is not only used to determine the molecular mass of a compound, but also to identify ligands. Additionally, the ionization energy as well as the energies of the metal ligand bonds can be measured.

The molecular mass is determined by observing the energy at which a single electron is expelled, i.e. that of the parent molecule ion.

The parent molecule ion can henceforth fractionate in one of the following ways:

i) A complete ligand can split off – this will usually occur if the ligand is classified as "readily removable", e.g. CO or NO [38];

ii) Part of a ligand can fractionate intact, e.g. a methyl group;

iii) Part of a ligand can fractionate and undergo further reaction.

The parent molecule ion is, however, not always observed: sometimes the peak corresponding to the largest fragment ion is that of the molecule deficient of one "readily removable" ligand.

The π–accepting ability of a ligand has an important influence on the fragmentation pattern of a compound. As the positive charge of the parent molecule ion is mainly located on the metal atom, the donation of electron density towards π–accepting ligands is severely hampered. These metal–ligand bonds become considerably weakened causing them to fractionate easily. The metal–ligand bonds of σ–donor ligands, on the other hand, become enforced resulting in the postponement of their detachment.

CHAPTER 3

THE SYNTHESIS AND CHARACTERIZATION OF [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$)

3.1 INTRODUCTION.

In this chapter, the synthesis of compounds of the type [$Me_3SnCo(CO)_3L$] starting from the dimers [$Co(CO)_3L]_2$ is described. The new compounds are studied spectroscopically and compared with other compounds of the type [$XCo(CO)_3L$].

3.2 COMPOUNDS OF THE TYPE [$Co(CO)_3L]_2$.

Dimers of the type [$Co(CO)_3L]_2$ are synthesized according to the method of Manning [39], using two equivalents of L (L = PPh_3, $P(OPh)_3$, $P(OMe)_3$, $AsPh_3$) for every equivalent of [$Co_2(CO)_8$]:

$$[Co_2(CO)_8] \quad + \quad 2L \quad \longrightarrow \quad [Co(CO)_3L]_2 \quad + \quad 2CO$$

The derivatives of PPh_3, $P(OPh)_3$ and $AsPh_3$ are insoluble in benzene and precipitate from the reaction mixture. Purification is then accomplished by repeated washing with warm benzene or hexane. The trimethylphosphite derivative, on the other hand, is soluble in benzene as well as in saturated hydrocarbon solvents, which limits the method of purification to that of crystallization. Although attempts at crystallization in hexane at -20^0C leads to the recovery of some crystals, the yield is very low and the remainder of the product decomposed in solution. The trimethylphosphite compound was therefore not investigated further. It is assumed that other small phosphines or phosphites (such as PMe_3, $P(OEt)_3$) will give a similar result.

The prepared dimers are characterized by comparing the carbonyl regions of their ir spectra with those in the literature. The results are shown in table 3.1.

TABLE 3.1 Observed carbonyl stretching frequencies for the complexes $[Co(CO)_3L]_2$ (L = PPh_3, $P(OPh)_3$, $AsPh_3$, $P(OMe)_3$).

L	$\nu(CO)$ $(cm^{-1})^a$		Reference[c]
	$A'_1{}^b$	E'	
PPh_3	1977 (w)	1950 (vs)	41
$P(OPh)_3$	1989 (w)	1966 (vs)	39
$AsPh_3$	1972 (w)	1949 (vs)	40
$P(OMe)_3$	1995 (w)	1972 (vs)	39

a) Obtained as a Nujol mull.

b) Ir inactive.

c) Data with which results are compared.

3.3 COMPOUNDS OF THE TYPE [$Me_3SnCo(CO)_3L$].

3.3.1 Introduction.

A literature study of compounds of the type [$R_3SnCo(CO)_3L$] reveals the existence of some triphenyltin complexes (i.e. R = Ph) where L is a phosphine or phosphite – commonly PPh_3, PBu_3 or $P(OPh)_3$ [42]. These complexes were usually studied by means of ir spectroscopy. It was decided to attempt the syntheses of the trimethyltin analogues (which are of lesser stability owing to the absence of the bulky phenyl groups) in order to determine the effects of R and L on these compounds.

Preparation of compounds of the type [$R_3SnCo(CO)_3L$] is accomplished either by cleavage of the dimer, followed by addition of the electrophilic reagent (method 1):

Method 1.

$$[Co(CO)_3L]^- + R_3MX \longrightarrow [R_3MCo(CO)_3L] + X^-$$

or by a carbonyl substitution between L and [$R_3MCo(CO)_4$] (method 2):

Method 2.

$$[R_3MCo(CO)_4] + L \longrightarrow [R_3MCo(CO)_3L] + CO$$

The method of salt elimination (method 1) is the more convenient, as the anions $[Co(CO)_3L]^-$ are readily prepared and normally used *in situ*. A disadvantage (a result of the amalgam) is the possibility of the formation of mercury salts of the anion. In some instances substantial amounts of mercury byproducts have been identified [42]. The major disadvantage of method 2 is that the large excess of L required to obtain a reasonable yield impeded purification of the product.

3.3.2 The synthesis of [$Me_3SnCo(CO)_3L$]. (L = PPh_3 (I), $P(OPh)_3$ (II), $AsPh_3$ (III)).

For the syntheses method 1 (as outlined in section 3.3.1) is followed. Initially, the procedure described by Curtis for the preparation of [$Ph_3SiCo(CO)_3PPh_3$] [43] was used, but it soon became apparent that considerable changes would have to be made.

The experiment is briefly discussed below. Firstly, the low solubilities (even in THF) of the dimers have to be taken into account. Reduction of the dimer is accomplished by suspension thereof in a large volume of THF followed by addition to the freshly prepared sodium amalgam (scheme 3.1, steps A and B). The time required for the reduction to reach completion appears to be related to the solubility of the particular dimer in THF. Some of the reaction conditions are summarized in table 3.2.

The reduced compound (scheme 3.1, step C) is removed from the amalgam before addition of the electrophilic reagent. The salts Na[$Co(CO)_3L$] have a limited stability and although they are routinely handled at –30^{0}C, a certain degree of decomposition always occurs. It is thus important to add the trimethyltinchloride as soon as possible – this renders the filtration of the salt impractical.

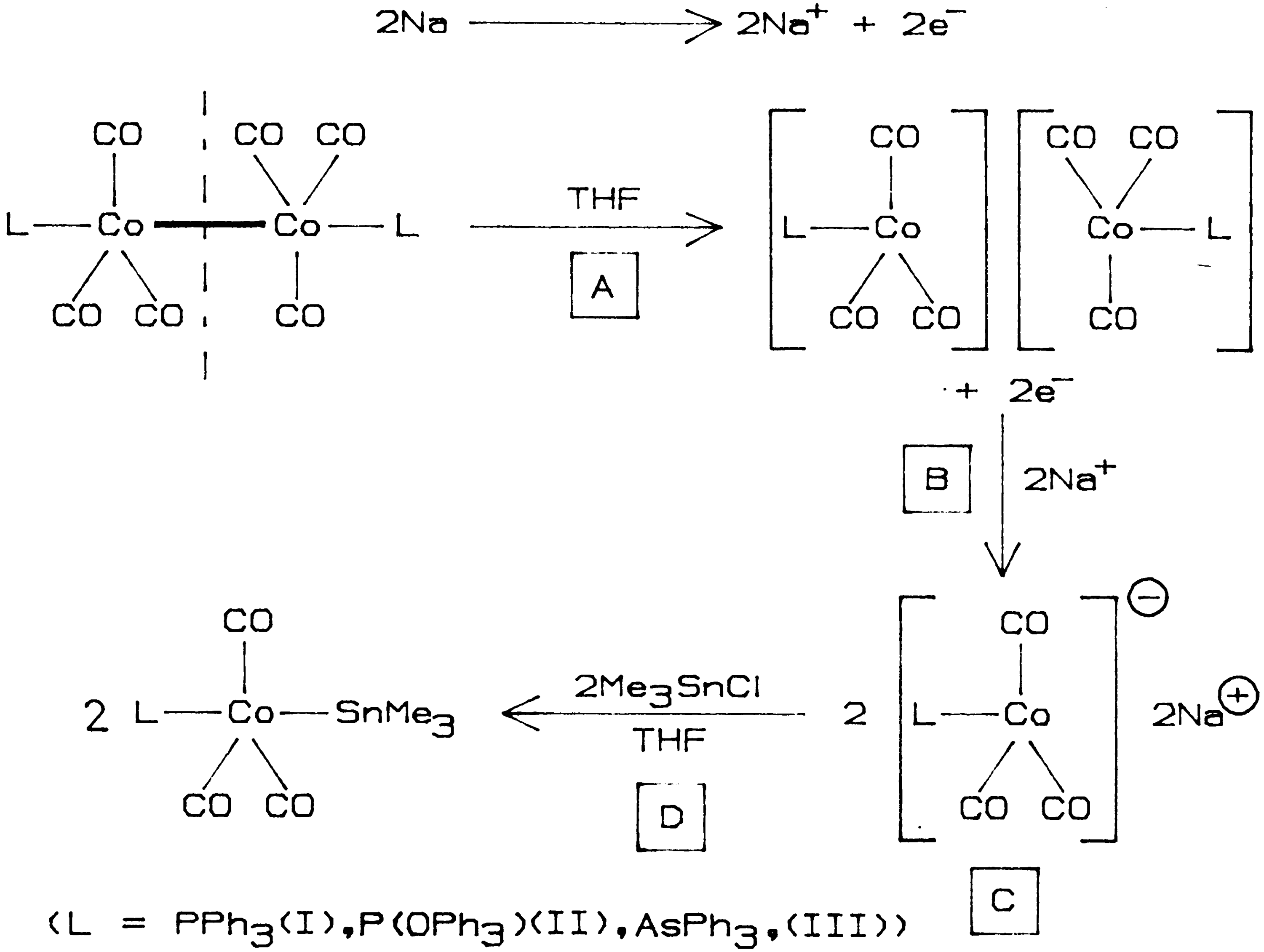
TABLE 3.2 Some reaction conditions: the reduction of $[Co(CO)_3L]_2$ on a sodium amalgam.

L	Mercury (g)	Solubility in THF	Reaction time
PPh_3	500	very poor	16 h
$AsPh_3$	250	poor	40 min
$P(OPh)_3$	300	reasonable	20 min

After the treatment of $Na[Co(CO)_3L]$ with Me_3SnCl at room temperature (scheme 3.1, step D) the reaction mixture is chilled upon which the formed NaCl precipitates more rapidly. Decantation of the crude product solution, removal of the solvent and subsequent extraction procedures are all carried out at reduced temperatures to prevent decomposition. (The exact procedure differs for each of L = PPh_3, $P(OPh)_3$ and $AsPh_3$ and is described in detail at the end of this chapter.)

Apart from the formation of I, II and III, a small amount of bright yellow product (insoluble in benzene and soluble in dichloromethane) also forms. From the reaction of I, it is possible to isolate a portion of this byproduct. An ir spectrum (obtained as a KBr pellet) shows two peaks in the carbonyl region: $\nu(CO)$ = 1991.1 cm^{-1}(w) and 1939.6 cm^{-1}(vs). This points to the presence of the $[Co(CO)_3PPh_3]^-$ anion at least, possibly with another counterion. During an investigation of the reaction of $[Co_2(CO)_8]$ with organomercuric halides [44], Seyferth identified the byproduct $Hg[Co(CO)_3PPh_3]_2$ which gave $\nu(CO)$ = 1992 cm^{-1}(w) and 1944 cm^{-1}(s) (KBr–pellet).

SCHEME 3.1



(L = PPh_3(I), P(OPh_3)(II), $AsPh_3$, (III))

The existence of a byproduct renders necessary the purification of the desired products by means of column chromatography. Some physical properties of the products are given in table 3.3.

TABLE 3.3 Some physical properties of [$Me_3SnCo(CO)_3L$]
(L = PPh_3 (I), $P(OPh)_3$ (II), $AsPh_3$ (III)).

Compound	Colour	Mp (^{0}C)	Anal. calc.		Found	
			C	H	C	H
I	yellow	173–175 (dec)	50.66	4.25	50.86	4.30
II	pale yellow	91–92	46.72	3.92	46.73	3.89
III	primrose	122–124 (dec)	47.03	3.95	47.08	3.88

It is interesting to note that although the triphenyltin analogues of I and II, i.e. [$Ph_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$) were previously prepared [42, 43], no such analogue of the triphenylarsine derivative existed. In fact, a search of the literature does not reveal any compounds of the type [$R_3MCo(CO)_3L$] (L = AsR_3; R = Me, Ph; M = Si, Ge, Sn) which are prepared by initial reduction of the dimers [$Co(CO)_3AsR_3$]$_2$ followed by the addition of R_3MCl as shown in scheme 3.1. The only two arsine derivatives which exist, [$Cl_3MCo(CO)_3AsPh_3$] (M = Ge, Sn), were prepared differently by starting from [$Cl_3MCo(CO)_4$]. This was treated with $AsPh_3$ to substitute a carbonyl [45].

The lack of these arsine derivatives can probably be ascribed to the immense instability of the precursor salt, Na[$Co(CO)_3AsPh_3$]. A published attempt to cleave [$Co(CO)_3AsPh_3$]$_2$ reductively led to complete decomposition [46]:

$$2[Co(CO)_3AsPh_3]_2 \longrightarrow Na[Co(CO)_4] + 4AsPh_3 + [Co(THF)_6][Co(CO)_4]_2$$

This failure seems inexplicable, as the authors noticed a colour change from dark red to brown to red during the first 40 min of the reduction step – in this work a colour change from dark red to pale yellow is observed in the corresponding period of time, whereupon the reaction is considered to be complete.

3.4 A SPECTROSCOPIC STUDY OF [$Me_3SnCo(CO)_3L$].

3.4.1 Infrared spectroscopy.

Number of bands: The observance of a single strong band (E–band) in the carbonyl region indicates that the three carbonyl ligands are symmetrically arranged in the molecule occupying the three equatorial sites of the trigonal bypiramid (compare appendix 1). The A_1 band, vanishingly weak in intensity as it represents a symmetrical vibration mode, is actually infrared inactive, but is observed due to the three CO–groups being slightly non–coplanar (see section 3.4.4). The molecules can therefore be said to belong to the C_{3v} point group.

TABLE 3.4 Infrared spectroscopic data for [$R_3SnCo(CO)_3L$] (R = Me, Ph; L = PPh_3, $P(OPh)_3$, $AsPh_3$).

R	L	ν(CO)[a]		Approx. force const.[b]	
		A_1	E	k	k_i
Me	PPh_3	2013 (w)	1936 (vs)	1554	123
Me	PPh_3[c]	2007 (w)	1925 (vs)	1540	130
Me	$P(OPh)_3$	2030 (w)	1961 (vs)	1590	111
Me	$AsPh_3$	2015 (w)	1946 (vs)	1566	110
Ph[ce]	PPh_3	2000 (w)	1945 (vs)	1557	88
Ph[d]	$P(OPh)_3$	2041 (w)	1975 (vs)	1611	107

a. In hexane unless otherwise stated.

b. Calculated using the "Cotton–Kraihanzel" approximation [23, 24].

c. Measured as a KBr–disc.

d. Measured in benzene – taken from reference 42.

e. Taken from reference 43.

Position of bands: The vibrational frequency of a C≡O bond can be related to the "tightness" of bonding of a carbonyl ligand. That is, by measuring frequency at which the C≡O bond vibrates and comparing this with the frequencies of known analogues, it is possible to predict whether the carbonyl ligand will undergo substitution or not. Replacement of a carbonyl ligand in [$Me_3SnCo(CO)_4$] weaker π–acceptor such as a phosphine, phosphite or arsine leads to an increase of electron density on the metal centre. This in turn makes more electron density available for the remaining carbonyl ligands which respond by increasing their degree of back bonding and thereby strengthening the metal–carbon bond. The CO bands for the substituted complexes I, II and III (table 3.4) appear at significantly lower values than that of [$Me_3SnCo(CO)_4$] (E–band: ν(CO) = 1988 cm^{-1}).

A comparison of **I** with its triphenyltin analogue [$Ph_3SnCo(CO)_3PPh_3$] shows that the R–groups on tin also have an influence on the frequency of C≡O. As can be expected, electron donating methyl groups, which cause an increase in back bonding to the carbonyl ligands, result in a lowering of the frequency of the carbonyl bands upon going from Ph_3Sn– to Me_3Sn–.

Vibrations other than C≡O are not assigned. The Co–Sn vibration has been observed at 177 cm^{-1} for [$Me_3SnCo(CO)_4$] [47] and was not found to mix with modes of lighter atoms. (Due to the lack of appropriate instrumentation, the far infrared spectra of **I**, **II** and **III** have not been recorded.)

3.4.2 Mass spectroscopy.

The fragmentation of the ligands of compounds of the type [$Me_3SnCo(CO)_3L$] occurs in the order i) strong π–acceptors, ii) the Me_3Sn moiety, iii) weak π–acceptors. This is the expected order (see section 2.4.3).

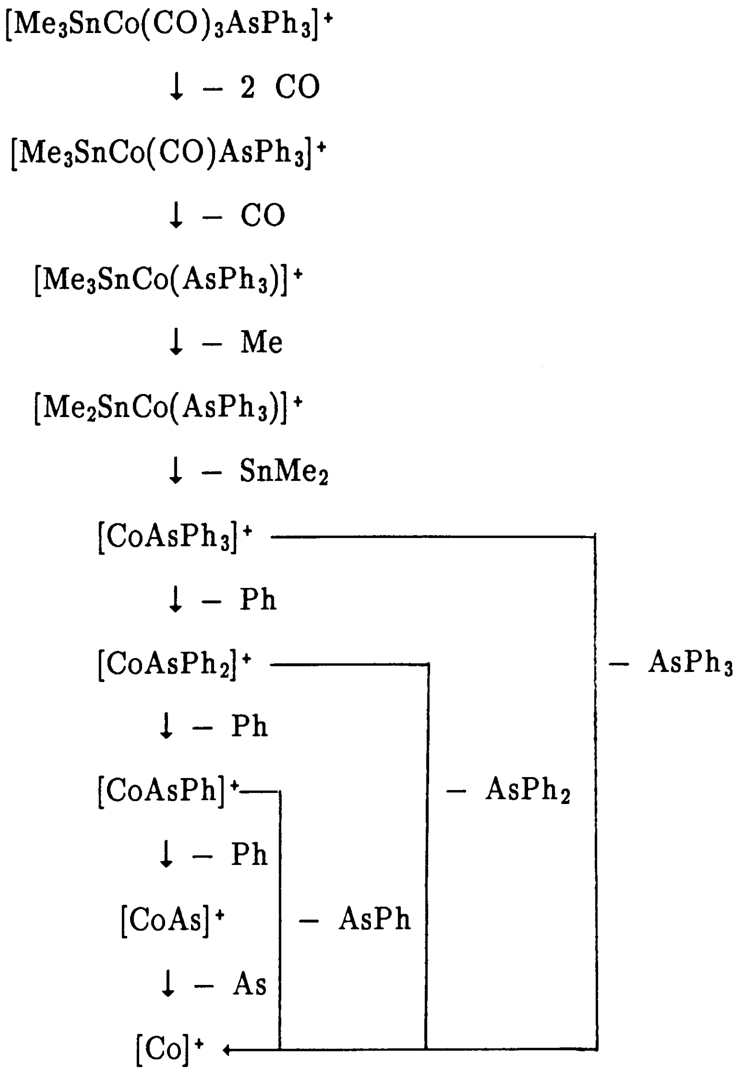
On the mass spectra of **I** and **III** the molecular ion is observed as a low intensity peak. **III** exhibits a simple fragmentation pattern (scheme 3.2). Initial loss of the carbonyl ligands is followed by fragmentation of the trimethyltin moiety and finally the triphenylarsine ligand. Although no competing fragmentation pathways are observed, fragment peaks for [$AsPh_3$]$^+$, [$AsPh_2$]$^+$ and [AsPh]$^+$ are detected; these most probably being the result of loss of parts of the arsine ligand from Co or the recombination of arsenic with phenyl fragments. A peak at $^m/_z$ 326 indicates the probable combination of two Me_3Sn fragments to form

$Sn_2(Me)_6$, which is a likely explanation for the insoluble white substance often seen plated on the walls of the reaction vessel.

Although fragmentation of **I** mainly occurs along the same route as **III**, other pathways of fragmentation are found to be competitive. $[Me_3SnCo(CO)_3PPh_3]^+$ mainly fragments by way of the consecutive loss of the three carbonyl ligands, but a small amount of the compound fragments by initially losing the three methyl groups (scheme 3.3). The principal ion peak is $[CoPPh_3]^+$. The numerous low intensity peaks between $^m/_z$ 183 and 364 can possibly be explained in terms of the recombination of methyl fragments with $[CoPPh_3]^+$, $[CoPPh_2]^+$ and $[CoPPh]^+$.

(Owing to the poor handling characteristics of **II** it was at the time not possible to obtain its mass spectrum.)

