

Chapter 1: General Introduction

1.1. Carbene ligand

The chemistry of metal carbene complexes and of related complexes was introduced by Nobel Laureate Ernst Otto Fischer in 1964¹. Today, carbene complexes similar to those original Group 6 carbene complexes are referred to as Fischer carbene complexes. In this study, the somewhat neglected low-valent Fischer carbene complexes of rhenium were synthesized and studied and aspects of their chemistry were investigated.

1.1.1 Free carbene species

A free carbene molecule is comprised of a carbon with two substituents. One of the four carbon valence electrons is involved in σ -bonding to each of the substituents. The remaining two valence electrons are available for bonding. The carbene carbon atom therefore represents a six-electron species and is very reactive (unfilled octet). The two electrons not involved in bonding may be paired in one of the remaining orbitals and such a carbene is defined as a singlet carbene. In a triplet carbene, on the other hand, the two electrons each occupy its own orbital. Reactive carbene moieties can be stabilized by coordination to transition metals and Arduengo² and Bertrand³ pioneered research in the isolation of free carbenes (Figure 1.1).

The bent structure of the carbene ligand comes from the carbene carbon atom being sp^2 hybridized.

¹ E.O. Fischer, A. Maasböl; *Angew. Chem., Int. Ed. Engl.*, **1964**, 3, 580–581

² A. J. Arduengo, R. L. Harlow, M. Kline; *J. Am. Chem. Soc.*, **1991**, 113, 361–363

³ (a) A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand; *J. Am. Chem. Soc.*, **1988**, 110, 6463–6466; (b) A. Igau, A. Baceiredo, C. Trinquier, G. Bertrand; *Angew. Chem. Int. Ed. Engl.*, **1989**, 28, 621–622; (c) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand; *J. Organomet. Chem.*; **2004**, 689, 3857–3865

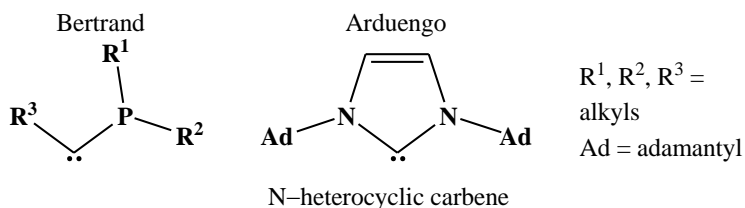


Figure 1.1: The Bertrand and Arduengo carbenes

1.1.2 Low-valent metal carbene complexes

The carbene function of a Fischer carbene complex can be generated from the stepwise reaction of a metal carbonyl precursor with organolithium agents (which nucleophilically attack a carbonyl ligand), followed by alkylation. After alkylation the carbene displays an alkoxy substituent. A Fischer carbene complex in this context can be seen as an organometallic analogue of an organic ester. The nature of bonding, however, is different than that of an ester. The bonding of the carbene ligand is shown in Figure 1.2⁴.

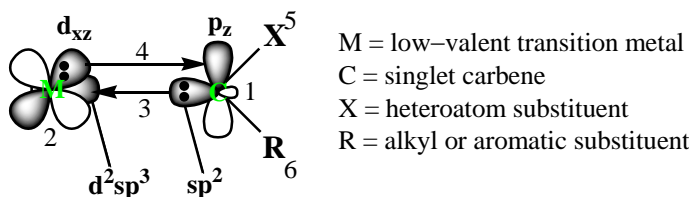


Figure 1.2: Typical Fischer carbene complex showing the bonding between the carbene carbon and its substituents

In a typical Fischer carbene complex, the sp^2 singlet carbene ligand (1) is an L-type ligand (Green classification⁵), bonding to the transition metal (2), which is formally in a low oxidation state, by dative σ -donation of an electron-pair in a sp^2 -hybrid orbital (3).

⁴ In an ester, electrons are shared in normal covalent bonds, but in the Fischer carbene complex the electron-pairs are donated by the two partners in a synergic fashion, i.e. the metal atom and the carbon atom.

⁵ M. L. H. Green; *J. Organomet. Chem.*, **1995**, 500, 127–148

A second dative back-donation from the metal (t_{2g} -orbitals) into the empty p-orbital on the carbene carbon makes a π -bond (4). Commonly, oxygen or nitrogen (with their own substituents) is the heteroatom (5). These heteroatoms contain electron lone-pairs (Lewis bases) that can be donated into the carbene carbon's empty p-orbital. The competition for π -stabilization between the metal and the heteroatom might be depicted by the following resonance forms (Scheme 1.1).



Scheme 1.1: π -Bonding interactions in Fischer carbene complexes

Because nitrogen has a lower electronegativity than oxygen, nitrogen will more effectively participate in backbonding to the carbene carbon atom. If the substituents of the carbene carbon can dominate the stabilization of the carbene carbon through π -donation, the metal back-donation into the carbene carbon p-orbital is of only minor relevance. Under these circumstances the bond between the metal atom and carbon atom is longer, and one would not necessarily draw the bond as containing double bond character. This is the case with N-heterocyclic carbene ligands (NHCs), which are quite stable as free uncomplexed molecules⁶ – they are usually stabilized by bulky nitrogen substituents. As another example, consider a high-valent metal species that has no t_{2g} electrons⁷ available in a low-lying orbital to π -donate into the carbene carbon p-orbital.

1.1.3 Applications of Fischer carbene complexes

Fischer carbene complexes have current impact in chemistry in template reactions in

⁶ M. F. Lappert; *J. Organomet. Chem.*, **2005**, 690, 5467–5473

⁷ W. A. Herrmann, K. Öfele, M. Elison, F. E. Kuhn, P. W. Roesky; *J. Organomet. Chem.*, **1994**, 480, C7–C9

organic chemistry⁸, in catalysis⁹ and in materials science¹⁰. NHCs, that are superior to phosphines in many respects, are found as ancillary ligands for coupling–reaction catalysts¹¹ and metathesis (Grubbs) catalysts¹².