SCHEME 3.2


$[Me_3SnCo(CO)_3AsPh_3]^+$
$-2\ CO$
$[Me_3SnCo(CO)AsPh_3]^+$
$-CO$
$[Me_3SnCo(AsPh_3)]^+$
$-Me$
$[Me_2SnCo(AsPh_3)]^+$
$-SnMe_2$
$[CoAsPh_3]^+$
$-Ph$
$[CoAsPh_2]^+$
$-Ph$
$[CoAsPh]^+$
$-Ph$
$[CoAs]^+$
$-As$
$[Co]^+$
$-AsPh_3$
$-AsPh_2$
$-AsPh$

SCHEME 3.3

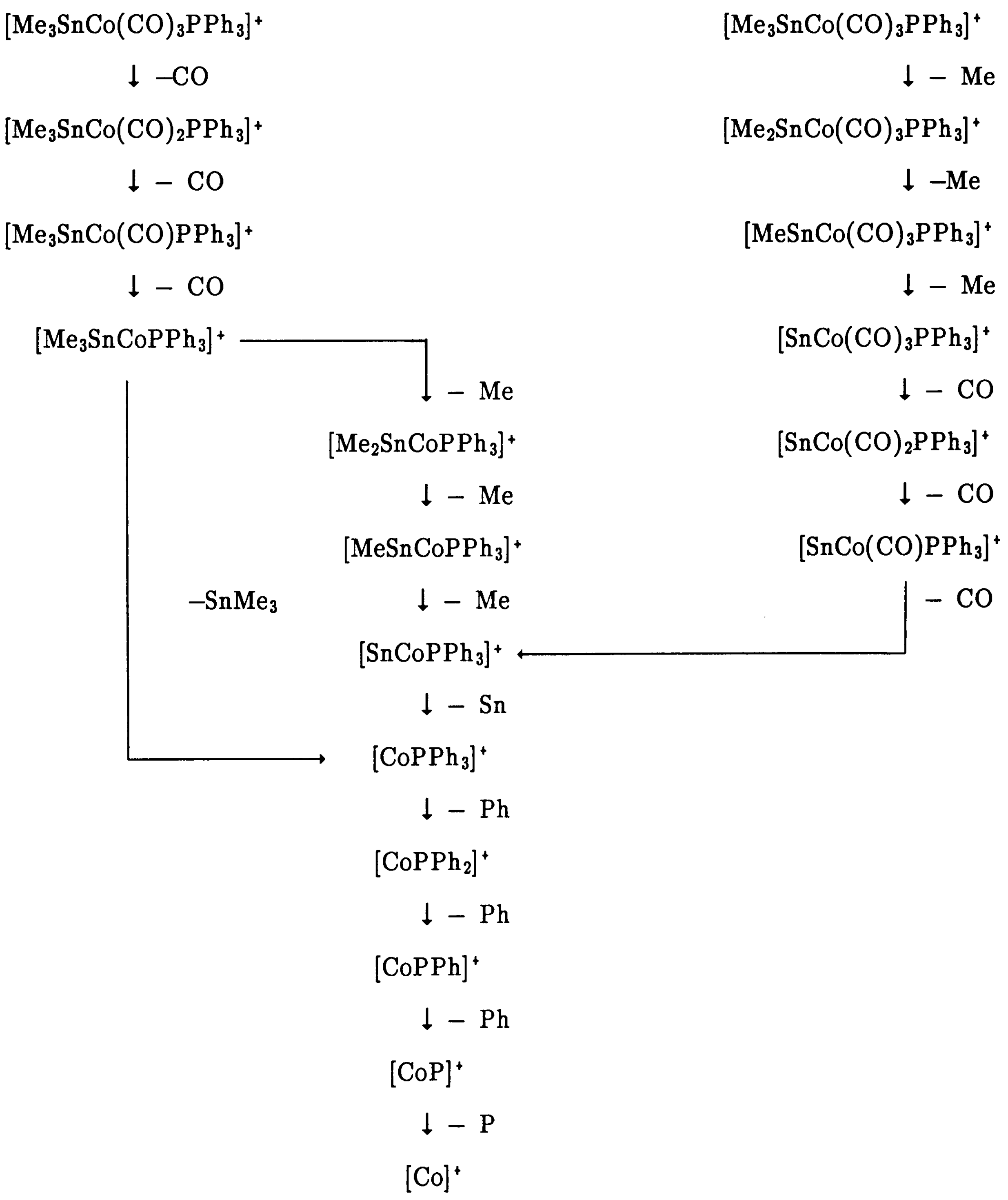

$[Me_3SnCo(CO)_3PPh_3]^+$
↓ –CO
$[Me_3SnCo(CO)_2PPh_3]^+$
↓ – CO
$[Me_3SnCo(CO)PPh_3]^+$
↓ – CO
$[Me_3SnCoPPh_3]^+$
– Me
$[Me_2SnCoPPh_3]^+$
↓ – Me
$[MeSnCoPPh_3]^+$
–SnMe₃
↓ – Me
$[SnCoPPh_3]^+$
↓ – Sn
$[CoPPh_3]^+$
↓ – Ph
$[CoPPh_2]^+$
↓ – Ph
$[CoPPh]^+$
↓ – Ph
$[CoP]^+$
↓ – P
$[Co]^+$
$[Me_3SnCo(CO)_3PPh_3]^+$
↓ – Me
$[Me_2SnCo(CO)_3PPh_3]^+$
↓ –Me
$[MeSnCo(CO)_3PPh_3]^+$
↓ – Me
$[SnCo(CO)_3PPh_3]^+$
↓ – CO
$[SnCo(CO)_2PPh_3]^+$
↓ – CO
$[SnCo(CO)PPh_3]^+$
– CO

TABLE 3.5 Mass fragments of $[Me_3SnCo(CO)_3L]$ (L = PPh_3, $AsPh_3$).[a]

Fragments	$^m/_z$	Rel. intensity
L ≡ PPh_3		
$[Me_3SnCo(CO)_3PPh_3]^+$	568	1
$[Me_3SnCo(CO)_2PPh_3]^+$	541	3
$[Me_3SnCo(CO)PPh_3]^+$	514	9
$[Me_3SnCoPPh_3]^+$	486	7
$[Me_2SnCoPPh_3]^+$	471	4
$[MeSnCoPPh_3]^+$	456	5
$[CoPPh_3]^+$	321	100
$[CoPPh_2]^+$	243	38
$[CoPPh]^+$	167	16
$[Co]^+$	59	11
L ≡ $AsPh_3$		
$[Me_3SnCo(CO)_3AsPh_3]^+$	613	5
$[Me_3SnCo(CO)AsPh_3]^+$	557	30
$[Me_3SnCoAsPh_3]^+$	529	40
$[Me_2SnCoAsPh_3]^+$	514	12
$[CoAsPh_3]^+$	365	93
$[Sn_2(Me)_6]^+$	326	1
$[CoAsPh_2]^+$	288	22
$[CoAsPh]^+$	213	17
$[Co]^+$	59	100

a. Fragments of main route only for L = PPh_3.

3.4.3 **Nmr spectroscopy.**

3.4.3.1 ^{1}H nmr

Compounds I, II and III exhibit simple ^{1}H nmr spectra, with the methyl protons showing sharp singlets in the range 0.4 – 0.8 ppm (table 3.7) and the phenyl protons showing multiplets in the range 6.8 – 7.6 ppm (table 3.6). In spite of their simplicity, the spectra contain some interesting features.

<u>Phenyl protons</u>: The phenyl protons of phosphines or arsines are usually observed as second–order multiplets. However, if the spectrum is obtained in an aromatic solvent such as benzene, the so–called "ring current" of the benzene influences the chemical shifts of some protons considerably, while those of other protons may remain unchanged. Accordingly, the expected multiplets for free PPh_3 and $AsPh_3$ are each split into two multiplets (in the ratio 2:3), the resonance of the *ortho* protons occurring on average 0.32 ppm downfield from the combined *meta* and *para* resonances. This is observed for I and III. The spectrum of II (fig. 3.1(b)) displays three distinct resonances for the *ortho*, *meta* and *para* protons of the coordinated $P(OPh)_3$ due to the presence of the electronegative oxygen. It is possible to obtain $^nJ(HH)$ coupling constants from the spectrum of II – assignments are made by comparing these with coupling constants obtained from the spectrum of free $P(OPh)_3$ (fig.3.1(a)).

TABLE 3.6 **^{1}H nmr data for [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$). (phenyl protons)[a]**

Compound	Coordinated L			Free L		
	H_o	H_m	H_p	H_o	H_m	H_p
I	7.60 (m,6H)	6.97 (m,9H)		7.38 (m,6H)	7.05 (m,9H)	
II	7.31[b] (d,6H)	7.03 (t,6H)	6.87 (t,3H)	7.15[c] (d,6H)	7.00 (t,6H)	6.83 (td,3H)
III	7.58 (m,6H)	6.98 (m,9H)		7.37 (m,6H)	7.05 (m,9H)	

a) In benzene–d_6; chemical shifts in ppm relative to TMS; coupling constants in Hz.

b) $^3J(H_pH_m) = 7.4$; $^3J(H_oH_m) = 7.9$; $^4J(H_oH_p) < 1$.

c) $^3J(H_pH_m) = 7.4$; $^3J(H_oH_m) = 8.0$; $^4J(H_oH_p) < 1$.

<u>Methyl protons</u>: The methyl protons of I, II and III are observed as sharp singlets, with that of the triphenylphosphite derivative occurring 0.3 ppm downfield from those of I and III (table 3.7). A characteristic feature on the ^{1}H nmr spectra of compounds containing a tin atom, are the satellites of the two isotopes ^{117}Sn and ^{119}Sn which appear as sharp, low intensity peaks arranged symmetrically on either side of the proton resonance line. Unfortunately resolution does not always permit distinction between the two isotopes, but in the case of III the values of $^2J(^{117}SnH)$ and $^2(J^{119}SnH)$ could be obtained. For transition metal

trimethyltin compounds, these coupling constants are typical (30 Hz – 60 Hz [48]). At an even greater distance from the proton resonance line two yet smaller peaks are visible on either side thereof. These are the ^{13}C satellites from which $^{1}J(CH) = 117.6$ Hz is obtained. These satellites are the consequence of the chance occurrence of a ^{13}C atom next to the proton:

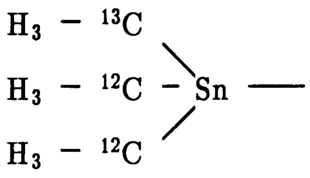


TABLE 3.7 **^{1}H nmr data for [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$). (methyl protons)**

Compound	$\delta(H)^b$	$^{2}J(^{119}SnH)$	$^{2}J(^{117}SnH)$
I	0.72 (s,9H)	48.0	
II	0.45 (s,9H)	50.0	
III	0.73 (s,9H)	50.6	49.0

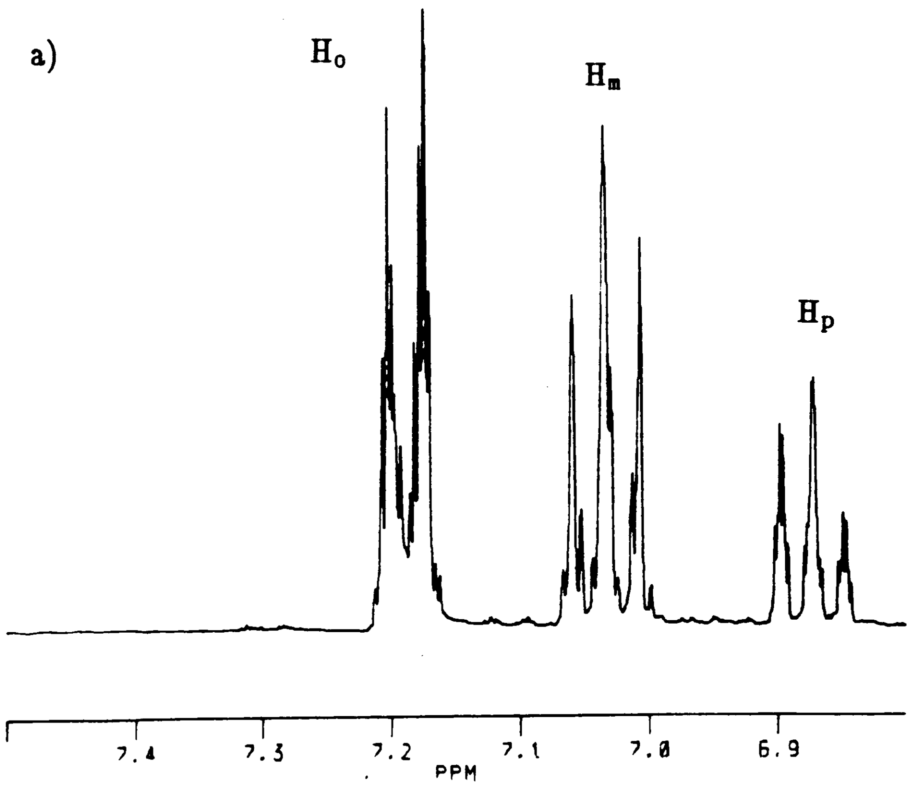
a) In benzene–d_6; chemical shifts in ppm relative to TMS; coupling constants in Hz.

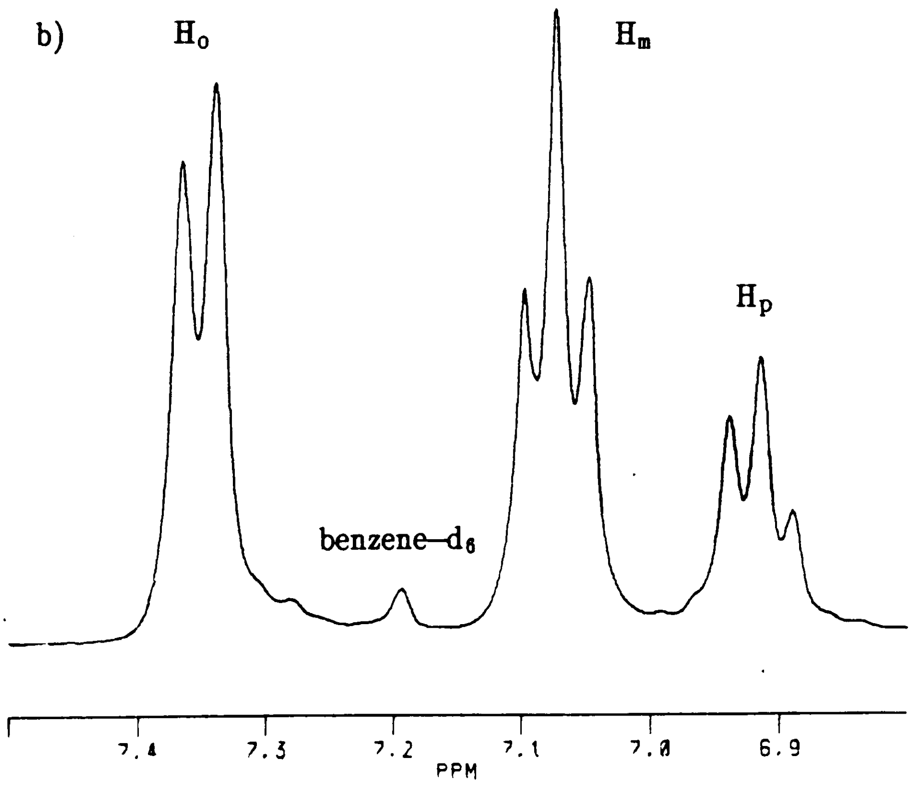
b) $Me_3SnC\ell$: $\delta = 0.32$ ppm; $^{2}J(^{119}SnH) = 58.6$; $^{2}J(^{117}SnH) = 56.1$.

FIGURE 3.1 ^{1}H nmr spectrum (phenyl region) of

a) $P(OPh)_3$

b) $[Me_3SnCo(CO)_3P(OPh)_3]$ (II)





3.4.3.2 ^{13}C nmr.

High quality $^{13}C\{^{1}H\}$ nmr spectra of I (fig. 3.2), II and III (fig. 3.3) are obtained by carefully selecting instrumental parameters.

<u>Phenyl carbons</u>: The phenyl carbons resonate in the region 150 ppm – 120 ppm. Assignments are made using one or more of the following as guidelines:

i) the $^{13}C\{^{1}H\}$ nmr spectra of free PPh_3, $P(OPh)_3$ and $AsPh_3$;
ii) relative peak intensities;
iii) the magnitude of $^{n}J(CP)$.

In general the chemical shifts of the phenyl carbons do not differ much from those of the free ligand. Also, the deshielding effects of phosphorus and arsenic on these carbons are similar: the chemical shifts of the phenyl carbons of I and III differ little.

<u>Methyl carbons</u>: The methyl carbons are shifted slightly upfield relative to those of $Me_3SnC\ell$ ($\delta(^{13}C)$ = 5.1 ppm) showing the $[Co(CO)_3L]^-$ anion to be a weaker nucleophile than $C\ell^-$. There seems to be no major movement of electron density across the Sn–Co bond: this has led to the suggestion that the Sn–Co bond is of a covalent and not a donor / acceptor nature [49].

Use of the Sn–satellite peaks on the ^{13}C spectra enables the calculation of the tin–carbon coupling constants which are found to lie in the range 265 Hz to 280 Hz. Unfortunately the resolution does not always permit distinction between ^{117}Sn and ^{119}Sn whereupon an average value is taken. Previous work on compounds with transition metal–tin bonds [34, 35] does not contain any $\delta(^{13}C)$ or $^{1}J(SnC)$ values. More recent work on compounds of the type $[Ph_3SnCo(CO)_3L]$ (L = carbene) [50, 51] showed $^{1}J(SnC)$ ranging from 280 Hz to 320 Hz.

FIGURE 3.2 $^{13}C\{^1H\}$ nmr spectrum of $[Me_3SnCo(CO)_3PPh_3]$ (I).

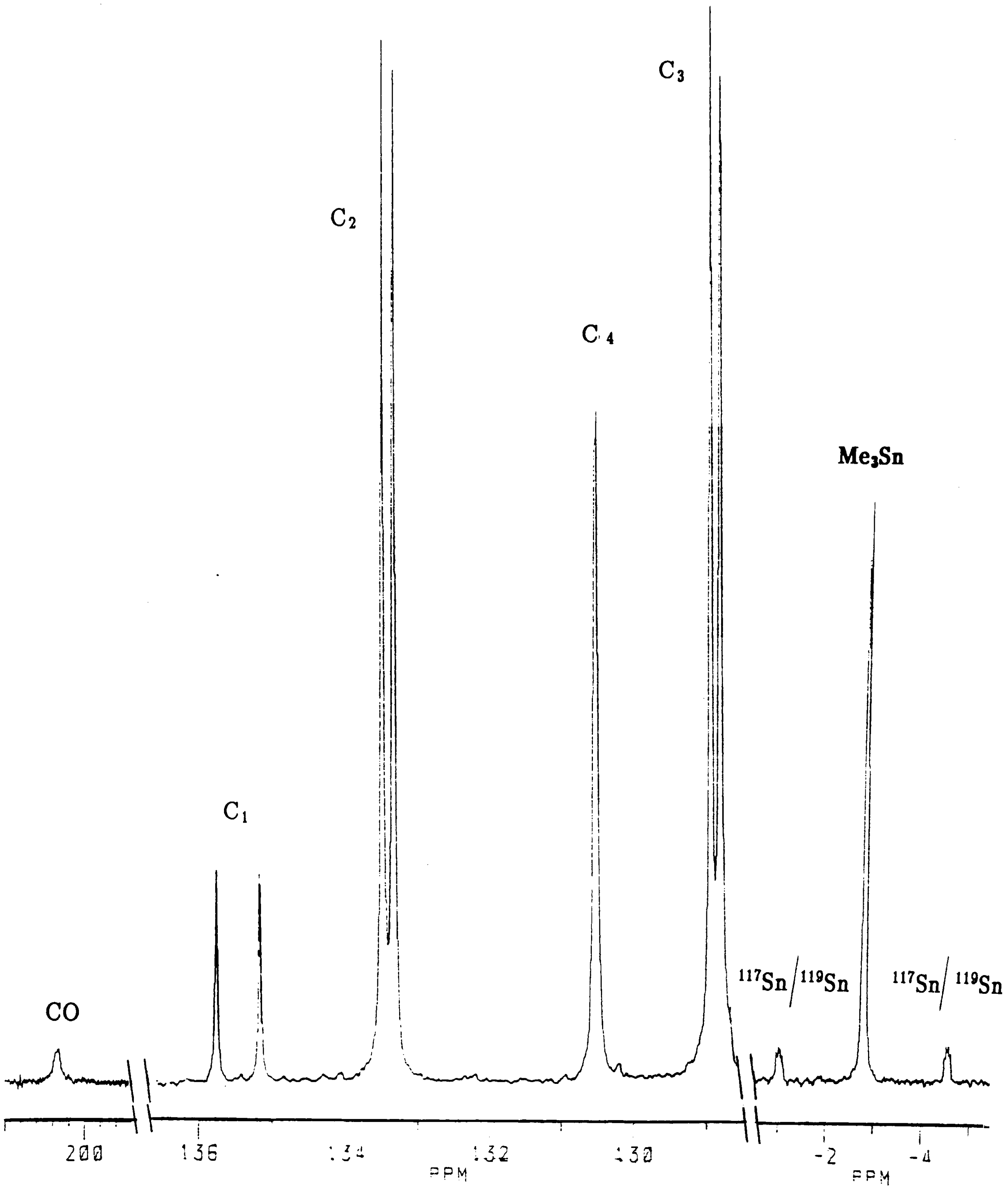
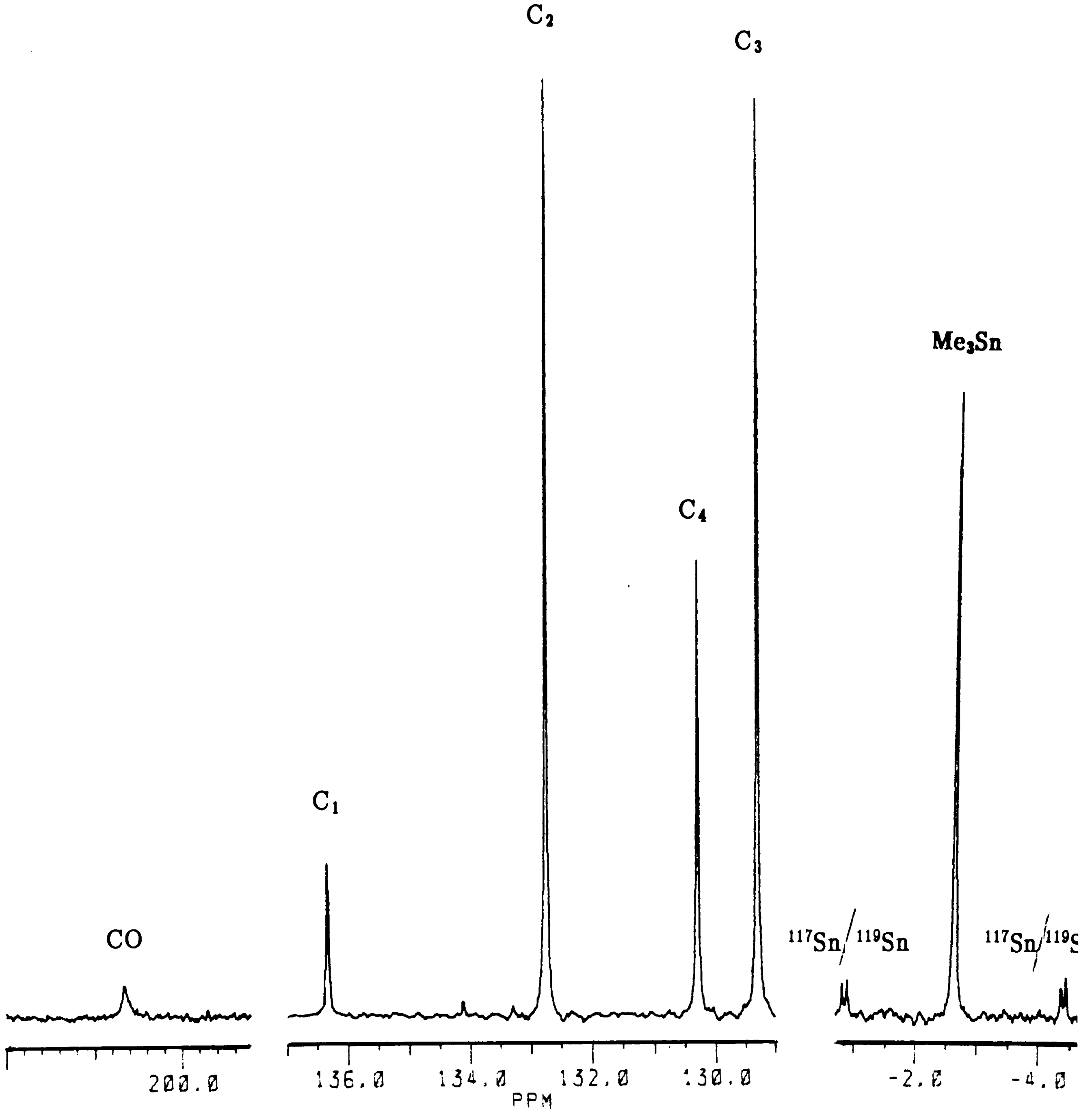


FIGURE 3.3 $^{13}C\{^1H\}$ nmr spectrum of $[Me_3SnCo(CO)_3AsPh_3]$ (III).