A metal–carbene connection can be made by attachment of the free carbene species at a vacant coordination site on a metal, which is an application of free carbenes¹³. This is not the most common method of carbene complex synthesis, because free carbenes are difficult to work with as they tend to dimerize¹⁴.

1.2. Group 7 metal carbene complexes

1.2.1 Background/Introduction

Group 7 transition metals have an uneven number of valence electrons and thus require at least one X–type ligand (see Green classification of ligands⁵). Synthesis of Group 7 carbene complexes, in this study, involved low–valent dirhenium decacarbonyl or rheniumpentacarbonyl bromide. The X–type ligand of each rhenium in the dimer complex $(\text{CO})_5\text{Re–Re}(\text{CO})_5$ is “ $\text{Re}(\text{CO})_5$ ” and in $[\text{Re}(\text{CO})_5\text{Br}]$, it is the bromo ligand. For

⁸ J. W. Herndon; *Coord. Chem. Rev.*, **2000**, 206–207, 237–262

⁹ C. W. Bielawska, R. H. Grubbs; *Progress in Polymer Science*, **2007**, 32, 1–29

¹⁰ J. Barluenga, D. de Saa, A. Gomez, A. Ballesteros, J. Santamara, A. de Prado, M. Tomas, A. L. Suarez–Sobrino; *Angew. Chem. Int. Ed.*, **2008**, 47, 6225–6228

¹¹ R. Chinchilla, C. Najera; *Chem. Rev.* **2007**, 107, 874–922

¹² a) S. T. Nguyen, R. H. Grubbs, J. W. Ziller; *J. Am. Chem. Soc.*, **1993**, 115, 9858–9859; b) G. C. Fu, S. T. Nguyen, R. H. Grubbs; *J. Am. Chem. Soc.*, **1993**, 115, 9856–9857; c) T. M. Trnka, R. H. Grubbs; *Acc. Chem. Res.*, **2001**, 34, 18–29; (d) P. Schwab, M. B. France, J. W. Zille, R. H. Grubbs; *Angew. Chem., Int. Ed. Engl.*, **1995**, 34, 2039–2041; (e) E. L. Dias, S. T. Nguyen, R. H. Grubbs; *J. Am. Chem. Soc.*, **1997**, 119, 3887–3897; (f) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann; *Angew. Chem., Int. Ed. Engl.*, **1999**, 38, 2416–2419; (g) S. F. Vyboishchikov, M. Buhl, W. Thiel; *Chem. Eur. J.*, **2002**, 8, 3962–3975

¹³ A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R. H. Crabtree; *J. Am. Chem. Soc.*, **2007**, 129, 12834–12846

¹⁴ W. Kirmse; *Angew. Chem. Int. Ed. Engl.*, **2005**, 44, 2476–2479

different complexes $[M(CO)_4LX]$ ($L = CO, C(OR)R'$; $X = \text{halide, H, } M(CO)_5$), we have isolobal relationships for the X-type ligands, as indicated below¹⁵:



1.2.2 X-ligands in Group 7 metal carbene chemistry

Halogen substitution is a common tool in chemical transformation. As an example: a charged organic nucleophile can replace a halogen ligand of a Group 7 metal complex¹⁶. Then there are examples of an organic group bearing a halogen that couples with an anionic metal complex¹⁷. Shown in Scheme 1.2 is a reaction that was reported by King¹⁸; the reaction of the metal carbonyl anionic complex, $[Mn(CO)_5]^-$, with 1,3-dibromopropane. The structure of the product was assigned incorrectly by King, as indicated in Scheme 1.2, because three signals in the proton NMR spectrum were misinterpreted. Proton NMR spectroscopy was later employed by Casey to assign the correct structure¹⁹.

The true structure of the complex that was obtained by King raises the interesting question of how it might have formed. A mechanism for the formation of the dimanganese monocarbene complex is provided in Scheme 1.3. It shows a replacement of one of the 1,3-dibromopropane bromines by $[Mn(CO)_5]^-$. The new alkyl ligand on the manganese migrates to a carbonyl ligand and a vacant coordination site is created. An attack by $[Mn(CO)_5]^-$ on this intermediate complex induced electron movement and bond-formation between the acyl oxygen atom and the farthest carbon atom (with bromide expulsion), produced the final Fischer carbene complex. King was correct in

¹⁵ R. Hoffmann; *Angew Chem. Int. Ed. Engl.*, **1982**, 21, 711–724

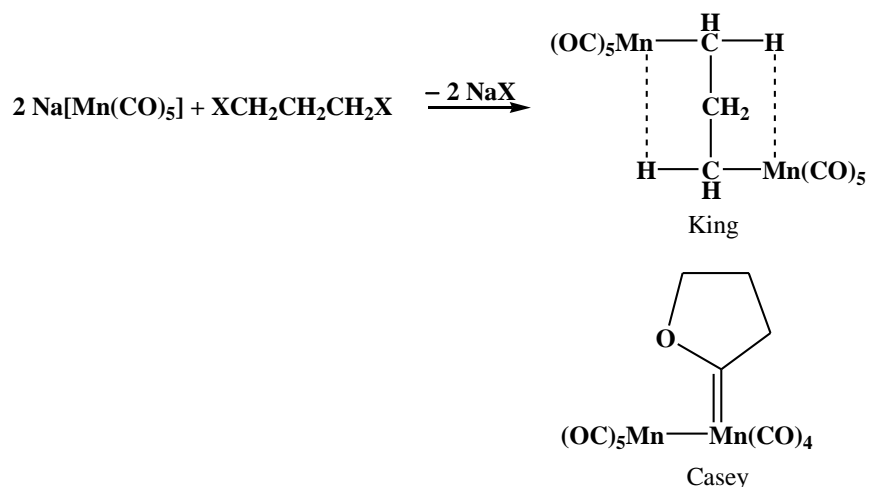
¹⁶ (a) S. Lotz, M. Schindehutte, P. H. Van Rooyen; *Organometallics*, **1992**, 11, 629–639; (b) T. A. Waldbach, P. H. van Rooyen, S. Lotz; *Organometallics*, **1993**, 12, 4250–4253; (c) T. A. Waldbach, P. H. van Rooyen, S. Lotz; *Angew. Chem. Int. Ed. Engl.*, **1993**, 32, 710–712

¹⁷ Y. Matsuo, Y. Kuninobu, A. Muramatsu, M. Sawamura, E. Nakamura; *Organometallics*, **2008**, 27, 3403–3409

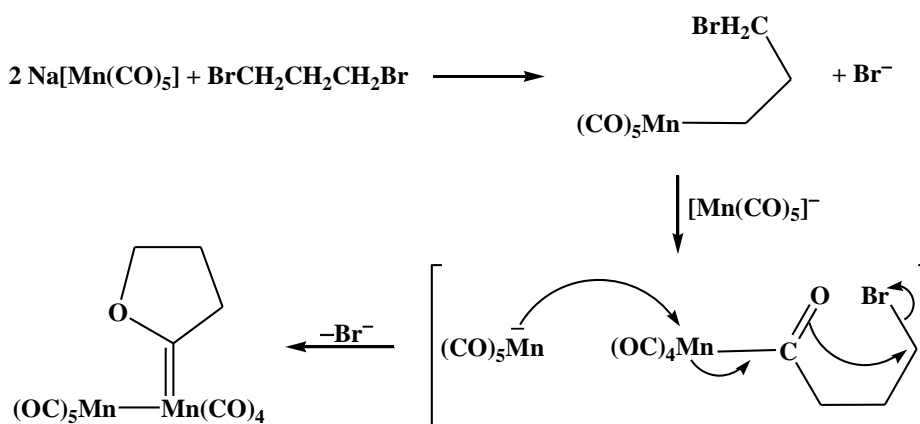
¹⁸ R. B. King; *J. Am. Chem. Soc.*, **1963**, 85, 1922–1926

¹⁹ C. P. Casey; *J. C. S. Chem. Comm.*, **1970**, 1220–1221

assuming a path where both the halogen atoms were lost from the reagent, as the final carbene complex is indeed without any halogens.



Scheme 1.2: King and Casey structures for the dimanganese carbene complex

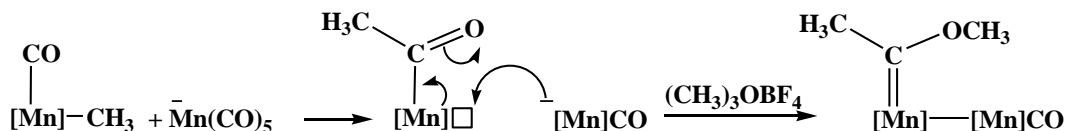


Scheme 1.3: A mechanism for the formation of the ‘King’ complex

Casey also showed that the anionic complex $[\text{Mn}(\text{CO})_5]^-$ attacks on the manganese complex $[\text{Mn}(\text{CO})_5(\text{CH}_3)]$, induces the alkyl ligand to migrate to a carbonyl ligand, and then binds to the manganese. Alkylating agent was added and the carbene complex

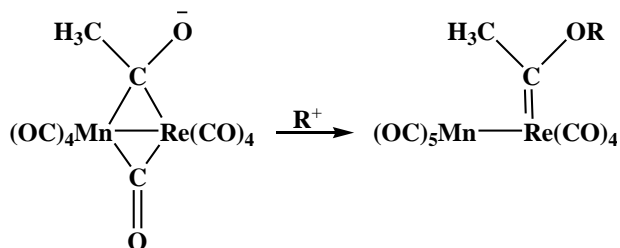
formed²⁰, as illustrated in Scheme 1.4.

[Mn] = Mn(CO)₄ □ = vacated coordination site



Scheme 1.4: Nucleophilic attack induces methyl migration

Interestingly, in the reaction of Na[Re(CO)₅] and [Mn(CO)₅CH₃], the carbene ligand of the resulting mixed Mn–Re complex is found on the rhenium fragment. An intermediate (Scheme 1.5) with a bridging acylate ligand was postulated.

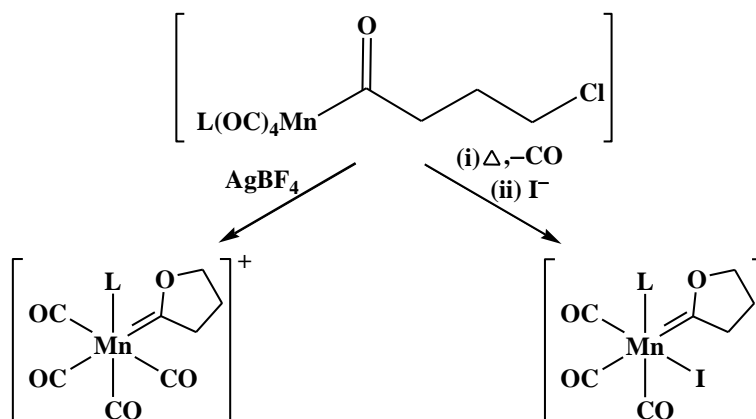


Scheme 1.5: Mn–Re carbene complex

Monomanganese carbene complexes were synthesized by reacting Na[Mn(CO)₄L] with 4-chlorobutyryl chloride (has carbonyl functionality built into the organic substrate), to give an intermediate chloro acyl compound. Abstraction of the terminal chlorine of the acyl ligand by AgBF₄ gave a cationic carbene complex, whilst heating and reacting with iodide gave a neutral carbene complex²¹ (Scheme 1.6).