Carbonyl carbons: The carbonyl carbons resonate close to 200 ppm (table 3.8) and are difficult to detect. The n.q.m. of Co causes a reasonable amount of broadening of these peaks making it impossible to obtain the two–bond coupling with the phosphorus.

TABLE 3.8 $^{13}C\{^{1}H\}$ nmr data for $[Me_3SnCo(CO)_3L]$
(L = PPh_3 (I), $P(OPh)_3$ (II), $AsPh_3$ (III))[a]

Compound	$Sn(CH_3)_3$[b]	$P(C_6H_5)_3$; $P(OC_6H_5)_3$; $As(C_6H_5)_3$				CO[e]
		C_1	C_2	C_3	C_4	
I	-2.8[c] $^{1}J(SnC)=267.2$	135.4 (d) $^{1}J(PC)=44.4$	133.4 (d) $^{2}J(PC)=11.7$	128.8 (d) $^{3}J(PC)=10.2$	130.5 (s) $^{4}J(PC)=0$	201.7 (br)
II	-3.1[d] $^{1}J(SnC)=278.2$	151.5 (d) $^{2}J(PC)=5.9$	122.1 (d) $^{3}J(PC)=4.3$	130.0 (s) $^{4}J(PC)=0$	125.7 (s) $^{5}J(PC)=0$	199.5 (br)
III	-2.6 $^{1}J(^{119}SnC)=276$ $^{1}J(^{117}SnC)=263$	136.3 (s) -	132.8 (s) -	129.3 (s) -	130.3 (s) -	201.6 (br)

a. Obtained in benzene-d_6; chemical shifts in ppm relative to solvent ($\delta = 128.00$ ppm); coupling constants in Hz.

b. $^{1}J(SnC)$ is the average of $^{1}J(^{119}SnC)$ and $^{1}J(^{117}SnC)$.

c. $^{3}J(PC) = 3.0$ Hz.

d. $^{3}J(PC) = 5.5$ Hz.

e. $^{2}J(PC)$ cannot be obtained due to extensive broadening of the CO resonance by Co.

3.4.3.3 ^{31}P and ^{119}Sn nmr.

$^{31}P\{^1H\}$ nmr spectra of I and II and $^{119}Sn\{^1H\}$ nmr spectra of I, II and III are obtained by using broad–band proton noise decoupling. The ^{31}P resonances exhibit considerable broadening owing to the cobalt, whereas the ^{119}Sn peaks seem uninfluenced.

The $^{31}P\{^1H\}$ spectra of I and II each consist of a singlet ($\nu^1/_2$ = 50 Hz (I) and 160 Hz (II)) and the spectrum of I displays the Sn satellites as broadened peaks on either side of the ^{31}P signal (fig. 3.4). From this spectrum an approximate coupling constant of $^2J(PSn)$ = 236 Hz is obtained, which compares favourably with the more accurate value of 240.8 Hz obtained from the ^{119}Sn spectrum (fig. 3.5). The Sn–satellites are not as prominent on the ^{31}P spectrum of II.

In view of the weak π–acceptor abilities of phosphines and phosphites, a shift of $\delta(^{31}P)$ towards low field can be anticipated when these ligands coordinate to the metal. Experimentally, this shift is indeed found to be considerable for phosphines (table 3.9) illustrating the sensitivity of the phosphorus nucleus to its environment.

This sensivitivity is also displayed by the ^{119}Sn nucleus: the influence of Y in Me_3SnY on the shielding of the ^{119}Sn nucleus (see section 2.3.2.4) is clearly demonstrated when $[Me_3SnCo(CO)_4]$ ($\delta(^{119}Sn)$ = 151 ppm) is compared with the compounds listed in table 3.9. The stabilising influence of L on the remaining three carbonyl ligands becomes apparent as the electron density is moved away from the metal centre towards the carbonyls.

TABLE 3.9 $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ nmr data of $[Me_3SnCo(CO)_3L]$

($L = PPh_3$ (I), $P(OPh)_3$ (II), $AsPh_3$ (III)).[a]

Compound	$\delta(^{31}P)$[b]	$\delta(^{119}Sn)$	$^2J(PSn)$[c]
I	53.4[d] (–6.5)	117.3 (d)	240.8
II	130.6 (br) (121.9)	136.2 (d)	418.7
III	–	143.6 (s)	–

a. $\delta(^{31}P)$ in ppm relative to 85% H_3PO_4; $\delta(^{119}Sn)$ in ppm relative to Me_4Sn; measured in benzene–d_6; coupling constants in Hz.

b. Chemical shift of the free ligand in parentheses below.

c. Coupling constants obtained from $^{119}Sn\{^1H\}$ spectra.

d. See text.

FIGURE 3.4 $^{31}P\{^{1}H\}$ nmr spectrum of $[Me_3SnCo(CO)_3PPh_3]$ (I).

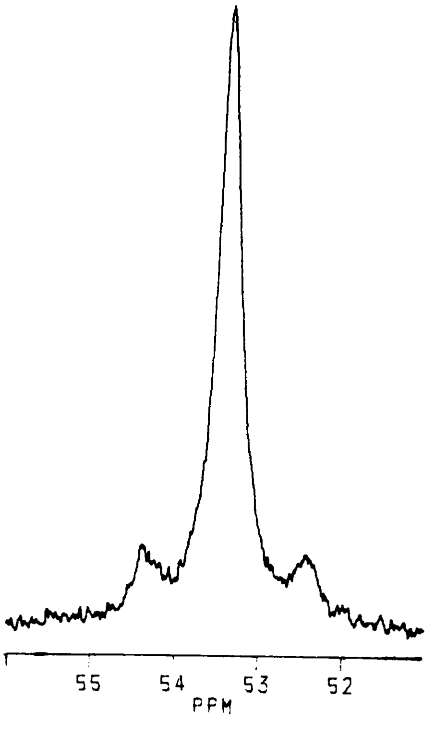
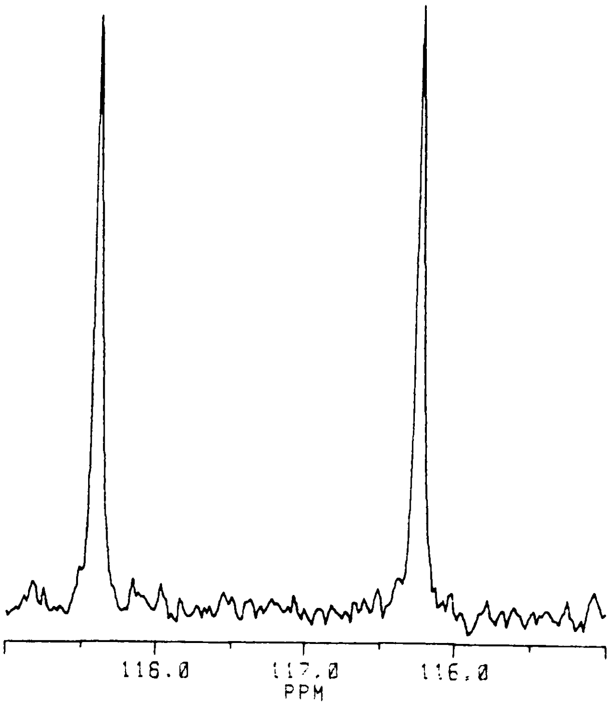


FIGURE 3 5 $^{119}Sn\{^{1}H\}$ nmr spectrum of $[Me_3SnCo(CO)_3PPh_3]$ (I).



3.4.4 **Structural considerations.**

X–ray crystal structural studies of [$Ph_3GeCo(CO)_3PPh_3$] [48, 52] and also the fact that spectroscopic data for [$Me_3SnCo(CO)_3L$] is consistent with a near ideal trigonal bipyramidal structure, deem a structural determination of **I**, **II** and **III** unnecessary. An incomplete study of the structure of [$Ph_3SnCo(CO)_3PPh_3$] was published in a journal not readily accessible [53] and only the abstract was located.

The above–mentioned X–ray study of [$Ph_3GeCo(CO)_3PPh_3$] revealed the OC–Co–CO angles to be 120^0 and the Ge–Co–P angle to be 173^0 [49]. A comparison of the structures of [$C\ell_3GeCo(CO)_4$] [54] and [$Ph_3GeCo(CO)_3PPh_3$] showed the PPh_3 to influence the OC_{eq}–Co–Ge angles. In the unsubstituted compound the equatorial carbonyls are bent away from the axial one with OC_{eq}–Co–CO_{ax} of 95^0. In the substituted compound the tendency of the carbonyls to lean towards the second metal atom is greater – even more so when going from the triphenyl to the trimethyl compound. This led some researchers to believe [49] that this tendency was merely a consequence of the need to fill space more efficiently and not of electronic factors.

3.5 CONCLUSION.

In this chapter L is spectroscopically shown to have a considerable influence on the redistribution of electron density in, and hence the stability of, compounds of the type [$XCo(CO)_3L$]. The stabilities of these compounds decrease in the order X = Ph_3Sn > Me_3Sn and L = PPh_3 > $AsPh_3$ > $P(OPh)_3$. Not only is the triphenyltin ligand a better electrophile, but it is more bulky than Me_3Sn, explaining the greater stability of its derivatives. This notwithstanding, it is shown that it is possible to prepare the trimethyltin analogues and that they are sufficiently stable to be studied spectroscopically.

Subsequent work is presented in the following chapter where the reactivity of these compounds is put to test.

3.6 EXPERIMENTAL.

All reactions are carried out under inert atmosphere using the Schlenk tube technique [55]. Solvents are distilled under nitrogen atmosphere after which they are pre–dried in the usual manner. Commercial $[Co_2(CO)_8]$ and phosphine, phosphite and arsine ligands are used without purification.

Melting points: are determined on a Gallenkamp melting point apparatus.

Elemental analyses: are determined at the DPCMT, CSIR, Pretoria or at the Mikroanalytisches Labor Pascher, Remagen, Fed. Rep. of Germany.

Infrared spectra: are recorded on a Bruker IFS 113v or a Bomem FTIR. Spectroscopic grade solvents are degassed by three freeze–thaw cycles prior to preparation of the sample solutions under N_2. Cells are purged with N_2 before introduction of the sample solutions.

Nmr spectra: are recorded on a Bruker AC300 MHz instrument at 303K. Deuterated solvents (except benzene) are degassed using liquid N_2 (as above) before use. Samples are prepared under N_2 and lids of sample tubes secured with PTFE ribbon to prevent air from entering. Spectra are obtained at the following frequencies:

^{1}H : 300.13 MHz.
^{13}C : 75.47 MHz.
^{31}P : 121.49 MHz.
^{119}Sn : 111.90 MHz.

For ^{13}C nmr spectra, approximately 20 mg sample is dissolved in 0.5 mℓ solvent. Data accumulation is done at 303K using a 45^{0} pulse delayed for 4 – 6 seconds. Usually 2000 scans are sufficient to give a high signal / noise ratio.

Mass spectra: are recorded on the Perkin–Elmer RMU–6H instrument (operating at 70 eV) at the Rand Afrikaans University.

Syntheses: Details of the syntheses have been submitted for publication [56].

3.6.1 The synthesis of [$Me_3SnCo(CO)_3PPh_3$] (I).

[$Co(CO)_3PPh_3]_2$ is poorly soluble in most common solvents. It is therefore convenient to prepare the required amount immediately prior to use and to convert the entire batch.

A solution of [$Co_2(CO)_8$] (3.42 g, 10 mmol) in 120 mℓ benzene is prepared in a 500 mℓ round bottomed flask. Triphenylphosphine (5.25 g, 20 mmol) is dissolved in 30 mℓ benzene and slowly added to the contents of the flask while vigorous stirring is maintained. The reaction mixture is refluxed for 1 hr at $80^{0}C$ until the initial orange brown colour has changed to red brown. The reaction mixture is allowed to cool whereupon the product settles out. The benzene layer is decanted and the product washed with benzene until the solvent remains colourless. The last traces of benzene are removed by washing with n–pentane. Finally the product is dried *in vacuo* (30^0C / 0.1 mm) for a few hours. (Yield > 95%; ir: ν(CO) = 1950 cm^{-1}(s), 1977 cm^{-1}(w)).

A 1% sodium amalgam is prepared in a 1ℓ two–necked round bottomed flask using 500 g mercury. The amalgam is allowed to cool to room temperature. The $[Co(CO)_3PPh_3]_2$ (prepared above) is suspended in 300 mℓ THF and added to the amalgam. The reaction mixture is stirred vigorously with a mechanical stirrer for 16 hr, whereupon it is left to stand for another 3 hr to allow the solid particles to settle. The dark yellow solution is decanted and filtered through a glass frit (porosity: fine).

Trimethyltin chloride (3.2 g, 16 mmol) – dissolved in 20 mℓ THF– is then added to the solution of $Na[Co(CO)_3PPh_3]$. This is stirred rapidly at room temperature for 30 min. After filtration (to remove NaCℓ), the solution is reduced to dryness with the aid of the vacuum pump. The residue is taken up in a minimum volume dichloromethane / hexane (1:1) and introduced to an alumina (neutral, activity III) column (15 x 3 cm) prepared in hexane. The product is eluated with hexane. Subsequent removal of the solvent under vacuum and further drying (30^0C / 0.1 mm / 1 hr) gives typically 4.4 – 5.0 g (40 – 45% based on $[Co(CO)_3PPh_3]_2$) golden yellow crystals.

3.6.2 The synthesis of $[Me_3SnCo(CO)_3P(OPh)_3]$ (II).

A solution of triphenylphosphite (5 mℓ, 19 mmol) in 10 mℓ benzene is added to a solution of $[Co_2(CO)_8]$ (3.42 g, 10 mmol) in benzene. This solution is stirred at 60^0C for 2 hr. The flask is cooled to room temperature and purification is accomplished as described for $[Co(CO)_3PPh_3]_2$ (section 3.6.1). The yield is typically 7.8 – 8.0 g (86% – 88%) $[Co(CO)_3P(OPh)_3]_2$.

A 1% (w/w) sodium amalgam is prepared in a 500 mℓ two–necked round bottomed flask using 300 g mercury. The $[Co(CO)_3P(OPh)_3]_2$ (prepared above) is suspended in 100 mℓ THF and added to the amalgam. Vigorous stirring with a mechanical stirrer (300 rpm) for 10 to 15 min followed by decantation and quick filtration reveals a yellow solution.

Trimethyltin chloride (2.32 g, 11.6 mmol) is dissolved in 20 mℓ THF and added to the filtered solution. After stirring at room temperature for 30 min, the THF is removed under vacuum (–20^{0}C / 0.1 mm). The residue is then repeatedly extracted with 20 mℓ portions of cold hexane until the latter no longer becomes yellow and the combined hexane fractions filtered and reduced to dryness to leave a dark yellow solid. Further purification is accomplished by way of repeated crystallization from hexane at –30^{0}C. The crystals are finally dried *in vacuo* (0^{0}C / 0.1 mm / 2 hr) to give 5.1 – 5.6 g (48% – 53% based on $[Co(CO)_3P(OPh)_3]_2$) of **II**.

3.6.3 The synthesis of $[Me_3SnCo(CO)_3AsPh_3]$ (III).

To a solution of $[Co_2(CO)_8]$ (1.5 g, 5 mmol) in 50 mℓ benzene a solution of triphenylarsine (2.7 g, 10 mmol) in benzene is added. After stirring at 60^{0}C for an hour, the heat is removed and the purple–red product allowed to settle. The product is purified in the same manner as $[Co(CO)_3PPh_3]$ (section 3.6.1). Yield: 3.2 g (71%) $[Co(CO)_3AsPh_3]_2$.

In a 500 mℓ two–necked round–bottomed flask a 1% sodium amalgam is prepared using 2.5 g sodium metal and 250 g mercury. The dimer (prepared above) is suspended in 100 mℓ THF and added to the amalgam. The suspension is mechanically stirred for 40 min, after which the dark red colour disappears. The suspension is quickly decanted and added to a solution of 1 g trimethyltin chloride in THF. After stirring for 30 min at room temperature, the THF is removed under reduced pressure and the residue repeatedly extracted with hexane until the latter remains colourless. The combined hexane portions are filtered and completely reduced to dryness (0^0C / 0.1 mm). The dark yellow product is taken up in 4 mℓ dichloromethane / hexane (1:1) and introduced to an alumina column (neutral, activity IV, 20 cm x 1 cm) prepared in hexane. The product is eluated with hexane which is subsequently removed under vacuum. Further drying (25^0C / 0.1 mm / 2 hr) yields 2.9 g – 3.2 g (66% – 73%) primrose yellow crystals of **III**.

CHAPTER 4

THE REACTION OF [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) WITH ISOCYANIDES.

4.1 INTRODUCTION.

Ater the successful preparation of [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) it was thought appropriate to investigate the reactivity of these compounds towards nucleophilic substitution, i.e. was it possible to replace a second carbonyl ligand? It seems that phosphines and phosphites will not replace another carbonyl. This necessitates the use of a ligand more closely resembling a carbonyl such as an isocyanide.

Although there are only subtle differences between the π–acceptor and σ–donor properties of isocyanides and carbonyls, isocyanides are polar and are good bases compared to carbonyls [57]. Also, the properties of isocyanides can be varied by changing the R–group: aryl isocyanides are better π–acceptors than alkyl isocyanides.

Considering the relative instability of the compounds [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) in solution, ways of replacing a carbonyl ligand without using forcing conditions have to be pursued.

In this chapter the reactions of [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) with CNR (R = t–Bu, Ph, 2,6–dimethylphenyl) are described.

4.2 THE REACTION OF [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) WITH CNR (R = t–Bu, Ph, 2,6–dimethylphenyl).

Attempts to replace a carbonyl ligand by heating in the presence of excess isocyanide merely leads to the recovery of starting material in the case of L = PPh_3 and to decomposition of the starting material when L = $P(OPh)_3$ and $AsPh_3$.

Although photoinduction has been used to prepare $CpMn(CNR)_3$ (R = Me, Ph) [58], it has a limited application, presumably because of the polimerization of isocyanides. It is therefore not unexpected that this method of attempted labilization of a carbonyl did not meet with any success.

Finally it was decided to employ a chemical reagent to enhance substitution. The oxidizing agent trimethylamine–N–oxide (Me_3NO) has been used extensively for this purpose [59]. This reagent is purified by initial azeotropic drying with toluene followed by sublimation (60°C / 0.1 mm). Although it has a limited solubility in non–polar solvents, it can either be added in the solid form or suspended in benzene prior to addition.

Me_3NO is added to [$Me_3SnCo(CO)_3L$] in the presence of excess isocyanide. Stirring at 40°C for 2 – 4 hours results in the slow evolution of CO_2 while a purple–blue solid plates out onto the reaction vessel. Nmr spectroscopy shows this compound to be paramagnetic – it also rapidly decomposes in the acetone–d_6 – presumably a Co(II) complex. A purple–blue compound has previously been observed in reactions of organocobalt compounds with isocyanides [60], but it could also not be identified. No further attempts are therefore made to characterise this byproduct.

Progress of the reaction is initially monitored with tlc, but during further reactions the advanced formation of the plated compound as well as the reaction mixture taking on a orange–brown colour is taken to indicate completion thereof. Before product separation on a column, the excess isocyanide has to be removed. In the case of 2,6–dimethyl isocyanide (which is a solid) this proves quite difficult and sometimes more than one column separation is necessary due to some of the remaining isocyanide causing the bands to tail. Column separation of each product mixture results in a smaller orange band followed by a larger orange band. The first band can be eluted with a dichloromethane / hexane mixture which indicates that it probably contains a neutral compound.

The reaction seems to be poorly reproducible as sometimes either none of the first product forms or the band is too small to be observed on the column. This possibly indicates that the first product is a precursor of the second product.

The second product is a salt and is precipitated with NH_4PF_6.

4.3 RESULTS AND DISCUSSION.

Nine reactions were attempted:

$$[Me_3SnCo(CO)_3L] + 4Me_3NO + 4CNR \longrightarrow Product_1 + Product_2$$

Reaction 1: L = PPh_3, R = t–Bu
Reaction 2: L = PPh_3, R = Ph
Reaction 3: L = PPh_3, R = 2,6–dimethylphenyl
Reaction 4: L = $P(OPh)_3$, R = t–Bu

Reaction 5: L = $P(OPh)_3$, R = Ph

Reaction 6: L = $P(OPh)_3$, R = 2,6–dimethylphenyl

Reaction 7: L = $AsPh_3$, R = t–Bu

Reaction 8: L = $AsPh_3$, R = Ph

Reaction 9: L = $AsPh_3$, R = 2,6–dimethylphenyl

Of these, both $product_1$ and $product_2$ obtained in reactions 3 to 9 are extremely unstable oils and numerous attempts to obtain spectra resulted in failure. Only reaction 1 results in solid products ($product_1$ = **IVA**, $product_2$ = **IVB**) which can be characterised without decomposing. From reaction 2, one of the products ($product_1$ = **V**) can be isolated. Some properties of these products are given in table 4.1.

TABLE 4.1 Some physical properties of IVA, IVB and V.

Compound	Reaction	Colour	State	Mp (^0C)
IVA	1	orange	solid	215–217 (dec)
IVB	1	orange	solid	230–233 (dec)
V	2	brown	oil	–

IVA gives confusing ^1H nmr spectra, but this is thought to be the result of varying amounts of a high–boiling organic compound which cannot easily be removed (cobalt is known to be a catalyst for the conversion of isocyanides into a variety of organic products [61]). Nevertheless, the ^1H nmr spectrum shows that **IVA** does not contain the trimethyltin ligand. This is confirmed with $^{119}Sn\{^1H\}$ nmr. Apart from this it can be confirmed that the complex contains two carbonyl (ir), one isocyanide (ir, ^{13}C nmr) and at least one triphenylphosphine ligand (^1H,

^{13}C and ^{31}P nmr).