²⁰ (a) C. P. Casey, R. L. Anderson; *J. Am. Chem. Soc.*, **1971**, 93, 3554–3555; (b) C. P. Casey, C. R. Cyr, R. L. Anderson, D. F. Marten; *J. Am. Chem. Soc.*; **1975**; 97; 3053–3059

²¹ C. H. Game, M. Green, J. R. Moss, F. G. A. Stone; *J.C.S. Dalton Trans.*, **1974**, 351–357



Scheme 1.6: Carbene ligand formation through cyclization

In another interesting reaction, the replacement of two of the carbonyl ligands of the manganese acyl complex $[\text{Mn}(\text{CO})_5\{\text{C}(\text{O})\text{Me}\}]$ by 1,2-bis(diphenylphosphino)ethane (dppe) facilitates the alkylation of the acyl ligand. The resultant complex, $[\text{Mn}(\text{CO})_3(\text{dppe})\{\text{C}(\text{O})\text{Me}\}]$, reacts with $\text{CF}_3\text{SO}_3\text{CH}_3$ and the monomanganese cationic carbene complex $[\text{Mn}(\text{CO})_3(\text{dppe})\{\text{C}(\text{OMe})\text{Me}\}]^+\text{OSO}_2\text{CF}_3$ forms²².

1.3 Reactions of Group 7 metal complexes with nucleophiles

1.3.1 Fischer carbene complexes

Nucleophiles (even halides²³) can transform carbonyl and isocyanide ligands into Fischer carbene ligands, by nucleophilic attack on the carbon atom of these ligands. The carbon of CO and CNR^{24} ligands donates an electron-pair to the metal and has a hetero-atom already bonded to it, similar to the Fischer carbene carbon atom.

E. O. Fischer synthesized dirhenium carbene complexes by his established method of reaction with a nucleophile (Nu^-), which attacks on a carbonyl ligand, and then

²² P. M. Treichel, K. P. Wagner; *J. Organomet. Chem.*, **1975**, 88, 199–206

²³ E. O. Fischer, J. Chen, K. Scherzer; *J. Organomet. Chem.*, **1983**, 253, 231–241

²⁴ F. E. Hahn, V. Langenhahn, T. Pape, *Chem. Commun.*, **2005**, 5390–5392

alkylation (electrophile: R⁺) of the intermediate²⁵:



In the same way Fischer prepared dimanganese monocarbene complexes, starting with $\text{Mn}_2(\text{CO})_{10}$ ²⁶, as well as equatorial technetium monocarbene complexes, starting with $\text{Tc}_2(\text{CO})_{10}$ ²⁷.

Schubert reported some very interesting dirhenium biscarbene complexes with silyl nucleophiles²⁸ (Figure 1.3). One of the complexes is the only example that we are aware of where two carbene ligands are coordinated to a dirhenium system, with one carbene ligand coordinated in an axial position and the other in an equatorial position.

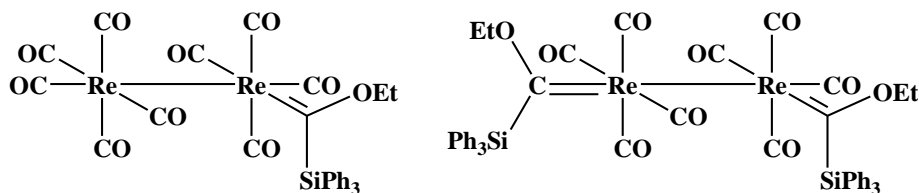


Figure 1.3: Rustemeyer dirhenium carbene complexes

1.3.2 Possible reaction intermediates

By contrast to Group 6 transition metal carbonyl complexes, more reactive intermediates are possible when Group 7 transition metal complexes react with the nucleophiles, because both L-type and X-type ligands are present in the precursors: “[Re(CO)₅X]”. With X being “Re(CO)₅”, the outcome of the Fischer carbene synthesis reaction is

²⁵ E. O. Fischer, E. Offhaus, J. Muller, D. Nöthe; *Chem. Ber.*, **1972**, *105*, 3027–3035

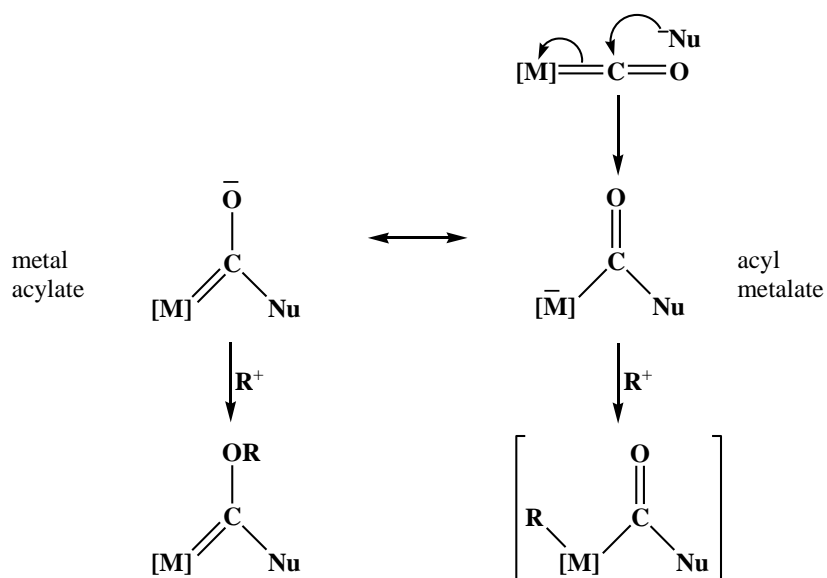
²⁶ E. O. Fischer, E. Offhaus; *Chem. Ber.*, **1969**, *102*, 2449–2455

²⁷ E. O. Fischer, E. Offhaus, J. Müller, D. Nöthe; *Chem. Ber.*, **1972**, *105*, 3027–3035

²⁸ E. O. Fischer, P. Rustemeyer; *J. Organomet. Chem.*, **1982**, *225*, 265–277; (b) U. Schubert, K. Ackermann, P. Rustemeyer; *J. Organomet. Chem.*, **1982**, *231*, 323–334; (c) E. O. Fischer, P. Rustemeyer, O. Orama, D. Neugebauer, U. Schubert; *J. Organomet. Chem.*, **1983**, *247*, 7–19

however the same as for Group 6 transition metal carbonyl complexes.

When the nucleophile attacks on the carbonyl carbon atom, the bond order of the bond between the carbon and the metal or of the bond between the carbon and the oxygen is affected (Scheme 1.7). The carbon is rehybridized from sp to sp^2 . The electrophile that is added, for instance an alkylating agent (oxonium salts like $[R_3O]BF_4$ are commonly used), will react with the atom of higher negative charge. A metalate normally forms if the anionic nucleophile attacks on the carbon atom of a carbonyl ligand. A metal acylate is a resonance form of the former. Both cases are illustrated in Scheme 1.7. The double bond location between the carbon atom and one of its three substituents is of consequence as it impacts on the nature of the σ -bonding around the carbon atom.

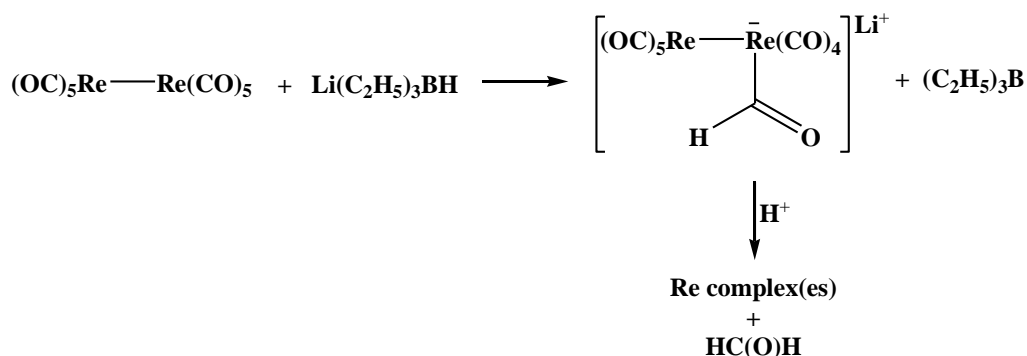


Scheme 1.7: Possible intermediates and products after attack of a nucleophile and subsequent alkylation

The alkylation on the metal of the acyl metalate species generally affords unstable complexes with two X-type ligands, whose reductive elimination gives an organic product (for instance ketones). Semmelhack showed that such iron tetracarbonyl phenyl carbene intermediates react with alkylating agents ($R-X$) to be alkylated at the metal –

PhCOR and PhCO₂R were obtained (FeCl₃ was added).²⁹

Gladysz and co-workers made X-type formyl ligands by reacting [Re₂(CO)₁₀] and [Mn₂(CO)₁₀] with a hydride source³⁰. Nucleophilic attack on a carbonyl ligand by the hydride resulted in the shift of an electron to the metal and not the oxygen atom. The complexes could then dissociate formaldehyde by reaction with acid (Scheme 1.8). The proton presumably bonds to the rhenium and is then reductively eliminated with the acyl ligand.



Scheme 1.8: Anionic formyl complex formation

The metal acylate form is found in most cases to be alkylated to give neutral Fischer carbene complexes. Fischer alkoxy-carbene carbon atoms generally display the following order of π -stabilization: M > O >> C(R).

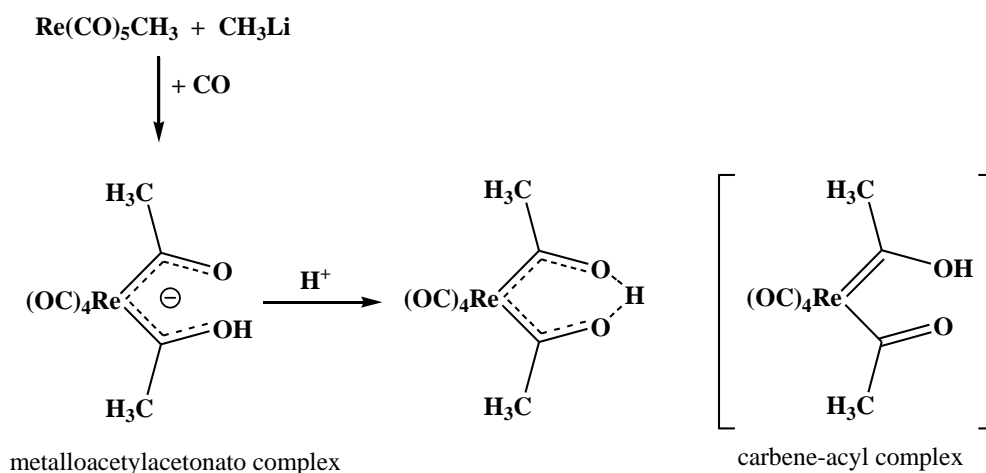
An alternative to alkylating the oxygen of the metal acylate is to protonate it with an acid, a process that produces hydroxycarbene complexes. In the 1960s E. O. Fischer prepared hydroxycarbene complexes and the carbene ligands were found to be transformed into