V is an unstable dark brown oil of which a ^{1}H nmr spectrum could be obtained in spite of it having a fleeting existence in the acetone–d_6.

IVB was characterised as *trans*–[Co(t–BuNC)$_3$(PPh$_3$)$_2$][PF$_6$]. This is a known compound which has previously been prepared from [Co(t–BuNC)$_5$]PF$_6$ though using much harsher reaction conditions [62].

The spectra of these compounds are discussed further in the following section on spectroscopy.

4.4 SPECTROSCOPY.

4.4.1 Infrared spectroscopy.

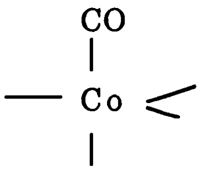
The presence of two bands in the carbonyl region points to two carbonyl ligands with OC–Co–CO < 180^0 for **IVA**.

TABLE 4.2 Infrared spectroscopic data for compounds IVA and IVB.[a]

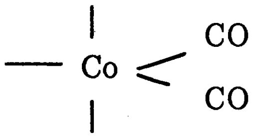
Compound	ν(CO) (cm^{-1})		ν(CN) (cm^{-1})
IVA	1884	1873	2071
IVB	–	–	2076

a) KBr pellet.

Structures consistent with this observation are the following:



1



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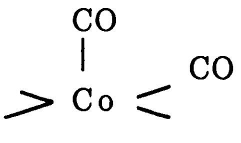

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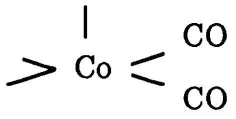
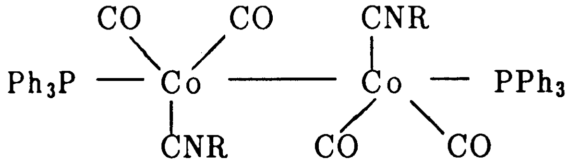


4

In view of the general preference especially for five–coordinate transition metal d^8 compounds to adopt trigonal bipyramidal configurations [63, 64] and the fact that the starting compounds have this geometry with the three carbonyls occupying equatorial sites, structure 2 is favoured for **IVA**. From ir data alone it is not possible to comment on the position of the isocyanide ligand, but presumably it occupies an equatorial site as it has replaced a carbonyl.

The lowering of ν(CN) by 73 cm^{-1} (as compared to 2144 cm^{-1} for the free ligand [65]) is rather small and shows the σ–donor influence of the isocyanide to overrule the π–acceptor influence in this particular case [66]. This is reflected in the considerable lowering of the carbonyl frequencies, which can only be a consequence of the replacement of the third carbonyl by a weaker π–acceptor. The possibility of **IVA** being a dimer cannot be ruled out:



but is not pursued further due to the lack of evidence. The phenyl isocyanide analogue, **V**, unfortunately is too unstable to obtain an infrared spectrum.

For **IVB** a single band is observed in the C≡N region, while no bands due to C≡O bonds are detected. A literature search reveals that the ir spectrum of this compound corresponds with that of an existing compound, *trans*–$[Co(t{-}BuNC)_3(PPh_3)_2]PF_6$ [62].

4.4.2 **Mass spectroscopy.**

Interpretation of the mass spectrum of **IVA** is complicated by the fact that it is not known whether the molecular ion peak is observed or not, but it is nevertheless possible to assign some of the mass peaks (table 4.3).

TABLE 4.3 Mass spectral data for IVA (incomplete).

Fragment	$^m/_z$	Rel. intensity
M^+	n.o.	
$[Co(CO)_2(t{-}BuNC)PPh_3]^+$	460	2
$[Co(t{-}BuNC)PPh_3]^+$	404	2
$[Co(PPh_3)]^+$	321	1
$[PPh_3]^+$	262	100
$[CoP]^+$	90	3
$[Co]^+$	59	2

From the relative intensities of the mass peaks, it is obvious that the complex disintegrates completely upon impact with the electron beam. Although the mass spectrum does not provide conclusive evidence towards identifying **IVA**, the absence of mass peaks at $^m/_z$ 119 (Sn) and $^m/_z$ 164 (Me_3Sn) confirms the absence of the trimethyltin ligand.

No mass spectra were obtained of **IVB** and **V**.

4.4.3 Nmr spectroscopy.

4.4.3.1 ^1H nmr.

The spectrum of **IVA** is consistent with one triphenylphosphine and one isocyanide ligand per molecule, whereas that of **IVB** integrates for three isocyanide and two triphenylphosphine ligands. The ^1H nmr spectrum of free t–BuNC consists of a triplet ($J \approx 2Hz$) which is due to long–range coupling of the ^{14}N nucleus ($I = 1$) with the protons. Upon coordination this triplet collapses to a singlet with a concomitant upfield shift. This is observed for **IVA** as well as for **IVB** and is not unusual for coordinated alkyl isocyanides [57].

The ^1H spectrum of **V** shows several peaks due to decomposition products as a consequence of its instability in acetone solution. The protons of the isocyanide ligand occur as three well–resolved peaks upfield from those of the PPh_3 ligand. By way of comparison with the spectrum of free PhNC, coupling constants can be obtained for **V**.

As before, the protons show little change in chemical shift upon coordination of the ligands.

TABLE 4.4 **^{1}H nmr data for IVA, IVB and V.^{a}**

Compound	t–BuNC	PPh_3	PhNC		
			H_o	H_m	H_p
IVA	0.72	7.61	–	–	–
	(s,9H)	(m,15H)	–	–	
IVB	0.72	7.59	–	–	–
	(s,27H)	(m,15H)	–	–	–
V	–	7.56	7.21	7.46	6.93
		(m,15H)	(td,2H)	(dt,2H)	(tt,1H)
			$^4J(H_oH_p)=1$	$^3J(H_oH_m)=8$	$^3J(H_pH_m)=7$
Free	1.43	7.32	7.06	6.66	6.60
ligand	(t)	(m)	(td,2H)	(dt,2H)	(tt,1H)
	$^4J(^{14}NH)=2$		$^4J(H_oH_p)=1$	$^3J(H_oH_m)=7$	$^3J(H_pH_m)=7$

a) Obtained in acetone–d_6; chemical shifts in ppm relative to the solvent (δ = 2.04 ppm); coupling constants in Hz.
Abbreviations: td = triplet of doublets; dt = doublet of triplets; tt = triplet of triplets.

4.4.3.2 ^{13}C nmr.

The ^{13}C nmr spectra of numerous isocyanide complexes have been recorded. In many cases difficulties were, however, experienced in observing the sp carbon [67]. The chemical shift of the sp carbon is known to exhibit considerably greater sensitivity to changes in bonding and molecular structure than carbonyls, but is generally observed in the range 105 – 175 ppm [68]. In this work, the sp isocyanide carbon of **IVA** and **IVB** is observed as a broad triplet with a chemical shift not much different from that of the free ligand, but with a considerably larger nitrogen–carbon coupling constant (table 4.5). Due to the lack of published data specifically on cobalt isocyanide complexes (even in recent work the sp carbon of the isocyanide seems not to have been observed [60, 61]) it is difficult to make generalizations regarding the distribution of electron density in the molecules. In $[Co_2(t\text{–}BuNC)_8]$ [69] where a great extent of metal⟶ligand back bonding can be expected, a downfield shift of approximately 20 ppm was observed for the sp carbons of the terminally bonded ligands. It can thus be concluded that π–back bonding to the isocyanide ligand does not play an important role in **IVA** and **IVB**.

The appearance of the phenyl carbon resonances as triplets can only be the result of the presence of a second spin–$^1/_2$ nucleus other than C or H in the complex. This is a good example of what is known as a deceptively simple spectrum, but where each carbon actually forms the X–part of an AA'X spin system (A and A' are the other two nuclei with $I = {}^1/_2$). The resonance of C_1 is a 1:2:1 triplet (fig.4.1) which implies quite a large value for J(AA') (a few hundred Hz) [25]. This is consistent with two phosphines in a *trans* arrangement. These spectra do not allow the calculation of first order coupling constants (see chapter 5) – only average values can be obtained (table 4.4).

The remarkable resemblance of the ^{13}C spectra of **IVA** and **IVB** remains inexplicable in view of the different physical properties and ir spectra of these two compounds.

FIGURE 4.1 $^{13}C\{^{1}H\}$ nmr spectrum of IVA (low field region).

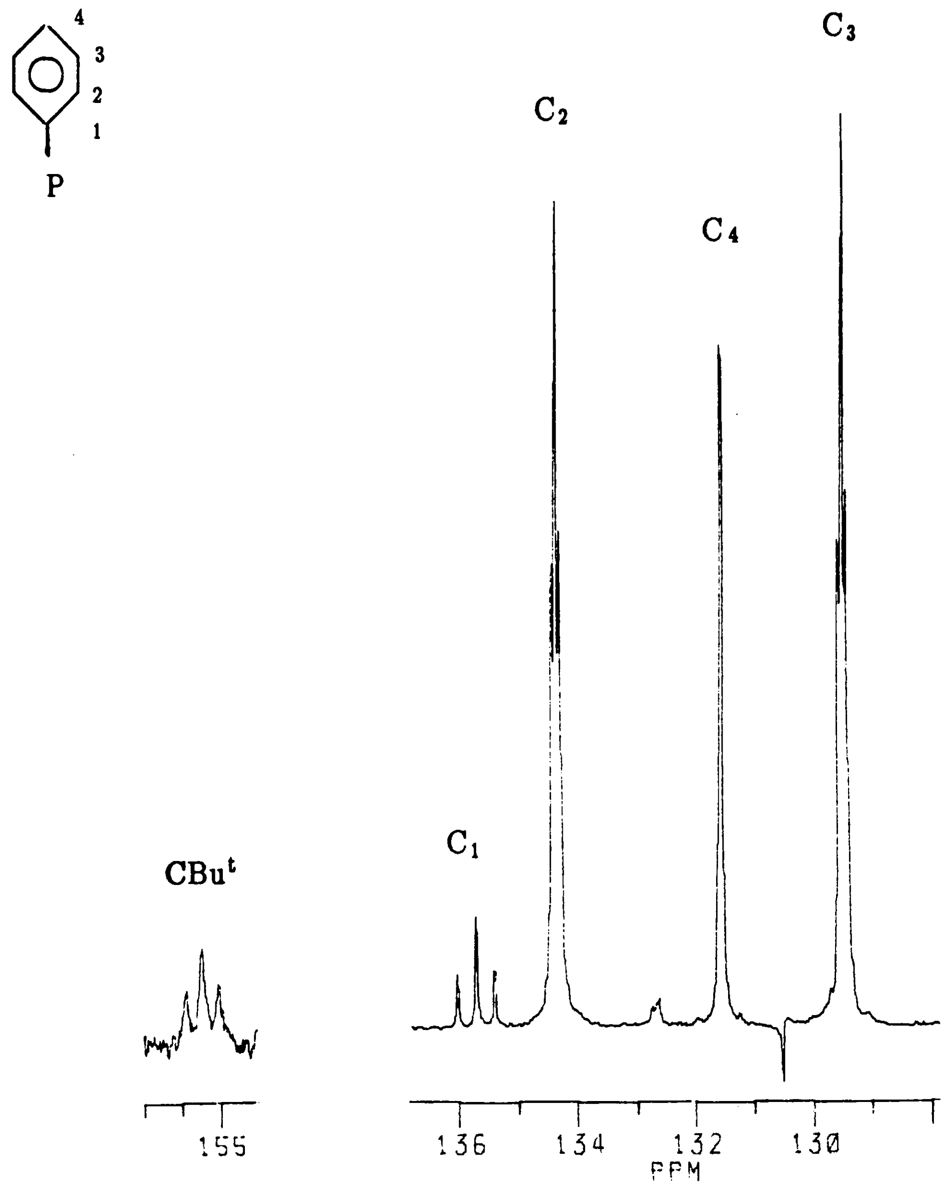


TABLE 4.5 $^{13}C\{^1H\}$ nmr data for the isocyanide complexes IVA and IVB.[a,b]

Compound	t–BuNc			PPh$_3$				CO[d]
	CBu^t	CNCMe$_3$	CNC(CH$_3$)$_3$	C$_1$	C$_2$	C$_3$	C$_4$	
IVA	155.4 (t) J=33.3[e]	56.9 (s)	29.5 (s)	135.5 (t[c]) J=24	134.4 (t[c]) J=5.1	129.5 (t[c]) J=4.7	131.5 (s)	153.6 (br)
IVB	155.4 (t) J=34	56.9 (s)	29.7 (s)	135.7 (t[c]) J=24	134.3 (t[c]) J=5.2	129.5 (t[c]) J=4.8	131.5 (s)	–
Free ligand	154.9 (t) J=3.4[e]	54.4 (s) J<1	30.8 (s) –	137.9 (d) J=–11.6	134.1 (d) J=20	129.1 (d) J=7	129.3 (s)	

a. Chemical shifts in ppm relative to acetone–d$_6$ (δ = 29.8 ppm); coupling constants in Hz.

b. No ^{13}C spectrum was obtained for **V**.

c. Spin–system: AA'X (see text).

d. $^2J(PC)$ could not be obtained as a result of broadening of the resonance by ^{59}Co ($I = {}^7/_2$).

e. $^1J(^{14}NC)$

4.4.3.3 ^{31}P nmr.

A single severely broadened resonance is observed on each of the ^{31}P spectra of **IVA** and **IVB**. It is thus not possible to comment on the number of equivalent phosphorus nuclei per molecule. Further, each resonance shows the usual large downfield shift of δP for coordinated PPh_3.

TABLE 4.6 $^{31}P\{^1H\}$ nmr data for IVA, IVB and V.[a]

Compound	$\delta(P)$
IVA	70.6
IVB	70.6
V	b
Free ligand	–6.5

a) Chemical shifts in ppm relative to 85% H_3PO_4; measured in acetone–d_6.

b) Not obtained owing to instability of the compound.

4.5 CONCLUSION.

Conflicting spectral evidence does not enable the products to be identified unanimously. Although four of the five ligands of **IVA** can be identified, the nature of the fifth remains evasive.

Even though crystals suitable for an X–ray structure determination were obtained and measured, considerable difficulties encountered during attempts to resolve the structure eventually resulted in failure to do so.

The reactivity of the compounds [$Me_3SnCo(CO)_3L$] (L = PPh_3, $P(OPh)_3$, $AsPh_3$) warrants comment. Attempts to substitute the third carbonyl by an isocyanide ligand are not successful as at least the trimethyltin group is also replaced and in the extreme case the cobalt is even oxidized. The question still remains: what is the influence of X on the reactivity of compounds of the type [$XCo(CO)_3L$]? This will be discussed in the following chapter.

4.6 EXPERIMENTAL.

The instruments / conditions used are described in section 3.5.

^{13}C nmr spectra: Approximately 60 mg sample is dissolved in 0.7 ml acetone–d_6. Data accumulation is done at 303K using a 45^0 pulse of duration 24 μs which is delayed for 2s. Although a satisfactory signal/ noise ratio is obtained after a few hundred scans, detection of the carbonyl resonance requires a few thousand scans.

Syntheses: The following general method is used to prepare all the isocyanide complexes:

[$Me_3SnCo(CO)_3L$] (0.5 g, 0.87 mmol) is dissolved in 10 mℓ benzene. To this is added Me_3NO (0.264 g, 3.5 mmol) suspended in 3 mℓ benzene, as well as 3.5 mmol of the isocyanide. After stirring at 40^0C for 3 hours, the reaction mixture is filtered and its volume reduced to 3 mℓ. Upon the addition of an equal volume of hexane, the product mixture separates as an oily brown mass. This is washed with 2x10 mℓ hexane.

The product mixture is then dissolved in a minimum volume dichloromethane / hexane (1:1) and introduced to a 12 cm x 1 cm alumina column (neutral, activity V) packed in hexane. Unreacted starting compound is eluated with hexane and an orange band (product$_1$) with dichloromethane / hexane (1:1). This band yields 0.06 – 0.195 g of product.

A second orange band (product$_2$) is eluated with ethanol / dichloromethane (1:5). This solution is reduced to dryness and the contents dissolved in ethanol. NH_4PF_6 (0.1 g) is dissolved in 5 mℓ ethanol and added to this solution dropwise whilst stirring. For reaction 1 (see section 4.3) an orange solid and for the other reactions an orange oil starts precipitating. Stirring is continued for an hour at room temperature. The ethanol is decanted and the precipitate washed with more ethanol until the solvent remained colourless. Further drying (30^{0}C / 0.1 mm) yielded 0.07 – 0.085 g product$_2$.

CHAPTER 5

THE REACTION OF BIS(TERTIARY PHOSPHINES) WITH π–ALLYL TRICARBONYL COBALT

5.1 INTRODUCTION

In view of difficulties experienced with the tin ligand in complexes of the type [$Me_3SnCo(CO)_3L$] (e.g. its tendency to detach itself from the cobalt), the quest for a suitable electrophilic reagent had to continue. In the event of such an electrophilic ligand coordinating to the cobalt by way of a single bond, bulkiness was found to be the factor determining the stability of the resulting neutral complex. It was therefore decided to employ a ligand which was, apart from the single σ–bond, capable of forming a second bond to the metal centre possibly rendering bulkiness superfluous. Although the η^5–cyclopentadienyl ligand is excellently suited for this purpose, its use in this regard has been extensive. The η^3–allyl ligand, though not invoking a comparable stability, has been far less extensively used, leaving great scope for the preparation of new complexes.

Also, from an nmr point of view, the allyl ligand with its variety of magnetically inequivalent nuclei makes interesting study material.

5.2 REVIEW.

Treatment of the cobalttetracarbonyl anion with an allylhalide results in compounds of the type (π–allyl)$Co(CO)_3$, which is the most common way in which these compounds have been prepared (method 1) [70]:

Method 1:

$$R–CH=CH–CH_2–X + Na[Co(CO)_4] \longrightarrow (\pi–RC_3H_4)Co(CO)_3 + NaX$$

Another method involves the reaction of 1,3–dienes with the cobalt hydride (method 2) [71]:

Method 2:

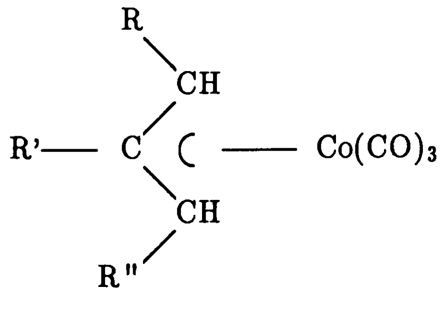
$$R–CH=CH–CH=CH_2 + H[Co(CO)_4] \longrightarrow (\pi–RC_3H_4)Co(CO)_4$$

More recently, the preparation was done by means of a phase transfer reaction to give excellent yields (method 3) [72]:

Method 3:

$$R–CH=CH–CH_2–X + Co_2(CO)_8 \xrightarrow[NaOH,\ benzene]{Et_3BzN^+Cl^-} (\pi–RC_3H_4)Co(CO)_3$$

Compounds of the type



have been the subject of quite a few studies in which the effect of the R–groups on the overall stability has been determined [70,84]. These compounds are unstable, volatile oils from which, given suitable conditions, the allyl group can detach itself with relative ease, making them excellent catalysts for organic syntheses [73,74].

Compounds of the type (π–RC_3H_4)Co(CO)$_3$ readily react with nucleophiles such as phosphorus donors to give complexes of the type (π–RC_3H_4)Co(CO)$_2$L which can be isolated in the solid state. Nucleophiles such as PPh_3 [76], PBu_3 [71], $PMePh_2$ [70], PEt_2Ph, $PEtPh_2$, PBu_2Ph, $P(OPh)_3$ and $AsPh_3$ [75] have been used, but isolation of the substituted product was only achieved in the first three cases – the others were identified in solution. These products were usually characterized by means of their infrared spectra: a crystal structure determination as well as some nmr data of (π–C_3H_5)Co(CO)$_2$(PPh_3) has only appeared more recently [76].

5.3 SYNTHESES.

5.3.1 Introduction.

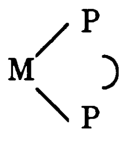
The reactions of (π–allyl)Co(CO)$_3$ with bis(tertiary phosphines) have not yet been investigated. It was decided to study the reactivity of (π–RC_3H_4)Co(CO)$_3$ towards dppm and dppe in order to make a comparison with the known compound (π–C_3H_5)Co(CO)$_2$(PPh_3) and to compare the stability of these compounds with those prepared in chapters 3 and 4.

An interesting possibility arising when a bis(phosphine) is used, is whether it coordinates as either

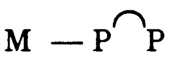
i) a bidentate ligand,

ii) a monodentate ligand with one coordinated phosphorus atom and one so–called "dangling" phosphorus atom,

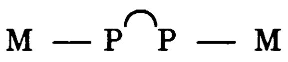
iii) a bridged ligand.



(i)



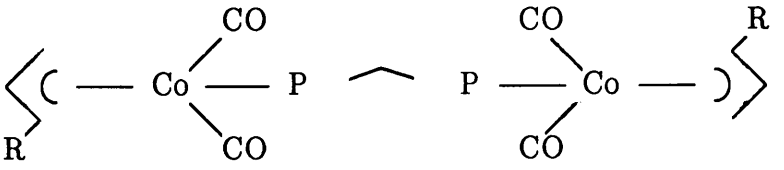
(ii)



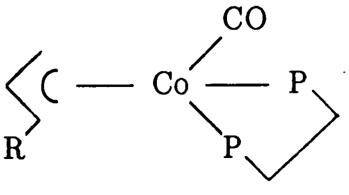
(iii)

The manner of coordination has been found to be dependent on the magnitude of n in $Ph_2P(CH_2)_nPPh_2$, the tendency to chelate being greatest for n = 2. For n = 1 the strain involved to form a four–membered ring often does not permit chelation. This is particularly so for metal atoms preferring square pyramidal or trigonal bipyramidal coordination geometries [77].