²⁹ (a) H. Alper, J-L. Fabre; *Organometallics* **1982**, *1*, 1037–1040; (b) W. Petz; *Organometallics*, **1983**, *2*, 1044–1046; (c) K. H. Dötz, U. Wenicker, G. Muller, H. G. Alt, D. Seyferth; *Organometallics* **1986**, *5*, 2570–2572; (d) M. F. Semmelhack, R. Tamura; *J. Am. Chem. Soc.*, **1983**, *105*, 4099–4100

³⁰ W. Tam, M. Marsi, J. A. Gladysz; *Inorg. Chem.*, **1983**, *22*, 1413–1421

aldehydes (a product one might expect if the protonation was on the metal)³¹.

Lukehart prepared a fascinating monorhenium compound displaying both acyl and hydroxycarbene ligands³² – the synthesis is shown in Scheme 1.9. The intermediate was referred to as a metalloacetylacetonato complex because it is the organometallic analogue of acac and may itself be a ligand to other metals. What is most interesting is that, where one might define one of the ligands in the final complex as being a hydroxycarbene ligand and the other as being an acyl ligand, both of the ligands actually have carbene and acyl character. It was illustrated in Scheme 1.7 that the intermediate forms of Fischer carbene complex synthesis may be a metal acylate or an acyl metalate species, depending on the location of the charge and of the double bond. In the Lukehart complex, the delocalization of negative charge and double bond is also evident.



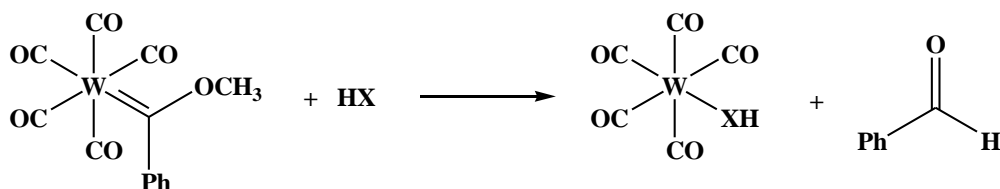
Scheme 1.9: Lukehart's rheniaacetylacetonato complex

The reaction between a tungsten Fischer carbene complex and a strong acid also leads to aldehydes and strong acid complexes being formed by cleavage of the metal–carbene

³¹ (a) E. O. Fischer, G. Kreis, F. R. Kreissl; *J. Organomet. Chem.*, **1973**, 56, C37–C40; (b) M. Ryang, I. Rhee, S. Tsutsumi; *Bull. Chem. Soc. Jpn.*, **1964**, 37, 341–343

³² (a) C. M. Lukehart, G. Paull Torrence, J. V. Zeile; *J. Am. Chem. Soc.*; **1975**; 97, 6903–6904; (b) C. M. Lukehart, J. V. Zeile; *J. Am. Chem. Soc.*; **1976**, 98, 2365–2367

bond³³:



Scheme 1.10: Aldehyde formation from Fischer carbene complexes

The carbene carbon is bonded to three atoms that may or may not stabilize it by π -donation into the empty carbene p-orbital. It has been shown how there may be double bonding between the metal and the oxygen atom. The former attacking nucleophile is usually a carbon substituent (sp , sp^2 , sp^3 -C) and less stabilization, through π -interaction, is expected to come from a carbon substituent than from the metal or oxygen substituent. If it is an aromatic ring, for instance, π -interaction between it and the carbene carbon would correspond to a loss of aromaticity, which would be energetically unfavourable. The third substituent may however also be a heteroatom that has available electron-pairs. Examples of these are the N-heterocyclic carbene complexes where the π -stabilization from the ring nitrogen atoms is greater than that from the metal.

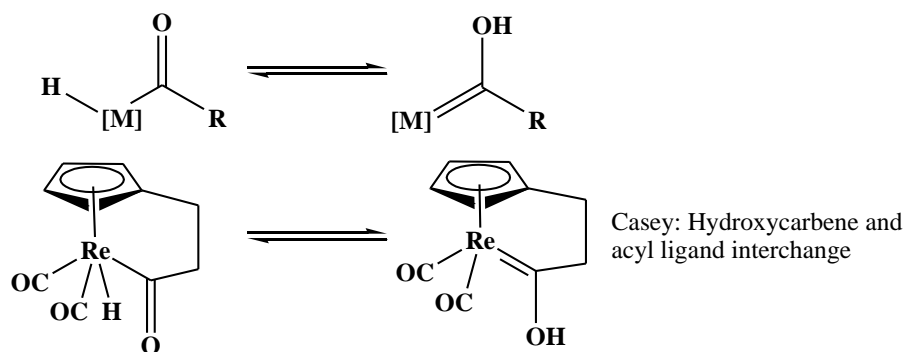
In the carbonyl transition metal complexes of transition metals that have an even number of valence electrons (complexes that may only have L-type ligands), the carbene synthesis could produce an acyl intermediate with a negative charge on the metal. Alkylation on the metal will then give a complex with two X-type ligands, which may both reductively eliminate. Group 7 metals differ in that they already have to have an X-type ligand or a ligand with X-functionality built in (for instance the L_2X Cp ligand) for an eighteen electron configuration. If $[Re(CO)_5Br]$ is reacted with a nucleophile, an interesting anionic intermediate may be obtained, which is the eighteen electron acyl intermediate $[Re(CO)_4\{C(O)Nu\}Br]^-$. If the bromo ligand is lost from the intermediate rhenium complex as bromide, one X-type ligand is lost, not two, as with reductive

³³ E. O. Fischer, S. Walz, G. Kreis, F. R. Kreissl; *Chem. Ber.*, **1977**, *110*, 1651–1658

elimination. An unsaturated neutral acyl complex is left. This occurrence represents an added dimension of reactivity that does not exist with Group 6 or 8 metal carbene intermediates and it forms an integral part of this study.

1.4 Dual nature of ligands (L, X) in Group 7 metal complexes

The hydroxycarbene ligand of a Fischer carbene complex is an L-type ligand, formed by oxygen protonation of the metal acylate intermediate. If the hydrogen atom that is bonded to the oxygen substituent migrates to the metal, the carbene ligand is transformed into two X-type ligands, i.e. the acyl and hydride (Scheme 1.11). These interchangeable species are organometallic analogues of keto–enol tautomerization in organic chemistry (Scheme 1.11). Casey showed that a hydroxycarbene complex and a metal acyl–hydride complex are in equilibrium (the favoured form depends on the solvent)³⁴. The carbene could be converted to a non–heteroatom stabilized amphiphilic carbene complex (can behave like a Fischer or a Schrock carbene)³⁵.



Scheme 1.11: “Metallo–keto” and “metallo–enol” tautomers

It has been discussed that a rhenium ligand can show properties intermediate between

³⁴ C. P. Casey, C. J. Czerwinski, R. K. Hayashi; *J. Am. Chem. Soc.*; **1995**, *117*, 4189–4190

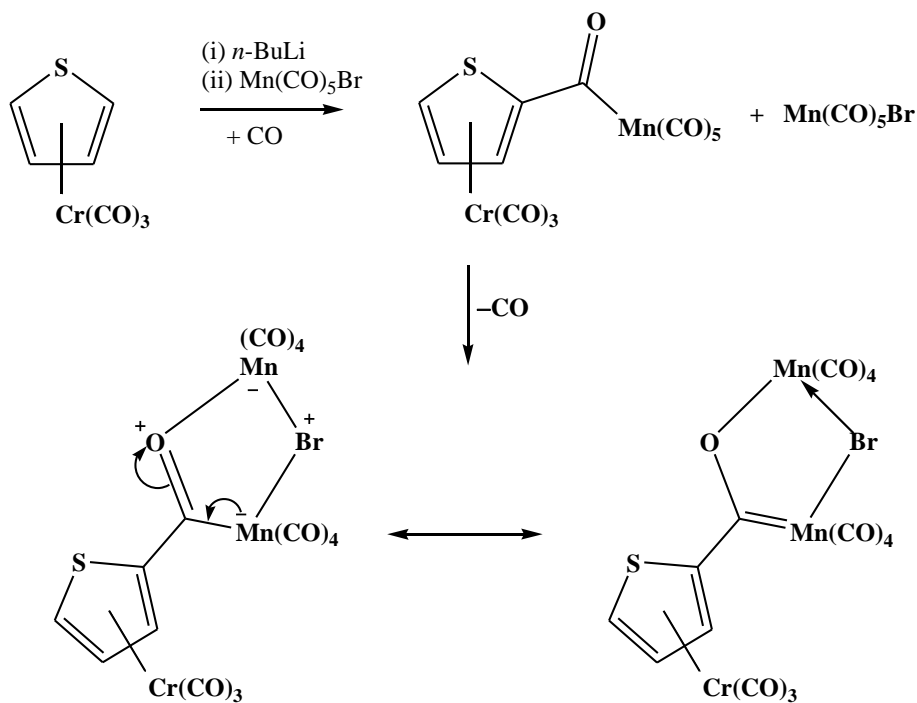
³⁵ (a) C. P. Casey, C. J. Czerwinski, K. A. Fusie, R. K. Hayashi; *J. Am. Chem. Soc.*, **1997**, *119*, 3971–3978;

(b) C. P. Casey, C. J. Czerwinski, D. R. Powell, R. K. Hayashi; *J. Am. Chem. Soc.*, **1997**, *119*, 5750–5751;

(c) C. P. Casey, H. Nagashima; *J. Am. Chem. Soc.*, **1989**, *111*, 2352–2353; (d) C P. Casey, P. C. Vosejпка,

F. R. Askham; *J. Am. Chem. Soc.*, **1990**, *112*, 3713–3715

those of a carbene and an acyl ligand³². Manganese also has seven valence electrons, like rhenium. The reaction of lithiated $[\text{Cr}\{\eta^5\text{-C}_4\text{H}_4\text{S}\}(\text{CO})_3]$ with $[\text{Mn}(\text{CO})_5\text{Br}]$ was studied in our laboratories and a major product was a bimetallic manganese acyl complex (Scheme 1.12)³⁶. Reaction with additional manganesepentacarbonyl bromide led to the formation of a novel trimetallic complex, which displays two $\text{Mn}(\text{CO})_4$ fragments bridged by an acyl and a bromo ligand. The manganese–carbon and carbon–oxygen bond lengths of the complex are intermediate and describe two contributing structures for the dimetallacycle: those of a bridging acyl and a bridging carbene–oxy ligand, as shown in Scheme 1.12.

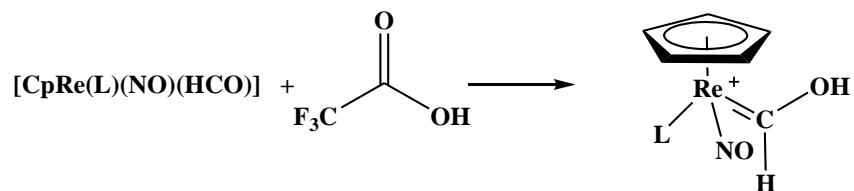


Scheme 1.12: Carbene and acyl ligands in a dimanganese complex

Gladysz and co-workers also showed that formyl ligands of Re could be transformed into hydroxycarbene ligands by reactions with strong organic acids³⁷.