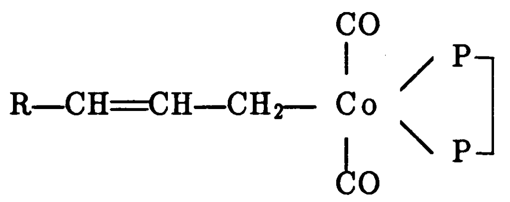
It was therefore anticipated that the reaction of $(\pi\text{–}RC_3H_4)Co(CO)_3$ with dppm would afford dimers of the type



and that its reaction with dppe would possibly result in the formation of

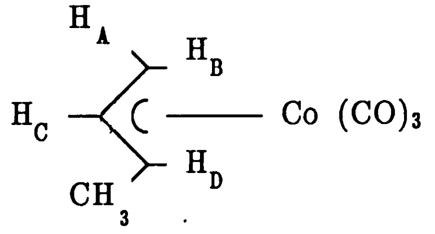


or perhaps in the enforced ring opening of the π–allyl to give:



5.3.2 The synthesis of (π–RC_3H_4)$Co(CO)_3$.

(π–RC_3H_4)$Co(CO)_3$ (R = H, CH_3) is synthesised according to a modified version of that of Heck [70]. This is best done by the addition of 1 eq of the allylchloride to a freshly prepared solution of $Na[Co(CO)_4]$ in THF at –10°C [78]. After stirring overnight, (π–C_3H_5)$Co(CO)_3$ can be obtained in good yield. The reaction of the methylallyl chloride ("crotyl" chloride) with $Na[Co(CO)_4]$ requires stirring overnight at –10°C and additional stirring at room temperature for 4 – 6 hours. The latter reaction can conveniently be monitored by means of ^1H nmr spectroscopy: a 3 mL sample is removed from the reaction mixture, reduced to dryness and a spectrum obtained in acetone–d_6. The disappearance of the broad peaks at δ = 1.78 ppm and δ = 3.61 ppm and the appearance of doublets at δ = 1.63 ppm (CH_3,3H), δ = 2.20 ppm (H_B,1H) and δ = 3.10 ppm (H_A,1H), a multiplet at δ = 3.4 ppm (H_D,1H) and a septet at δ = 4.9 ppm (H_C,1H) indicates the formation of the desired product:



Alternatively, (π–RC_3H_4)Co(CO)$_3$ is prepared by making use of a phase–transfer catalyst. This is a well–known way to prepare various organometallic compounds; a review has appeared [82]. This method [72] was successfully used to prepare (π–RC_3H_4)Co(CO)$_3$ (R = H, CH_3). However, the authors offered little advice on obtaining the compounds in a pure state which appeared to be of the utmost importance for further reaction. This will be discussed further in section 5.3.3.

5.3.3 The reaction of (π–RC_3H_4)Co(CO)$_3$ with bis(tertiary phosphines).

This can be done in one of the following ways:

i) initial preparation of the cobalt phosphine dimer, followed by cleavage
   (as described in chapter 3) and treatment with the allylchloride;

ii) preparation of the (π–allyl)Co(CO)$_3$ followed by addition of the phosphine.

i) The dimer [Co(CO)$_2$(P–P)]$_2$, obtained after the treatment of [$Co_2(CO)_8$] with dppe, is an unstable brown solid which is not suitable for reduction on an amalgam [80]. The reaction of [$Co_2(CO)_8$] with dppm resulted in the formation of [$Co_2(CO)_6$(μ–dppm)] [81] which would, upon reductive cleavage, lead to more than one product and not necessarily to the desired monomer [Co(CO)$_3$(η^1–dppm)]$^-$ as monodentate bis(phosphines) are known to be quite unstable. This route to the preparation of π–allyl cobalt phosphines was therefore not investigated any further.

ii) Compounds of the type (π–allyl)Co(CO)$_2$(phosphine) are prepared by adding an equimolar amount of the phosphine to the (π–allyl)Co(CO)$_3$ in THF. Reactions are taken to be complete when the evolution of CO is no longer visible and the solutions have taken on a bright orange colour. Subsequent work–up leads to the recovery of pale orange to orange solids in reasonable yields. The characterisation of these compounds will be discussed in section 5.3.4.

Alternatively, the compounds (π–allyl)Co(CO)$_3$ are prepared using a phase–transfer catalyst after which they are reacted with the phosphine. Preparation of (π–allyl)Co(CO)$_3$ in this way results in an impure benzene solution of the compound from which a pure benzene solution thereof can be obtained by vacuum distillation.

Treatment of these solutions of (π–allyl)Co(CO)$_3$ with the bis(phosphines) dppm and dppe result in only minute amounts of the substituted product and mainly recovery of unreacted phosphine as determined with ^{31}P nmr. It appears that the substitution of a carbonyl ligand by the phosphine in benzene is either i) very slow so that the (π–allyl)Co(CO)$_3$ decomposes at ambient temperature in solution before it can be stabilised by the phosphine or ii) that a non–polar solvent such as benzene does not facilitate substitution.

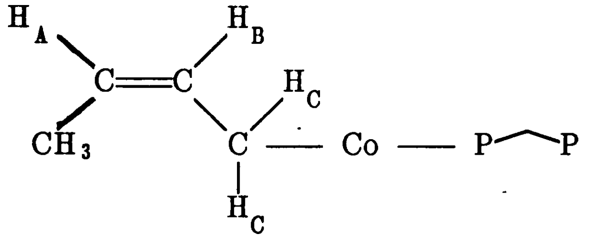
It was therefore attempted to labilise the carbonyl ligand. Addition of Me$_3$NO followed by addition of the bis(phosphine) to the solution of (π–RC$_3$H$_4$)Co(CO)$_3$ in benzene at 10^{0}C results in the rapid evolution of gas and the disappearance of the insoluble Me$_3$NO. Good yields of the substituted products are obtained as determined with ^{31}P{^{1}H} nmr and confirmed with ^{1}H nmr and ir spectroscopy. However, the reaction using Me$_3$NO appears to be of poor reproducibility as some attempts at substitution resulted in failure. The alternative method (in THF) was found to be less problematical and was therefore used in all subsequent preparations.

5.4 RESULTS AND DISCUSSION.

5.4.1 σ–Allyl compounds.

During some of the initial attempts to prepare the phosphine–substituted compounds, some pale yellow product, which rapidly turned brown at room temperature, was also obtained. In the case of the reaction of $(RC_3H_4)Co(CO)_3$ ($R = CH_3$) with dppm, the ^1H nmr spectrum did not reveal a π–coordinated allyl ligand and the ^{31}P nmr spectrum showed two doublets. Considering the known instability of cobalt alkyls, (σ–allyl)$Co(CO)_3$(η^1–dppm), **VI**, was thought to be a possibility. The absence of a carbonyl band below 1800 cm^{-1} on the ir spectrum confirmed that it was not an acyl, i.e. (σ–allyl)(CO)$Co(CO)_3$(η^1–dppm).

In order to obtain more information on this unstable compound, it was decided to specifically attempt the synthesis of the σ–allyl compound by adding allylchloride to a THF solution of $Na[Co(CO)_4]$ and dppm at –10°C. The ir, ^1H and $^{31}P\{^1H\}$ nmr spectra obtained from this pale yellow product are identical to those previously obtained. It thus appears that this product is the result of coordination of the phosphine to the σ–allyl complex:



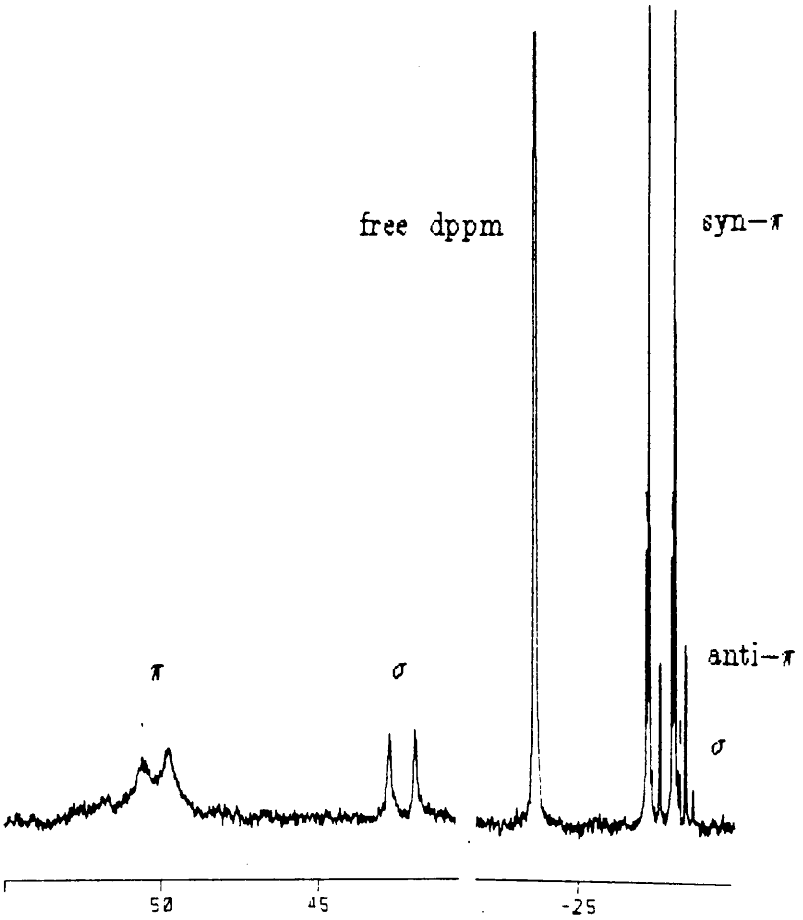
The ^1H nmr spectrum of this compound shows peaks at

δ = 1.27 ppm (br, 3H) for the methyl group
δ = 1.62 ppm (d, 2H) for H_C
δ = 3.44 ppm (dd, 2H) for the methylene group
δ = 3.64 ppm (br d, 1H) for H_A
δ = 5.48 ppm (m, 1H) for H_B

This can be compared with the ^1H nmr spectrum of (σ–C_3H_5)$Mn(CO)_5$ [83] which seems to be the only other σ–allyl carbonyl compound that has been isolated and characterised spectroscopically.

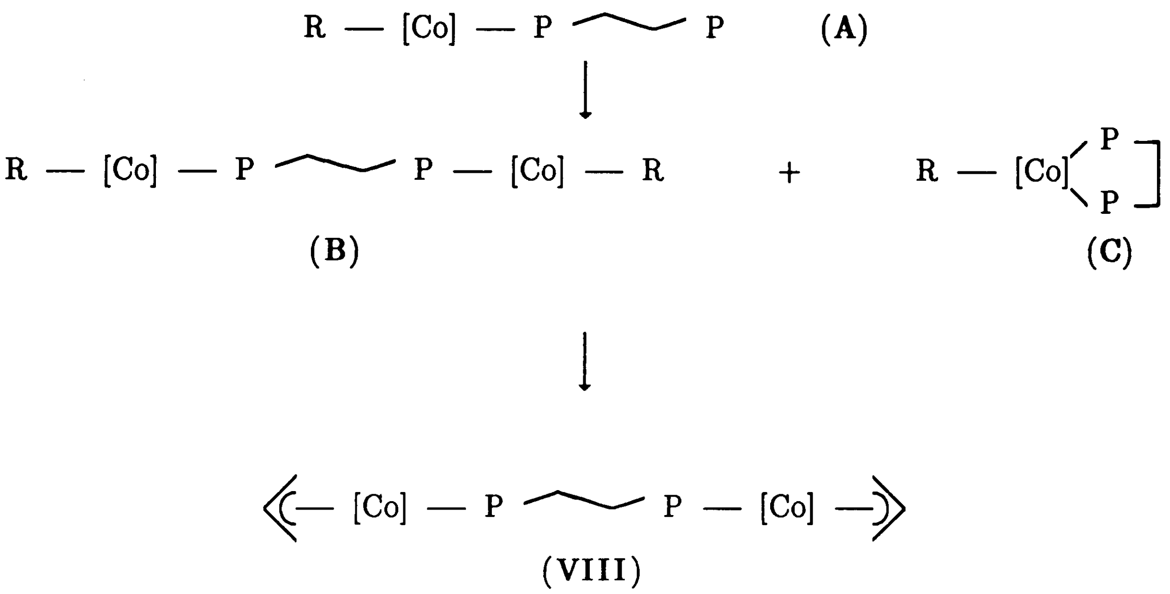
Also, the $^{31}P\{^1H\}$ nmr spectrum of **VI** (fig. 5.1) which shows a slightly broadened doublet at δ = 42.1 ppm and a doublet at δ = –27.1 ppm ($^2J(PP)$ = 98.1 Hz), points to a monodentate dppm ligand (the doublet of the coordinated phosphorus atom of the π–allyl complex occurs at δ = 50.1 ppm). The presence of some of the π–allyl product is thought to be a consequence of conversion of some of the σ–allyl product at the elevated temperature (30°C) at which the spectrum was obtained.

FIGURE 5.1 $^{31}P\{^1H\}$ nmr spectrum of $[(\sigma\text{–}C_4H_7)Co(CO)_3(\eta^1\text{–dppm})]$ (partially converted to IX in solution)



This reaction was repeated using dppe. A $^{31}P\{^1H\}$ nmr spectrum of the mixture, obtained in acetone–d_6, shows two doublets at δ = 28.5 ppm and δ = –13.9 ppm ($^3J(PP)$ = 47.4 Hz) which are most likely due to the monomer $(\sigma\text{–}C_3H_5)Co(CO)_3(\eta^1\text{–dppe})$ (A in scheme 5.1). A broad singlet at 29.6 ppm is thought to be due to the dimer $[(\sigma\text{–}C_3H_5)Co(CO)_3]_2(\mu\text{–dppe})$ (B in scheme 5.1), while the other broad singlet at δ = 68.7 ppm represents $(\sigma\text{–}C_3H_5)Co(CO)_2(\eta^2\text{–dppe})$ (C in scheme 5.1) as for a dppe ligand it is a known fact that transformation from η^1 to η^2 results in a downfield shift of between 20 and 40 ppm [98].

Scheme 5.1



([Co] = $Co(CO)_n$ (n = 2 or 3); R = σ–allyl)

Scheme 5.1 represents a possible pathway to the dimeric compound. The existence of these intermediate products can, however, not be verified as the ^1H nmr spectra are of poor quality exhibiting considerable broadening of peaks. An ir spectrum shows a collection of poorly resolved peaks in the carbonyl region, merely confirming the presence of more than one species.

5.4.2 π–Allyl compounds.

Products were characterised with the aid of micro–analyses and ir, ^1H nmr, ^{13}C nmr, $^{31}P\{^1H\}$ nmr and mass spectroscopy.

TABLE 5.1 Some physical properties of VII – X.

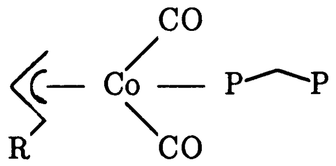
Compound	Colour	Mp (°C)
VII : $[(\pi\text{–}C_3H_5)Co(CO)_2(\eta^1\text{–dppm})$	pale orange	129–130 (dec)
VIII: $[(\pi\text{–}C_3H_5)Co(CO)_2]_2(\mu\text{–dppe})$	orange	145–147
IX : $[(\pi\text{–}C_4H_7)Co(CO)_2(\eta^1\text{–dppm})$	pale orange	> 125 (dwm)
X : $[(\pi\text{–}C_4H_7)Co(CO)_2]_2(\mu\text{–dppe})$	orange	159–160

TABLE 5.2 Micro–analytical data for compounds VII – X.

Compound	Anal.calc.		Found	
	C	H	C	H
VII	66.65	5.07	67.56	4.8
VIII	60.86	4.82	60.15	4.70
IX*	67.16	5.27	72.01	4.98
X	61.80	5.19	61.94	4.94

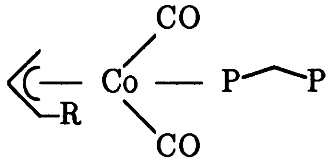
* Compound is extremely unstable and had decomposed partially before the determination could be done.

The reaction of $(\pi\text{–}RC_3H_4)Co(CO)_3$ (R = H, CH_3) with dppm yields the monomer with a "dangling" phosphine as the major product:

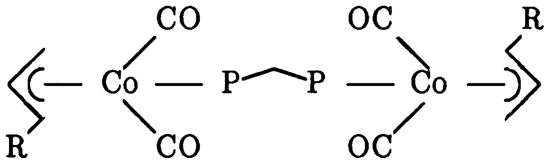


(R = H(VII), CH_3(IX))

In the case of the methylallyl ligand, where the formation of two isomers is possible, the more stable *syn*–isomer is found to be the major product while the remainder of the product mixture consists of some of the *anti*–isomer



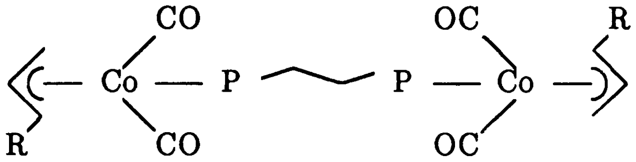
and a small amount of the dimer



The latter is thought to be the cause of a small severely broadened singlet upfield from the doublet of the coordinated phosphorus atom of **IX** on the ^{31}P nmr spectrum.

As past attempts to convert an isomeric mixture of (π–C_4H_7)Co(CO)$_3$ to the *syn*–isomer by prolonged heating produced conflicting results [83, 85], no such attempts were made with the phosphine–substituted products. It is, however, found that the *syn*–isomer (in both the case of **VII** and **IX**) can be purified on a short silica gel column (bands due to the other products are too small to isolate and characterise).

The reaction of (π–RC_3H_4)Co(CO)$_3$ with dppe also results in one major product (> 95% according to ^{31}P nmr)



(R = H(VIII), CH_3(X))

A small high field doublet on each of the $^{31}P\{^1H\}$ nmr spectra of impure **VIII** and **X** is thought to be due to the monomers $(\pi\text{–}RC_3H_4)Co(CO)_2(\eta^1\text{–dppe})$:

VIII: $\delta = -18.8$ ppm ($^3J(PP) = 38.5$ Hz)

X : $\delta = -18.7$ ppm ($^3J(PP) = 38.6$ Hz)

and that the low field doublet of the corresponding coordinated phosphorus atom is concealed by the intense broad singlet due to the dimers.

The stabilities of the compounds are found to decrease in the order:

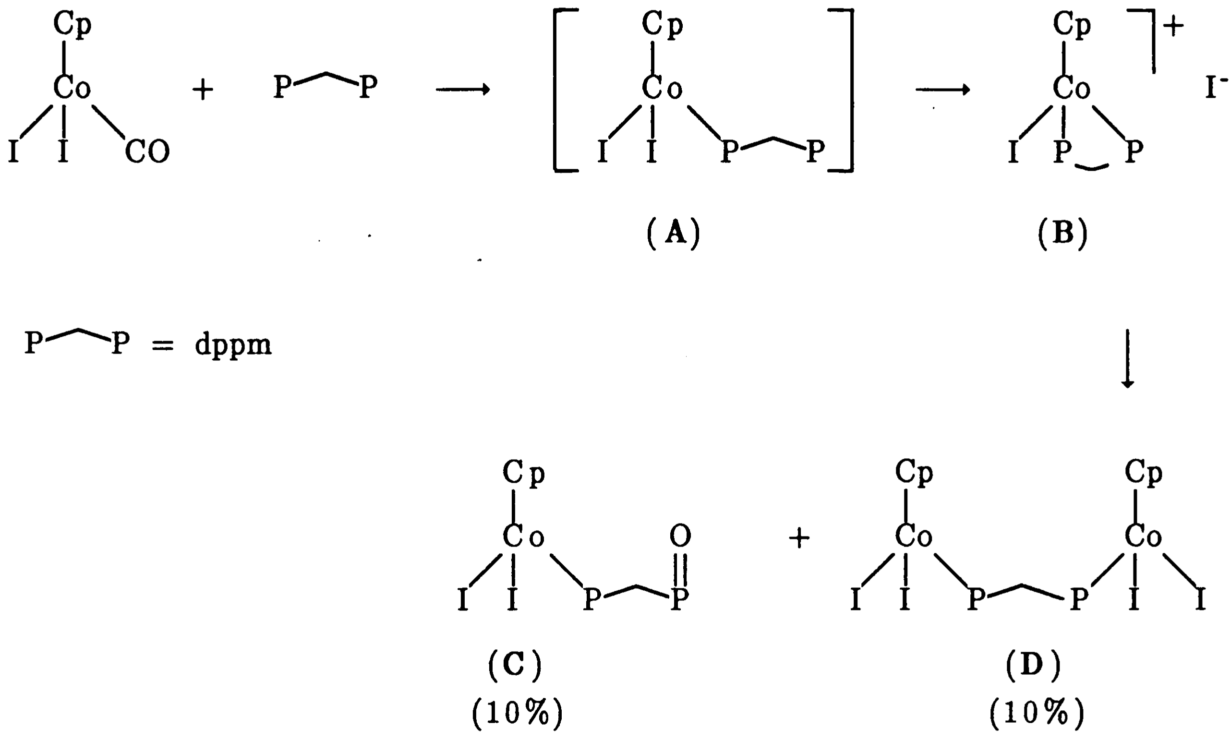
$[(\pi\text{–}C_3H_5)Co(CO)_2(PPh_3)]$ > **VIII** > **X** > **VII** > **IX** > **VI**

with the latter two decomposing in the solid state if kept above 0°C for longer than a few minutes (under N_2) and the first two being indefinitely stable at room temperature (under N_2)

These results are somewhat surprising in view of the known tendency of dppm to bridge two metal centres and the relatively few monodentate dppm complexes that have been prepared and isolated thus far [77]. Except for $[Cr(CO)_5(\eta^1\text{–dppm})]$ which is converted to the more stable $[Cr(CO)_4(\eta^2\text{–dppm})]$ in solution [86] and $[Mo(CO)_3(\eta^2\text{–dppm})(\eta^1\text{–dppm})]$ [89], other compounds with monodentate dppm ligands (e.g. $[CpFe(CO)(\eta^1\text{–dppm})][PF_6]$ [88] and $[CpNi(SPh)(\eta^1\text{–dppm})]$ [89]) are inherently more stable due to their high oxidation states and the presence of the cyclopentadienyl ligand.

Recently, a study by Brill and coworkers on cyclopentadienyl Co(III) complexes

[90] revealed the existence of the monodentate neutral dppm compound $[CpCo(\eta^1\text{–}dppm)I_2]$ (**A**) in solution. This could, however only be isolated as the bidentate salt **B**, which, upon standing in solution exposed to air, led to the isolation of small amounts of **C** and **D**:



Even more recently, the monodentate $[Fe(CO)_4(\eta^1\text{–}dppm)]$ [93] and $[Ru(CO)_4(\eta^1\text{–}dppm)]$ [92] were successfully prepared. The latter has only moderate stability and is slowly converted to $[Ru(CO)_3(\eta^2\text{–}dppm)]$. It also proved fluxional in solution which hampered nmr studies.

Apart from demonstrating the reluctance of dppm to remain monodentate, the immense instability of these compounds is also obvious from these studies.

The monodentate dppm compounds prepared in this work (**VII** and **IX**) therefore appear to be of exceptional stability as a fortuitous result of the combination of ligands and are the first examples of Co(I) complexes with a monodentate dppm ligand.

The formation of the bridged dppe complexes VIII and X is not as unexpected and, apart from some complexes of other transition metals, the bridged cobalt compound $[Co(NO)(CO)_2]_2(\mu\text{–dppe})$ [93] has been isolated. Starting from $[Co(NO)(CO)_3]$, the monodentate $[Co(NO)(CO)_2(\eta^1\text{–dppe})]$ was recognised spectroscopically to be the precursor of the bridged product, but could not be isolated.

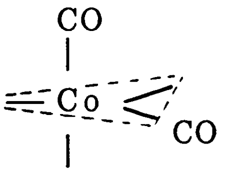
Spectroscopic studies conducted on VII – X (section 5.5) provide further information on these compounds.

5.5 A SPECTROSCOPIC STUDY OF $[(\pi\text{–}RC_3H_4)Co(CO)_2]_n(Ph_2P(CH_2)_nPPh_2)$ (n = 1, 2; R = H, CH_3).

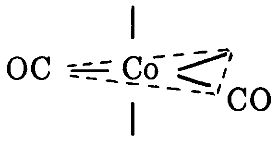
5.5.1 **Infrared spectroscopy**

Carbonyl bands.

For each of VII – X two intense bands are observed in the carbonyl region. This is consistent with two carbonyl ligands which occupy either one axial and one equatorial or two equatorial sites of a trigonal bipyramid:

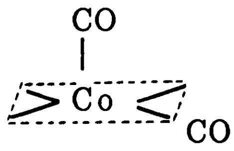


(A)



(B)

or the apical and the equatorial site of a square pyramid:



(C)

As it is not possible to comment on the geometry of the molecule by only considering the number of bands, the approximate angle between the two carbonyl ligands is calculated using the following equation:

$$\frac{I_{sym}}{I_{asym}} = \cot^2 \left(\frac{\theta}{2} \right)$$

$$\theta = 2 \tan^{-1} \left(\frac{I_{sym}}{I_{asym}} \right)^{-1}$$

Values are obtained by carefully tracing, cutting out and weighing bands recorded in absorbance mode. For this purpose, the spectra obtained in CH_2Cl_2 are used, as the bands of the solid samples are slightly broadened. Angles are given in table 5.3.

Although the calculated angles cannot be considered accurate, it is now possible to rule out geometry B. In order to make a distinction between A and C it would be necessary to consider the Co–CO bond lengths and OC–Co–CO angles: a considerable difference would point to geometry C. A crystal structure determination of (π–C_3H_5)Co(CO)$_2$(PPh$_3$) [76] revealed a distorted square pyramid with Co–C_{base} 175.8(3) pm and Co–C_{ap} 178.0(5) pm and although likely, does not mean that the compounds prepared in this work are similar.

TABLE 5.3 Observed carbonyl stretching frequencies and calculated angles for VII – X.

Compound	ν(CO) (cm^{-1})^a		ν(CO) (cm^{-1})^b		θ
	A_1	E	A_1	E	
VII	1977.3 (s)	1919.6 (s)	1984.4 (s)	1925.6 (s)	84
VIII	1977.7 (s)	1907.9 (s)	1983.8 (s)	1925.2 (s)	82
IX	1970.8 (s)	1912.0 (s)	1978.8 (s)	1919.3 (s)	81
X	1970.0 (s)	1919.2 (s)	1977.8 (s)	1919.1 (s)	78

a) KBr–pellet.

b) $CH_2C\ell_2$–solution.

As the two carbonyl groups are inequivalent, the force field is underdetermined and the two force constants could be quite different. This possibility renders the use of the relative peak intensities to find the force field inaccurate [22].

For compounds **VII** and **VIII** which contain the symmetrical allyl ligand, the E–band is degenerate. The methyl group on the 1–position of the allyl group in **IX** and **X**, on the other hand, introduces asymmetry causing a shoulder to appear on the E–band. In the case of **X** splitting of the E–band even occurs.

Other bands.

A detailed infrared study has been conducted on compounds of the type (π–allyl)Co(CO)$_3$ [84]. This is used as a guide to assign bands due to the allyl ligand. As coupling between vibrational modes was found to occur, assignment could only be done with care.

Even though some of the weaker bands are not observed in this work, the medium–intensity band occuring in the vicinity of 1025 cm^{-1} on each spectrum (assigned as the symmetrical ν(C–C–C)) is used to identify the allyl ligand and taken as proof of its delocalised nature.

Comparing reactivities.

On comparison with compounds **I**, **II** and **III** (which are described in chapter 3) the precursors of the compounds discussed in this chapter are more reactive from the point of view of carbonyl substitution. All these compounds are five–coordinated with three carbonyl ligands. The carbonyl bands of (π–allyl)Co$(CO)_3$ occur at higher frequencies than those of $[Me_3SnCo(CO)_3L]$. This is a result of the better π–accepting ability of the allyl ligands – the poor π–accepting ability of the tin ligand causes the cobalt to have a greater negative charge thereby facilitating back–bonding to the empty π^* orbitals of the carbonyl groups. This in turn lowers the C–O bond order and hence the frequencies and force constants. Whereas substitution of a carbonyl ligand of (π–allyl)Co$(CO)_3$ is readily achieved, the formation of the monodentate and bridged bis(phosphine) compounds **VII** – **X** show the substitution of a second carbonyl to be impossible under the reaction conditions used. This is reflected by the work in chapter 4 where attempts to labilise the third carbonyl with the aid of a special reagent only met with limited success.

Once again, the use of the CO frequency as an indicator as to whether a carbonyl ligand will undergo nucleophilic substitution or not becomes apparent (compare section 3.4.1).

5.5.2 **Mass spectroscopy.**

Attempts to obtain meaningful mass spectra of **VII** – **X** met with great frustration. Initially, spectra were obtained of solid samples, but this only resulted in decomposition during the process of volatilization.

Spectra obtained from solutions of the samples are a slight improvement. Results are shown in table 5.4. Although peaks due to larger fragments can be assigned, the fragile nature of the compounds is still evident from the large number of low intensity peaks below $^m/_z$ 200. The molecular ion peak is not observed on any of the spectra; the peak of highest $^m/_z$ is inevitably $M^+ - 2CO$ except for **IX** where it is $[Co(dppm)]^+$.

The compounds fragment by way of consecutive loss of ligands in the following order: i) CO ii) allyl iii) phosphine which is the expected order (see section 2.3.3). The dimers **VIII** and **X** are initially cleaved to give the fragments $[(\pi\text{–}RC_3H_4)Co(dppe)]^+$ and $[(\pi\text{–}RC_3H_4)Co]^+$ (R = H, CH_3) whereafter these fragment further.

Finally, the immense instability of **IX** is reflected in the low intensities of its mass peaks.

TABLE 5.4 Some mass spectral data of VII – X.

Compound	Fragment	$^m/_z$	Relative intensity
VII	M^+	n.o.	
	$[(\pi\text{–}C_3H_5)Co(dppm)]^+$	484	1
	$[Co(dppm)]^+$	443	3
	$[dppm]^+$	384	8
	$[Co]^+$	59	9
	$[C_3H_5]^+$	41	36
VIII	M^+	n.o.	
	$[(\pi\text{–}C_3H_5)Co(dppe)]^+$	498	17
	$[Co(dppe)]^+$	457	4
	$[dppe]^+$	398	2
	$[(\pi\text{–}C_3H_5)Co]^+$	100	13
	$[Co]^+$	59	29
	$[C_3H_5]^+$	41	34
IX	M^+	n.o.	
	$[Co(dppm)]^+$	443	1
	$[dppm]^+$	384	15
	$[Co]^+$	59	2
	$[C_3H_4]^+$	40	21
X	M^+	n.o.	
	$[(\pi\text{–}C_4H_7)Co(dppe)]^+$	512	33
	$[Co(dppe)]^+$	457	16
	$[dppe]^+$	398	8
	$[(\pi\text{–}C_4H_7)Co]^+$	114	14
	$[Co]^+$	59	72

5.5.3 **Nmr spectroscopy.**

5.5.3.1 ^{1}H nmr

Allyl protons.

By making use of the spectrum of the unsubstituted (π–C_3H_5)Co(CO)$_3$, it is possible to assign peaks for the phosphine substituted compounds by observing changes in the multiplicity and magnitudes of the coupling constants.

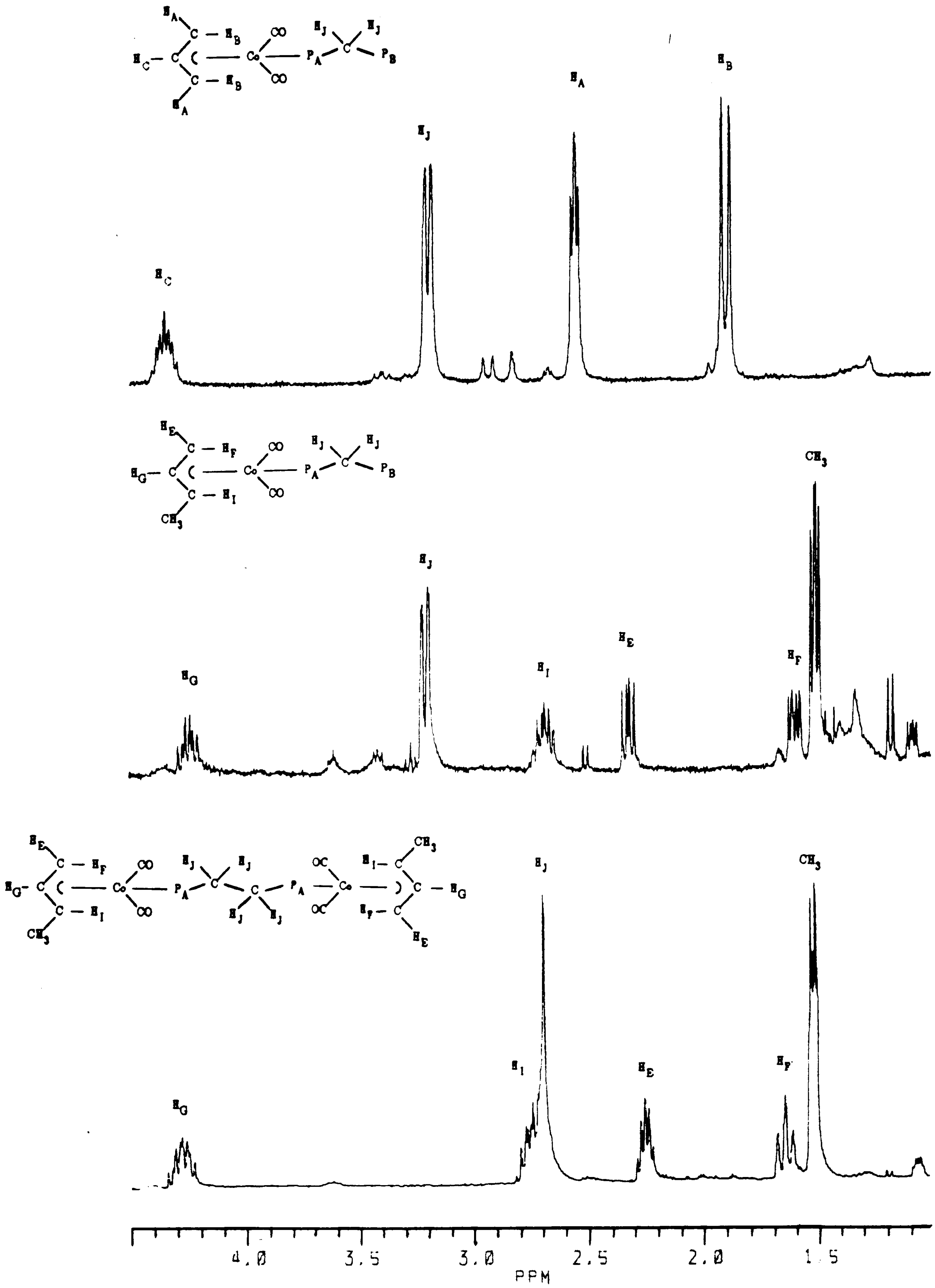
The spectrum of (π–C_3H_5)Co(CO)$_3$ shows doublets for H_A and H_B respectively, due to coupling with H_C as $J(H_AH_B) = 0$. Distinction between these doublets is made by observing the larger *trans* coupling $J(H_BH_C)$ as opposed to the smaller vicinal coupling $J(H_AH_C)$ which allows assignment of the lower field doublet to H_A (also referred to as the *syn*–proton). H_C occurs at $\delta = 4.42$ ppm and forms the X–part of the A_2B_2X spin system. Although the expected triplet of triplets for H_C is observed as a septet, the third and fifth peaks appear broadened on some spectra. The downfield shift of H_C relative to H_A and H_B is evidential of its aromatic character and is indicative of the allyl ligand resembling half a benzene ring.

From the upfield shift of the allyl resonances upon going from the unsubstituted (π–C_3H_5)Co(CO)$_3$ to **VII** and **VIII** it is obvious that π–backbonding to the allyl ligand has increased, demonstrating the stabilising influence of the phosphine. Although the coordinated phosphorus atom (P_A) transforms the spin system to that of A_2B_2MX, P_A only couples with H_A and not with H_B.

The resonance of H_B in **VII** is a simple doublet of doublets. For **VIII** it is observed as a broad triplet. On closer inspection, it seems that as a result of the involvement of both phosphorus nuclei, H_B forms part of an AA'XY spin system involving H_C. This spin system gives rise to a deceptively simple spectrum under conditions which require J(AA') and J(XY) to be large compared to δ(AA') amongst other things (δ here is the difference in chemical shift). A mathematical analysis of this spin system has been carried out [94]. The resonance of H_A, which also forms part of an AA'XY spin system, has a slightly different pattern as a result of J(AX) being larger for H_A than for H_B. These spin patterns do not readily permit the calculation of first–order coupling constants. Chemical shifts and some coupling constants for **VII** and **VIII** are given in table 5.5 and the ^{1}H nmr spectrum of **VII** is shown in fig. 5.2

FIGURE 5.2 ^{1}H nmr spectra of VII, IX and X

(phenyl region not included)



The presence of the methyl group in IX and X leads to additional splitting. Five resonances are observed for the allyl protons of each of these compounds. The spectrum of the unsubstituted $(\pi\text{–}C_4H_7)Co(CO)_3$ is used as a starting point in the assignment of chemical shifts. The spectrum of this compound has been discussed before [85] but the work seems ambiguous regarding coupling constants.

The allyl regions of the ^1H nmr spectra of IX and X are depicted in fig.5.2. Whereas the spectrum of the former appears well–resolved and allows the calculation of first–order coupling constants, the peaks on the spectrum of X exhibit second–order phenomena. The resonances of H_E and H_F resemble those of H_A and H_B respectively. The resonance of the methyl protons is split into a doublet due to coupling with H_I. Further, each line of the doublet is observed as a non 1:2:1 triplet which is indicative of the involvement of two other spin–$^1/_2$ nuclei. These protons do in fact form the X–part of an $AA'X_3$ spin system which only allows the calculation of the average coupling constant, $^1/_2$ [J(AX) + J(A'X)] [95].

The presence (or absence) of coupling between any two protons can be determined by recording the two–dimensional ^1H – ^1H correlated spectrum (COSY). This was done for IX (fig. 5.3) and X. In this way, it is found that H_G couples with H_E, H_F and H_I. As a result of $J(H_GH_F)$ and $J(H_GH_I)$ being of comparable magnitude, the resonance of H_G is observed as a doublet of triplets instead of the expected three overlapping doublets. The COSY also reveals the absence of coupling between H_E and H_F, H_E and H_I, and H_F and H_I. Also, from the increased multiplicity of their resonances, it can be seen that P_A couples with all the allyl protons except H_G.

FIGURE 5.3 ^1H – ^1H correlated spectrum (COSY) of IX.

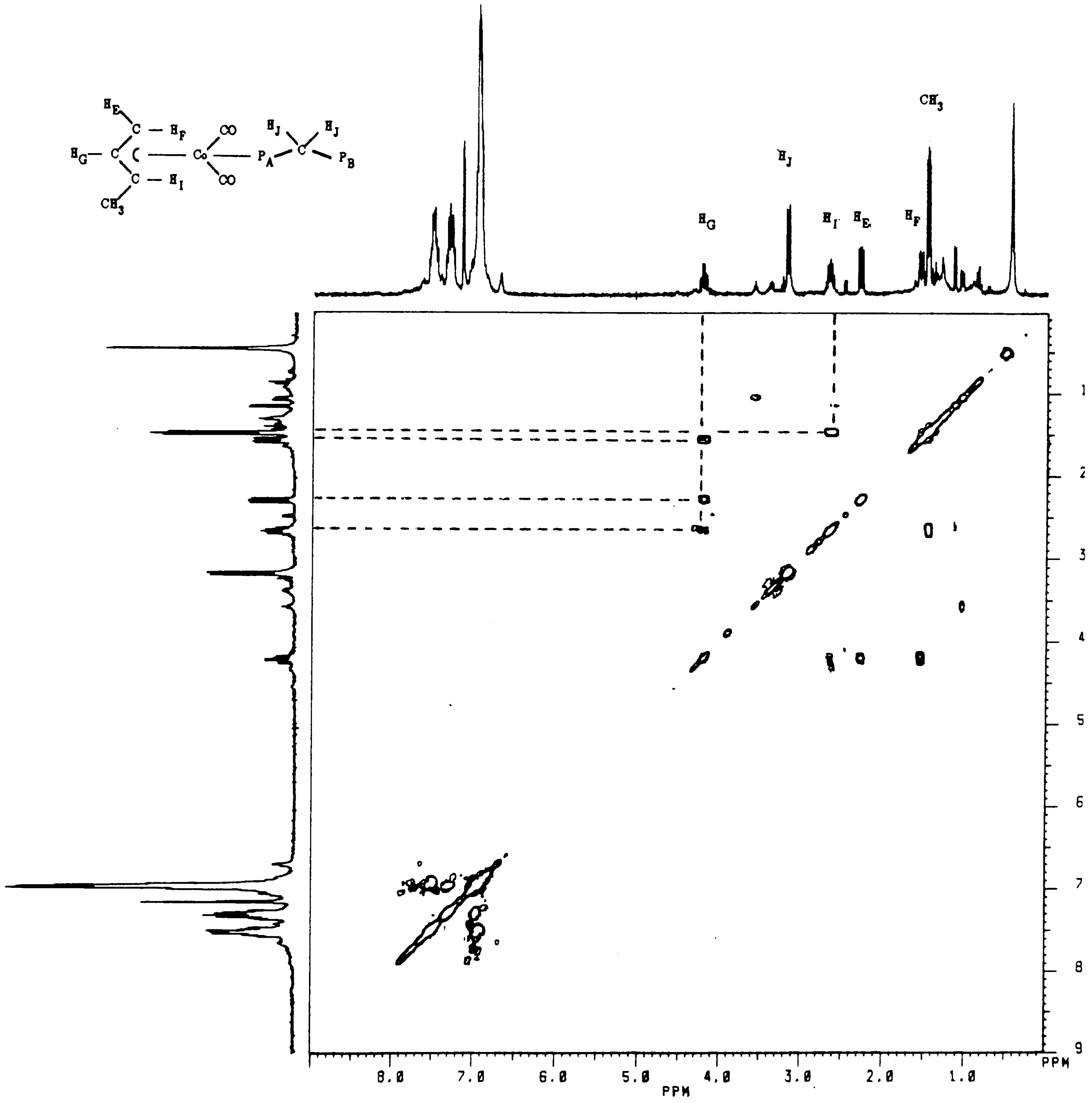
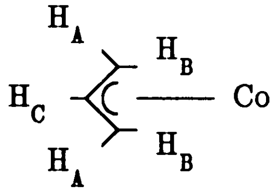


TABLE 5.5 ^1H chemical shift values and coupling constants for the allyl protons of VII and VIII.[a]



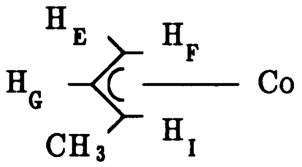
Compound	H_A	H_B	H_C
VII	2.51 (dd,2H) $^2J(H_AH_B)$[b] 0.0	1.85 (d,2H) $^3J(H_BH_C)$ 10.4	4.30 (sp,1H) $^3J(H_AH_C)$ 5.9
VIII	2.49 (dt,2H) $^2J(H_AH_B)$[c] 0.0	1.88 (d,2H) $^3J(H_BH_C)$ 10.4	4.31 (sp,1H) $^3J(H_AH_C)$ 5.9

a. Chemical shift in ppm relative to benzene–d_6 (δ = 7.15 ppm); coupling constants in Hz; abbreviations: dd = doublet of doublets, dt = doublet of triplets, sp = septet.

b. $^3J(P_AH_A)$ = 4.0 Hz.

c. $^3J(P_AH_A)$ = 2 Hz.

TABLE 5.6 ^{1}H chemical shift values and coupling constants for the allyl protons of IX and X.[a]



Compound	H_E	H_F	H_G	H_I	CH_3
IX	2.28 (dd,1H) $^2J(H_EH_F)$ 0.0 $^3J(P_AH_E)$ 9.6	1.55 (dd,1H) $^3J(H_FH_G)$ 10.2 $^3J(P_AH_F)$ 4.5	4.21 (dt,1H) $^3J(H_EH_G)$ 6.1 $^3J(P_AH_G)$ 0.0	2.65 (qn,1H) $^3J(H_GH_I)$ 9.9 $^3J(P_AH_I)$ b	1.46 (dd,3H) $^3J(H_ICH_3)$ 6.2 $^3J(P_ACH_3)$ 4.5
X	2.20 (qn,2H) $^2J(H_EH_F)$ 0.0 b	1.59 (t,2H) $^3J(H_FH_G)$ 10.3 b	4.24 (qn,2H) $^3J(H_EH_G)$ b $^3J(P_AH_G)$ 0.0	2.69 (m,2H) $^3J(H_GH_I)$ b b	1.46 (dt,6H) $^3J(H_ICH_3)$ 10.3 c 2.1

a. Chemical shift values in ppm relative to benzene–d_6 (δ = 7.15 ppm); coupling constants in Hz; abbreviations: dd = doublet of doublets, dt = doublet of triplets, qn = quintet.

b. Coupling constants not directly obtainable due to second order effects. (see text)

c. Average value: $^1/_2$ $[J(CH_3P_A^1) + J(CH_3P_A^2)]$.

Methylene protons.

The doublet of doublets observed for the methylene protons of **VII** and **IX** clearly demonstrates the inequality of the two phosphorus nuclei. The smaller coupling constant is ascribed to coupling with P_B, whereas the larger coupling is the result of coupling with P_A. The broad singlet observed for the methylene protons on the spectra of **VIII** and **X** seems to be the result of the coincidence of chemical shift and a relatively small ^{31}P coupling, a known problem with coordinated dppe [90].

TABLE 5.7 ^1H chemical shift values and coupling constants for the methylene and phenyl protons of VII and VIII.[a]

Compound	Methylene protons		Phenyl protons	
	δ(H)	J(PH)	H_o	$H_m + H_p$
VII	3.15 (dd,2H)	8.4 (P_A) 2.1 (P_B)	7.48 (P_A) (m,4H) 7.29 (P_B) (m,4H)	6.94 (m,12H)
VIII	2.63 (br,4H)	n.o.	7.48 (m,8H)	6.94 (m,12H)

a. Chemical shift values in ppm relative to benzene–d_6 (δ = 7.15 ppm); coupling constants in Hz.

TABLE 5.8 ^1H chemical shift values and coupling constants for the methylene and phenyl protons of IX and X.[a]

Compound	Methylene protons		Phenyl protons	
	δ(H)	J(PH)	H_o	$H_m + H_p$
IX	3.16 (dd,2H)	8.5 (P_A) 1.5 (P_B)	7.50 (P_A) (m,4H) 7.30 (P_B) (m,4H)	6.94 (m,12H)
X	2.64 (s br,4H)	b	7.50 (m,8H)	6.97 (m,12H)

a. Chemical shifts in ppm relative to benzene–d_6 (δ = 7.15 ppm); coupling constants in Hz; abbreviation: dd = doublet of doublets.

b. Coupling constant not directly obtainable.

Phenyl protons.

The observance of 3 distinct multiplets (in the ratio 4:4:12) is consistent with the different environments in which the two phosphorus nuclei in VII and IX find themselves. The resonance with the largest downfield shift is ascribed to the four *ortho* protons of the two phenyl rings on P_A, the higher field multiplet to the other four *ortho* protons and the large multiplet to the remaining phenyl protons.

In contrast, the spectra of VIII and X display only two multiplets (ratio 8:12) each.

5.5.3.2 ^{31}P nmr

$^{31}P\{^1H\}$ nmr spectroscopy can be used to establish rapidly whether a bis(phosphine) has coordinated in a monodentate, bidentate or bridged manner enabling the composition of reaction mixtures to be determined.

TABLE 5.9 $^{31}P\{^1H\}$ nmr data for VI – X.[a]

Compound	P_A	P_B[c]	$^2J(P_AP_B)$
VI[b]	42.2	–28.0	98
VII	46.8	–32.3	96
VIII	51.1	–	–
IX	45.6	–32.4	96
X	50.3	–	–

a. Chemical shifts in ppm relative to 85% H_3PO_4;
measured in benzene–d_6; coupling constants in Hz.
P_A is the coordinated phosphorus.

b. $[(\sigma\text{–}C_4H_7)Co(CO)_3(\eta^1\text{–dppm})]$, measured in acetone–$d_6$.

c. Chemical shifts of the free phosphines:
dppm: $\delta = -28.4$ ppm (benzene–d_6)
$\delta = -23.6$ ppm (acetone–d_6)
dppe: $\delta = -18.9$ ppm (benzene–d_6)
$\delta = -12.5$ ppm (acetone–d_6)

From the spectra of **VII** and **IX** (fig. 5.4) it is quite obvious that the higher field doublet results from the dangling phosphorus (P_B) as its chemical shift does not differ much from that of the free ligand. The lower field doublet exhibits considerable broadening due to it being directly attached to the cobalt (I = $^7/_2$). The $^{31}P\{^1H\}$ nmr spectrum of the *syn*–isomer of **IX** can be seen in fig. 5.4.

The ^{31}P spectra of **VIII** and **X** each consists of a single broad peak (table 5.9). it is thus not possible to distinguish between a bridged or a chelated dppe. ligand. A larger downfield shift would, however, be expected upon chelation

5.5.3.3 ^{13}C nmr

^{13}C nmr spectroscopy finds use in the identification of ligands and the study of the distribution of electron density within the complex. The general lack of detailed spectral data on cobalt compounds unfortunately makes it difficult to draw any meaningful conclusions by way of comparison with existing compounds.

Allyl carbons.

A number of $^{13}C\{^1H\}$ nmr spectra of allyl complexes of other transition metals have been recorded [25], including that of $(\pi\text{–}C_3H_5)Co(CO)_2(PPh_3)$ [77].

Assignment of the chemical shifts of the allyl carbons are made with the aid of the ^1H coupled ^{13}C spectra (the spectrum of **X** is shown in fig.5.5). The $^1J(CH)$ coupling constant provides information on the hybridization of a particular carbon atom: the delocalized nature of the carbon–carbon double bond is obvious from the fact that the coupling constants for C_2 and C_3 ($^1J(C_2H)$ = 166 Hz and $^1J(C_3H)$ = 164 Hz) are even greater than the normal range of 155 – 160 Hz for sp^2 carbons. The increase in p–character at C_1 is reflected by the lowering of $^1J(C_1H)$ from 164 Hz to 151 Hz upon substitution of one of its protons with a methyl group.

The expected two–bond coupling of P_A with C_1 and C_3 appears to be quite small and can, as a result of the n.q.m. of cobalt, not be resolved. This is ,however, an indication that the phosphine does not occupy a site directly *trans* to either C_1 or C_3. Rinze [76] obtained a value of $^2J(P_AC_1)$ = 2.9 Hz, but the accuracy thereof is doubtful as it was obtained from a spectrum recorded at room temperature at 25 MHz.

It is not necessarily possible to resolve coupling constants such as those described above by recording the spectrum at temperatures other than room temperature. Relaxation of a quadrupole nucleus such as cobalt essentially involves fluctuating fields arising from interaction between the quadrupole moment and the electrical field gradient at the quadrupole nucleus. The extremely short spin–lattice relaxation time of the cobalt nucleus can be increased by raising the temperature, which in turn will reduce the effect of this nucleus on the linewidths of resonances of neighbouring atoms. Allyl complexes, however, have the tendency to become fluxional upon increasing the temperature with the resulting broad resonances once again not permitting calculation of coupling constants.

FIGURE 5.5 ^{13}C nmr spectrum of X (only showing allyl and methylene resonances); a) ^1H decoupled; b) ^1H coupled.

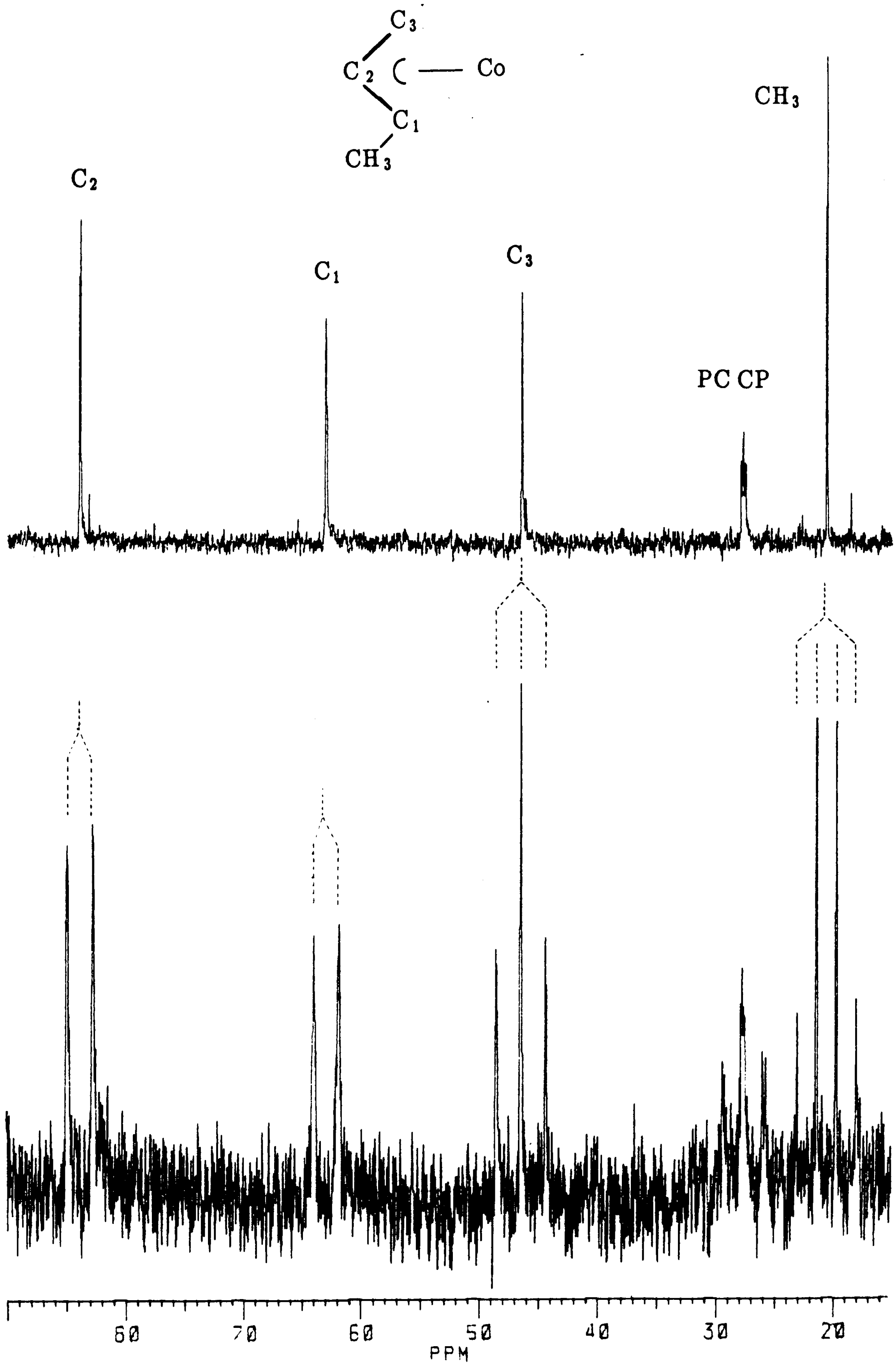
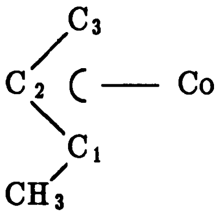


TABLE 5.10 ^{13}C nmr data for the allyl carbons of VII – X.^{a}



Compound	C_1	C_2	C_3	CH_3	$^2J(PC)$ and $^1J(CH)$
VII	47.3 (s)	80.8 (s)	47.3 (s)	–	b,d
VIII	47.3 (s)	81.0 (s)	47.3 (s)	–	b,d
IX	62.7 (s)	83.7 (s)	46.4 (s)	20.4 (s)	$^2J(P_AC_1)$:b; $^2J(P_AC_3)$:b $^1J(C_1H)=169.0$; $^1J(C_2H)=162.7$ $^1J(C_3H)=159.0$; $^1J(CH_3H)=126$
X	63.0 (s)	83.8 (s)	46.4 (s)	20.5 (s)	$^2J(P_AC_1)$:b; $^2J(P_AC_3)$:b $^1J(C_1H)=164.3$; $^1J(C_2H)=166.2$ $^1J(C_3H)=151.1$; $^1J(CH_3H)=127$
L = PPh_3^{c}	47.3 (d)	80.2 (s)	47.3 (d)	–	$^2J(PC_1) = 2.9$

a) Chemical shifts in ppm relative to benzene–d_6 ($\delta = 128.0$ ppm); coupling constants in Hz.

b) Resonances of carbons directly attached to Co do not permit calculation of $^2J(CP)$ (see text).

c) $[(\pi\text{–}C_3H_5)Co(CO)_2(PPh_3)]$; in toluene–$d_8$: from reference 76.

d) ^1H coupled spectra of VII and VIII were not recorded.

Methylene carbons.

The methylene carbons on average shift 10 ppm downfield upon coordination of the dppm, consistent with a withdrawal of electron density away from this ligand. In the bridged dppe complexes this effect is cancelled, resulting in no significant change.

Due to the dppm being monodentate in compounds **VII** and **IX**, the methylene carbon forms the X–part of a simple AMX spin system. This means that a doublet of doublets would be expected on the $^{13}C\{^{1}H\}$ spectrum, which is indeed observed ($^{1}J(CP_A) >> {}^{1}J(CP_B)$). Values are shown in table 5.11.

TABLE 5.11 ^{13}C nmr data for the methylene carbons of VII – X.[a]

Compound	δ(C)	J
VII	34.30 (dd)	$^{1}J(P_AC) = 31.8$ $^{1}J(P_BC) = 20.4$
VIII	27.64 (t)	$^{1+2}J(P_AC) = 14.1$
IX	34.18 (dd)	$^{1}J(P_AC) = 31.2$ $^{1}J(P_BC) = 19.4$ $^{1}J(HC) = 136.1$
X	27.64 (t) 27.57 (t)	$^{1+2}J(P_AC) = 13.7$

a) Chemical shifts in ppm relative to benzene–d_6 (δ = 128.0 ppm); coupling constants in Hz.

On the ^{1}H coupled ^{13}C spectrum of **IX**, each line of the triplet appears as a well resolved doublet of doublets with $^{1}J(CH) = 136.1$ Hz.

In compounds **VIII** and **X**, where the phosphine is bridged, the two phosphorus atoms are chemically equivalent, but magnetically non–equivalent due to the chance occurrence of a ^{13}C atom closer to one than the other. This makes it an AA'X spin system which results in more complicated spectra than the AMX system. The methylene carbon appears as a simple 1:2:1 triplet on the $^{13}C\{^1H\}$ spectrum. This is a second order phenomenon known to be due to the presence of two or more spin–$^1/_2$ nuclei other than ^{13}C or ^1H which are strongly coupled [25]. From this triplet it is thus not possible to obtain the magnitude of the coupling of the X–part with the A–part or B–part respectively, but only the average of these two values.

The two methylene carbons in **X** are slightly inequivalent (a consequence of the anisotropy introduced by the methyl group) giving rise to two overlapping triplets as opposed to the single triplet observed for **VIII**.

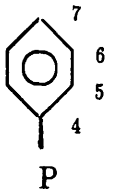
Phenyl carbons.

The carbons of the four phenyl rings resonate in the region 140 – 128 ppm. Although four distinct groups of resonances (representing C_4, C_5, C_6 and C_7) can be distinguished on each of the spectra of **VII** to **X**, broadening and overlapping of signals occurs in some cases. The latter phenomena are a result of:

i) second–order coupling due to the presence of two coupling phosphorus atoms;

ii) an increasing degree of dissimilarity of the phenyl rings upon going from **VIII** to **X** to **VII** to **IX** (see table 5.12).

TABLE 5.12 $^{13}C\{^{1}H\}$ nmr data of the phenyl carbons of VII – X.^{a}



Compound	C_4	C_5	C_6	C_7
VII^{d}	139.32 (dd) $^{1}J(P_AC_4) = 16.6$ $^{3}J(P_BC_4) = 7.8$ 137.22 (dd) $^{1}J(P_AC_4) = 37.7$ $^{3}J(P_BC_4) = 4.0$	133.40 (d,br) 132.53 (d)	128.6^{b} (s,br)	129.61 (s)
VIII^{e}	136.57 (vt) $^{1+4}J(P_AC_4)=19$	132.05 (t) $^{2+5}J(P_AC_5)=5$	128.72 (t) $^{3+6}J(P_AC_6)=4$	129.9
IX^{f}	140.0–136.6 (m)	133.51–132.7 (m)	128.7–128.2 (m)	131.6–129.4 (m)
X^{d}	137.25 (dd) $^{1}J(P_AC_4)=37.0$ 136.40 (dd) $^{4}J(P_AC_4)=19.0$	132.27 (t) $^{2+5}J(P_AC_5)=5$ 132.00 (t) $^{2+5}J(P_AC_5)=5$	128.69 (br)	129.85 (s) 129.70 (s)
L = PPh_3^{c}	not determined			

a) Chemical shifts in ppm relative to benzene–d_6 (δ = 128.0 ppm); coupling constants in Hz.

b) C_6–resonance partially obscured by strong solvent signal.

c) $[(\pi–C_3H_5)Co(CO)_2(PPh_3)]$; from reference 76.

d) 2 + 2 phenyl rings similar.

e) all 4 phenyl rings similar.

f) all 4 phenyl rings different.

This in effect means that the spectrum of **VIII** (fig.5.6) is the simplest of the four due to each of the different carbons in a phenyl ring being magnetically equivalent to the corresponding carbons of all the other rings. In spite of this, only C_4 of **VIII** displays a first–order doublet of doublets, which is also the case with **VII**. C_5 and C_6 of the dppe complexes invariably form the X–part of an AA'X spin system involving both ^{31}P nuclei, resulting in a deceptively simple triplet being observed for each carbon. The magnitudes of $^nJ(AX)$ and $^nJ(A'X)$ were shown to depend on the magnitude of $^nJ(AA')$ [97, 98] This dependence is illustrated in fig.5.6 where the change in the pattern of C_4 and C_5 upon going from free dppe to bridged dppe ($^3J(AA')_{free} > {}^3J(AA')_{bridged}$) can be seen. If $^nJ(AA')$ is known, it is possible to calculate the former two constants by simulating the spectra. The value of $^nJ(AA')$ can be determined experimentally by observing the ^{13}C satellites on the $^{31}P\{^1H\}$ spectrum, but this operation is once again hampered by the influence of Co. Some coupling constants could nonetheless be extracted from these resonances and are given in table 5.12.

The anticipated less complicated spin patterns (AMX spin system) for the phenyl carbons of the dppm complexes are complicated by the overlapping of peaks (fig 5.7).

<u>Carbonyl carbons</u>.

Although the ir spectra of **VII** and **VIII** show that there are two different carbonyl ligands on each metal centre, only one broadened signal can be observed on the $^{13}C\{^1H\}$ spectrum. This was also found in the case of $[(\pi\text{–}C_3H_5)Co(CO)_2(PPh_3)]$ [76] where, even upon cooling to 183K, only one signal emerged.

In contrast, the increased anisotropy in the methylallyl compounds seems to result in two distinct, albeit broad, carbonyl resonances being observed. The calculation of $^2J(PC)$ is unfortunately not permitted.

FIGURE 5.6 $^{13}C\{^{1}H\}$ nmr spectra (phenyl regions) of

i) free dppe

ii) bridged dppe (as in VIII)

showing the dependence of the spin pattern on $^{3}J(PP)$.

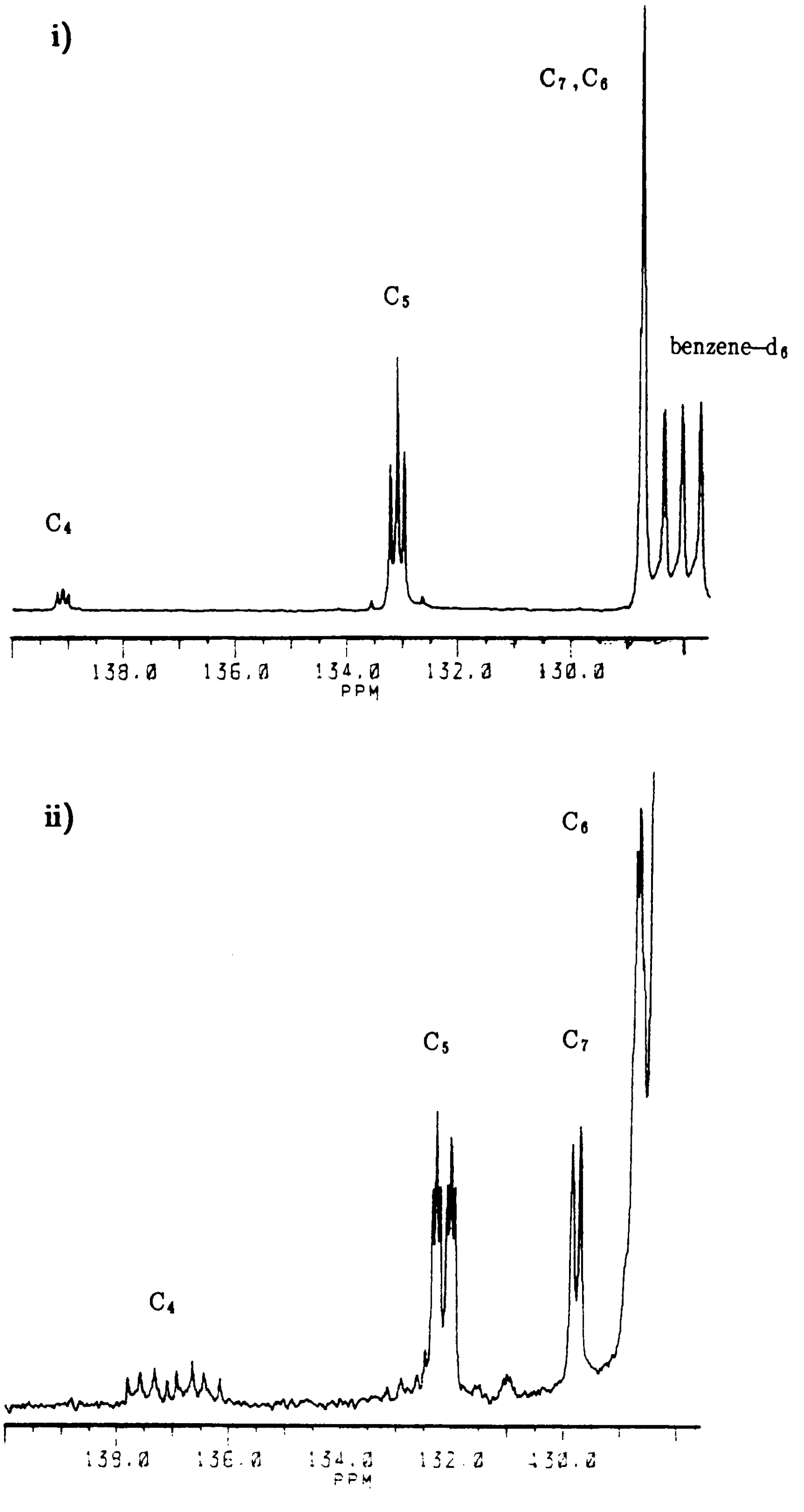


FIGURE 5.7 $^{13}C\{^1H\}$ nmr spectrum of $[(\pi\text{-}C_4H_7)Co(CO)_2(\eta^1\text{-dppm})]$ (IX).

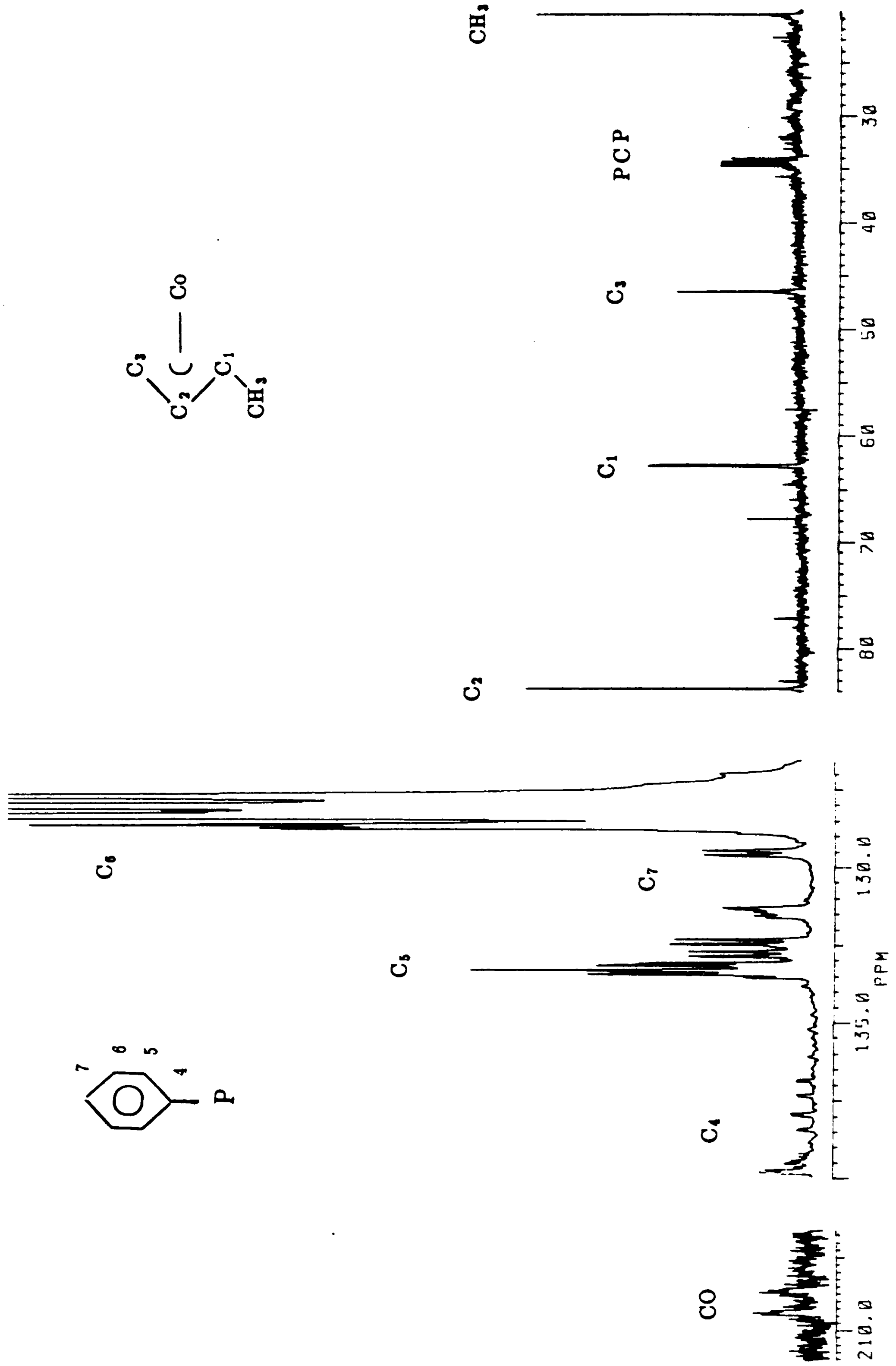


TABLE 5.13 $^{13}C\{^1H\}$ nmr chemical shifts for VII to X.[a]

Compound	$(CO)_1$	$(CO)_2$
VII	207.10 (br)	
VIII	207.02 (br)	
IX	207.29	208.72
X	207.44	208.44
L=PPh_3	206 (br)	

a) Chemical shifts in ppm relative to benzene–d_6 (δ = 128.0 ppm).

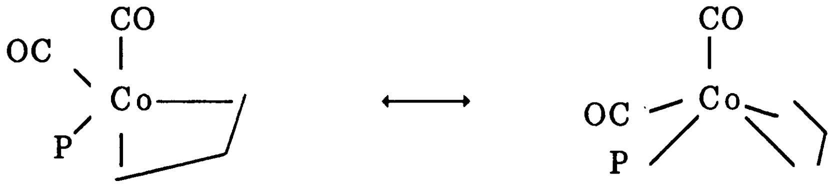
b) $[(\pi\text{–}C_3H_5)Co(CO)_2(PPh_3)]$ in toluene–d_8: from reference 76.

As far as can be determined the ^{13}C nmr spectra of the unsubstituted $[(\pi\text{–}RC_3H_4)Co(CO)_3]$ (R = H, CH_3) have not yet been recorded, probably because of their instability in solution. A comparison with the phosphine–substituted compounds is thus not possible.

5.5.4 Conclusions regarding geometry.

The hapticity of the bis(phosphine) ligands can be derived from the $^{31}P\{^1H\}$ nmr spectra and ^1H nmr shows the allyl ligands to be chelated, i.e. that they occupy two of the five coordination sites. This leaves two sites which are shown by ir and ^{13}C nmr spectroscopy to be occupied by carbonyls.

Although the geometry around the metal centre cannot unequivocally be predicted, spectral observations allow certain conclusions to be made. The absence of any strong coupling between an allyl carbon and the coordinated phosphorus atom indicates that the latter does not occupy a site *trans* to any one of these carbons. This suggests a distorted structure somewhere between a square pyramid and a trigonal bipyramid:



This will, however, have to be confirmed with an X–ray structure determination.

5.6 CONCLUSION.

In this study it is shown that it is possible to prepare stable derivatives of $[(\pi\text{–}RC_3H_4)Co(CO)_3]$ other than triphenylphosphine and that, even with dppe where expected ring closure does not occur, a second carbonyl ligand cannot be substituted.

These compounds offer unlimited possibilities for further study. Some reactions include:

i) attaching the dppm compounds to other metal centres by way of their free phosphorus atom;

ii) using strong nucleophiles to modify the allyl ligand;

iii) abstracting one or more of the methylene protons to give $[(Ph_2P)_2CH]^-$ which in itself has proved to be a good ligand [77].

5.7 EXPERIMENTAL.

The preparation of samples and the instruments / conditions used for characterization purposes are described in section 3.5 with the exception of those given below.

<u>^{13}C nmr spectra</u>.

Approximately 30 mg of sample is dissolved in 0.7 mℓ benzene–d_6. Data accumulation is done at 30°C using a 45° pulse delayed for 6s. 8000 to 12000 scans are found to give a satisfactory signal / noise ratio and enable detection of the carbonyl carbons.

<u>Mass spectra</u>.

These are recorded on a Varian MAT 212 mass spectrometer operating at 70 eV at the DPCMT, CSIR, Pretoria.

5.7.1 The synthesis of Na[Co(CO)$_4$].

Na[Co(CO)$_4$] is synthesized by essentially the same method as that of Edgell [79]. 0.342 g (1 mmol) $Co_2(CO)_8$ together with 0.08 g (2 mmol) NaOH in 20 mℓ THF is commonly used.

The salt is prepared immediately prior to further use: the THF–solution of Na[Co(CO)$_4$] is merely filtered into the flask to be used for the next reaction.

5.7.2 The synthesis of [(σ–C_4H_7)Co(CO)$_3$(η^1–dppm)] (VI).

A solution of Na[Co(CO)$_4$] (2 mmol) in THF is cooled to –10°C in a 100 mℓ Schlenk vessel. To this a solution of dppm (0.768 g, 2 mmol) in 2 mℓ

dichloromethane and 5 mℓ THF is added slowly. Crotyl chloride (0.19 mℓ, 2 mmol; freshly distilled and saturated with N_2) is dissolved in 5 mℓ THF and added to the reaction mixture in a dropwise fashion. After stirring at –10°C for an hour, the solvent is slowly removed with the aid of the vacuum pump (0.1 mm / –10°C). Separation from unreacted starting material is accomplished by washing twice with cold (–30°C) pentane whereafter the product is dissolved in cold diethyl ether and filtered to remove unreacted dppm. The clear yellow solution is reduced to dryness leaving a pale yellow powder. This is further dried *in vacuo* (0.1 mm / –30°C / 4 hr). The product can be stored below –80°C under N_2. Storage at or above –20°C for more than a few hours results in rapid decomposition. Because of its immense instability, the product is only characterized by its $^{31}P\{^1H\}$ nmr spectrum.

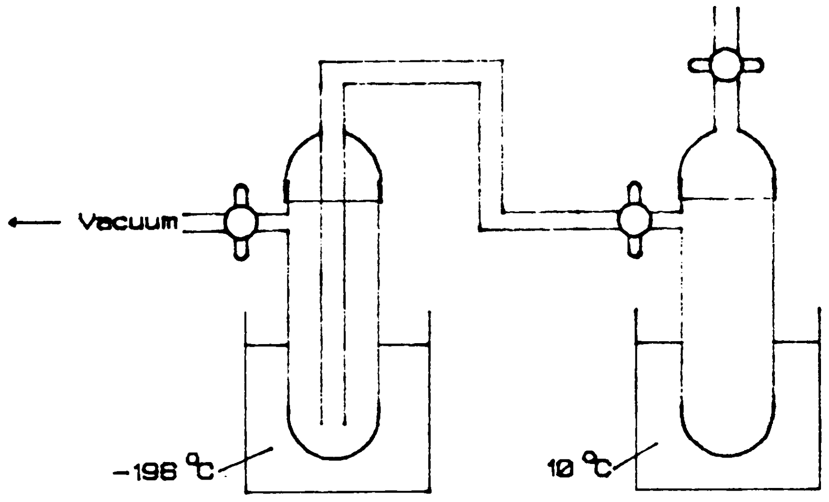
5.7.3 The synthesis of $[(\pi\text{–}RC_3H_4)Co(CO)_3]$ (R = H, CH_3).

A solution of $Na[Co(CO)_4]$ (2 mmol) in THF is chilled to –10°C. To this, 2 mmol of the particular allylchloride is added dropwise with a pipette upon which the pale yellow solution darkens somewhat. The solution is stirred overnight (12 – 14 hr) at 0°C, whereafter the temperature is raised to 30°C. Continued stirring for 3 hr (for R = H) or 6 – 8 hr (for R = CH_3) results in a dark orange solution consisting of approximately 70% of the π–allyl product as determined by ^1H nmr. After filtration to remove NaCl, these oily solutions are used without further purification.

5.7.4 The synthesis of $[(\pi\text{–}RC_3H_4)Co(CO)_3]$ (R = H, CH_3) with the aid of a phase–transfer catalyst.

0.114 g (0.5 mmol) benzyltriethylammoniumchloride is dissolved in 20 mℓ 5M

NaOH. A solution of 0.171 g (0.5 mmol) [$Co_2(CO)_8$] is rapidly added to the NaOH solution. Whilst stirring vigorously, the particular allylchloride (1 mmol) is added. After stirring for a further 15 min the reaction mixture is left to stand to allow separation of the phases. The benzene layer is decanted onto anhydrous Na_2SO_4, stirred for a few minutes and then filtered into a clean Schlenk vessel. The product is then purified by vacuum distillation (0.1 mm / 10°C) into a flask kept at the temperature of liquid nitrogen using the following apparatus:



The product is obtained as a clear yellow solution in benzene. This solution is used in subsequent reactions without further treatment.

5.7.5 The synthesis of $[(\pi\text{–}RC_3H_4)Co(CO)_2]_n(Ph_2P(CH_2)_nPPh_2)$
[R = H, n = 1 (VII); R = H, n = 2 (VIII);
R = CH_3, n = 1 (IX); R = CH_3, n = 2 (X)].

A solution of $[(\pi\text{–}RC_3H_4)Co(CO)_3]$ (R = H, CH_3) (2 mmol) in 30 mℓ THF is treated with the bis(phosphine) (2 mmol) in 5 mℓ dichloromethane. The pale orange solution is stirred for 30 min at room temperature after which the evolution of CO has ceased and the solution has taken on an orange–red colour.

The volume of the solution is reduced by half and an equal volume of hexane added. This process is repeated until an orange solid precipitates from the cold hexane. The solution is not reduced to dryness, but the last 10 mℓ of orange hexane solution removed with a pipette. The product is repeatedly washed with pentane (–20°C for **VII** and **IX**; 25°C for **VIII** and **X**) until the solvent remains clear, after which the product is dried *in vacuo*. **VIII** and **X** are further purified by recrystallization from dichloromethane / hexane. **VII** is purified on a short column (silica gel, 0.063 – 0.20 mm) packed in hexane under N_2. **IX** is too unstable to purify any further. All the products can be stored below –20°C under N_2. As reaction conditions are not optimized, yields are not determined, but they are reasonable (40% – 70%).

REFERENCES.

1. L Mond, H Hirtz and M D Cowap; J. Chem. Soc. (1910) 798.
2. W Hieber; Adv. Organomet. Chem. **8** (1970) 1.
3. V Galamb and G Palyi; Coord. Chem. Rev. **59** (1984) 203.
4. Y Wakatsuki, S Miya and H Yamazaki; J. Chem. Soc. Dalton Trans. (1986) 1207.
5. H Werner; Angew. Chem. **95** (1983) 932.
6. D Hargreaves and S Fromson; *World Index of Strategic Minerals*; Gower, New York, 1983.
7. A J Chalk and J F Harrod; *Catalysis by Cobalt Carbonyls*; Adv. Organomet. Chem. **6** (1968) 119.
8. C M Lukehart; *Fundamental Transition–Metal Organometallic Chemistry*; Brooks/Cole Publ. Co., Monterey California, 1985.
9. R L Pruett; Adv. Organomet. Chem. **17** (1979) 1.
10. C Masters; *Homogeneous Transition–Metal Catalysis*; Chapman and Hall, London, 1981 (pp 89 – 135).
11. J P Collman, L S Hegedus, J R Norton and R G Finke; *Principles and Applications of Organotransition Metal Chemistry*; Univ. Science Books, Mill Valley California, 1987.
12. L H Slaugh and R D Mullineaux; J. Organomet. Chem. **13** (1968) 469.
13. F A Cotton and G Wilkinson; *Advanced Inorganic Chemistry*, 5th ed.; Wiley–Interscience, New York, 1988. (Chapter 28)
14. R D W Kemmitt and D R Russell in *Comprehensive Organometallic Chemistry* (E W Abel, F G A Stone and G Wilkinson Eds) Vol 5 Pergamon, Oxford, 1981.
15. D A Buckingham and C R Clark in *Comprehensive Coordination Chemistry* (G Wilkinson ed–in–chief) Vol 4 (pp 636 – 882), Pergamon, Oxford, 1987.

16. Gmelin's Handbook of Inorganic Chemistry, Supplementary Work Vol 5: *Organocobalt Compounds*, *Part 1*: *Mononuclear Compounds*, 8th ed, Verlag Chemie, Weinheim, 1973.

17. Gmelin's Handbook of Inorganic Chemistry, Supplementary Work, Vol 6: *Organocobalt Compounds*, *Part 2*: *Polynuclear Compounds*, 8th ed, Verlag Chemie, Weinheim, 1973.

18. R F Heck; Adv. Organomet. Chem. **4** (1966) 243 and refs. therein.

19. C C Tso and A R Cutler; Organometallics **5** (1986) 1834.

20. K M Mackay and B K Nicholson in *Comprehensive Organometallic Chemistry* (E W Abel, F G A Stone and G Wilkinson Eds) Vol 6 (pp 1083 – 1090), Pergamon, Oxford, 1981.

21. E W Abel and F G A Stone; Quart. Rev. **23** (1969) 325.

22. P S Braterman; *Metal Carbonyl Spectra* (pp 36 – 94); Academic Press, London, 1975.

23. F A Cotton and C S Kraihanzel; J. Am. Chem. Soc. **84** (1962) 4432.

24. C S Kraihanzel and F A Cotton; Inorg. Chem. **2** (1963) 533.

25. P W Jolly and R Mynott; Adv. Organomet. Chem. **19** (1980) 257.

26. L J Schwartz; J. Chem. Ed. **65** (1988) 752.

27. R Benn and H Gunther; Angew. Chem. Int. Ed. Eng. **22** (1983) 350.

28. F W Wehrli and T Wirthlin; *Interpretation of carbon–13 nmr spectra*; Heyden and Son Ltd., London, 1980.

29. G C Levy and R A Komoroski; J. Am. Chem. Soc. **96** (1974) 678.

30. R D Bertrand, F B Ogilvie and J G Verkade; J. Am. Chem. Soc. **92** (1970) 1908.

31. D W Meek and T J Mazanec; Acc. Chem. Res. **14** (1981) 266.

32. F B Ogilvie, J M Jenkins and J G Verkade; J. Am. Chem. Soc. **92** (1970) 1916.

33. P J Smith and L Smith; Inorg. Chim. Acta Rev. **7** (1973) 11.

34. D H Harris, M F Lappert, J S Poland and W.McFarlane; J. Chem. Soc. Dalton Trans. (1975) 311.

35. V S Petrosyan; Progr. NMR Spectrosc. **11** (1977) 115.

36. R W Kiser in *Characterization of Organometallic Compounds, Part I* (M Tsutsui Ed); Interscience, New York, 1969. (Chapter 4, pp 137 – 211).

37. M I Bruce; Adv. Organomet. Chem. **6** (1968) 273.

38. J Muller; Angew. Chem. **84** (1972) 725.

39. A R Manning; J. Chem. Soc. (A) (1968) 1135.

40. W Hieber and W Freyer; Chem. Ber. **93** (1960) 462.

41. O Vohler; Chem. Ber. **91** (1958) 1235.

42. L M Bower and M H B Stiddard; J. Chem. Soc. (A) (1968) 706.

43. M D Curtis; Inorg. Chem. **11** (1972) 802.

44. D Seyferth and R J Spohn; J. Am. Chem. Soc. **91** (1969) 3037.

45. K Ogino and T L Brown; Inorg. Chem. **10** (1971) 517.

46. W Hieber and E Lindner; Chem. Ber. **94** (1961) 1417.

47. L F Wuyts and G P van der Kelen; Spectrochim. Acta, Part A **32** (1976) 1705.

48. R D George, K M Mackay and S R Stobart; J. Chem. Soc. Dalton Trans. (1972) 974.

49. B Y K Ho and J J Zuckerman; J. Organomet. Chem. **49** (1973) 1 (review).

50. A C Filippou, E O Fischer and H G Alt; J. Organomet. Chem. **330** (1987) 325.

51. A C Filippou, E O Fischer and G Muller; J. Organomet. Chem. **329** (1987) 223.

52. B J Aylett and J M Campbell; J. Chem. Soc. (A) (1969) 1910.

53. B Ziolkowska; Rozniki Chem. **43** (1969) 1781.

54. G C vd Berg, A Oskam and K Olie; J. Organomet. Chem. **80** (1974) 363.

55. D F Shriver; *The Manipulation of Air–sensitive Compounds*, McGraw–Hill, New York, 1969.

56. C Loubser and S Lotz; Inorg. Synth.; submitted for publication.

57. P M Treichel; Adv. Organomet. Chem. **11** (1973) 21.

58. P M Treichel and H J Mueh; Inorg. Chim. Acta **22** (1977) 265.

59. M O Albers and N J Coville; Coord. Chem. Rev. **53** (1984) 227.

60. M Scozzafava and A M Stolzenberg; Organometallics **7** (1987) 1073.

61. A M Stolzenberg, M Scozzafava and B M Foxman; Organometallics **6** (1987) 769.

62. R B King and M S Saran; Inorg. Chem. **11** (1972) 2112.

63. E L Muetterties and R A Schunn; Quart. Rev. Chem. Soc. **20** (1966) 245.

64. F H Westheimer; Acc. Chem. Res. **1** (1968) 70.

65. R W Stephany, M J A de Bie and W Drenth; Org. Magn. Res.**6** (1974) 45.

66. F A Cotton and F Zingales; J. Am. Chem. Soc. **83** (1961) 351.

67. D L Cronin, J R Wilkinson and L J Todd; J. Magn. Res. **17** (1975) 353.

68. E Singleton and H Oosthuizen; Adv. Organomet. Chem. **22** (1983) 209.

69. W E Carroll, M Green, A M R Galas, M Murray, T W Turney, A J Welch and P Woodward; J. Chem. Soc. Dalton Trans. (1980) 80.

70. R F Heck and D S Breslow; J. Am. Chem. Soc. **83** (1961) 1097.

71. W W Spooncer, A C Jones and L H Slaugh; J. Organomet. Chem. **18** (1969) 327.

72. H Alper, H. des Abbayes and D des Roches; J. Organomet. Chem. **121** (1976) C31.

73. L S Hegedus and Y Inoue; J. Am. Chem. Soc. **104** (1982) 4917.

74. L S Barinelli, K Tao and K M Nicholas; Organometallics **5** (1986) 588.

75. G Pregaglia, A Andreetta, G Ferrari, G Montrasi and R Ugo; J. Organomet. Chem. **33** (1971) 73.

76. P V Rinze and U Muller; Chem. Ber. **112** (1979) 1973.

77. R J Puddephatt; J. Chem. Soc. Rev. **12** (1981) 99.

78. W F Edgell and J Lyford IV; Inorg. Chem. **9** (1970) 1932.

79. A J Rest and D J Taylor; J. Chem. Soc. Dalton Trans. (1983) 1291.

80. D J Thornhill and A R Manning; J. Chem. Soc. Dalton Trans. (1973) 2086.

81. E C Lisic and B E Hanson; Inorg. Chem. **25** (1986) 812.

82. H Alper; Adv. Organomet. Chem. **19** (1980) 183.

83. W R McClellan and H H Hohn; J. Am. Chem. Soc. **83** (1961) 1601.

84. H L Clarke and N J Fitzpatrick; J. Organomet. Chem. **43** (1972) 405.

85. J A Bertrand, H B Jonassen and D W Moore; Inorg. Chem. **2** (1963) 601.

86. J A Connor, J P Day, E M Jones and G K McEwen; J. Chem. Soc. Dalton Trans. (1973) 347.

87. E E Isaacs and W A G Graham; Inorg. Chem. **14** (1975) 2560.

88. E E Isaacs and W A G Graham; J. Organomet. Chem. **120** (1976) 407.

89. F Sato, T Uemura and M Sato; J. Organomet. Chem. **56** (1973) C27.

90. Q–B Bao, S J Landon, A L Rheingold, T M Haller and T B Brill; Inorg. Chem. **24** (1985) 900.

91. X L Fontaine, G B Jacobsen, B L Shaw and M Thornton–Pett; J. Chem. Soc. Dalton Trans. (1988) 741.

92. G Kiel and J Takats; Organometallics **8** (1989) 839.

93. R J Mawby, D Morris, E M Thorsteinson and F Basolo; Inorg. Chem. **5** (1966) 27.

94. R J Abraham and H J Bernstein; Can. J. Chem. **39** (1961) 216.

95. M Akhtar, P D Ellis, A G MacDiarmid and J D Odom; Inorg. Chem. **11** (1972) 2917.

96. P E Garrou; Chem. Rev. **81** (1981) 229.

97. D A Redfield, L W Cary and J H Nelson; Inorg. Chem. **14** (1975) 50.

98. A W Verstuyft, J H Nelson and L W Cary; Inorg. Chem. **15** (1976) 732.