³⁶ T. A. Waldbach, R. van Eldik, P. H. van Rooyen, S. Lotz; *Organometallics*, **1997**, *16*, 4056–4070

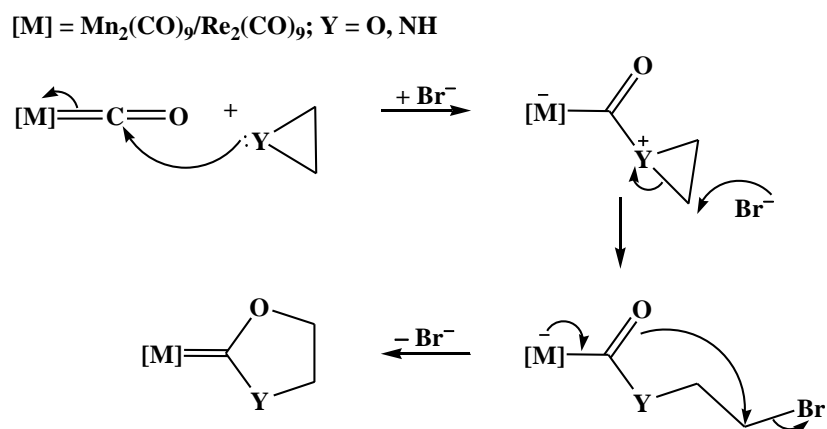
³⁷ W–K. Wong, W. Tam, J. A. Gladysz; *J. Am. Chem. Soc.*; **1979**, *101*, 5440–5442



Scheme 1.13: Formyl ligand transformed into carbene ligand

1.5 Carbene formation through halide catalysis

Angelici reported dirhenium and dimanganese carbene complexes, synthesized by using bromide to catalyze the ring-opening of oxirane and aziridine³⁸ (Scheme 1.14). Cyclic oxy-carbene complexes can also be prepared from Group 7 pentacarbonyl cationic species³⁹.



Scheme 1.14: Synthesis of carbene complexes using halide (X^-) as catalyst

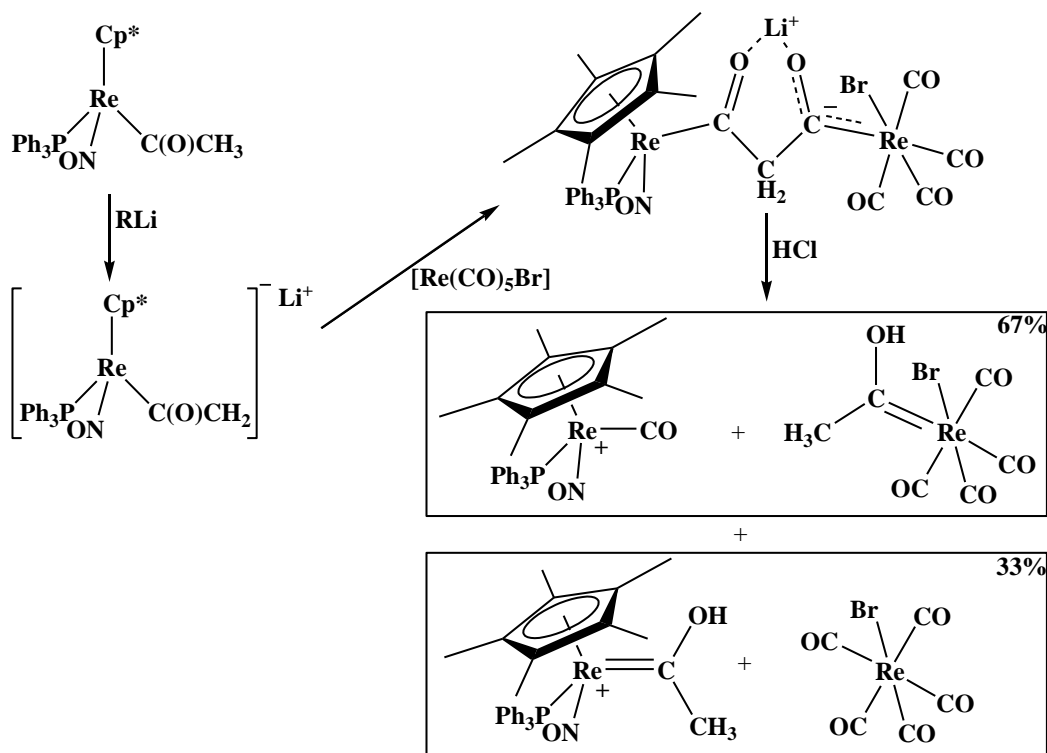
1.6 Hydroxycarbene complexes

An important goal of this study was to learn more about the fascinating relationship

³⁸ (a) M. M. Singh, R. I. Angelici; *Inorg. Chim. Acta*, **1985**, *100*, 57–63; (b) M. M. Singh, R. J. Angelici; *Inorg. Chem.*, **1984**, *23*, 2699–2705

³⁹ E. Fritsch, T. Kerscher, K. Polborn, W. Beck; *J. Organomet. Chem.*, **1993**, *460*, C25–C27

between acyl and carbene ligands. For an acyl ligand to be transformed into a hydroxycarbene ligand, a hydrogen atom is required. In a hydride–acyl metal complex the hydrogen atom is available as a metal ligand and its migration to the acyl oxygen atom leads to the formation of the hydroxycarbene complex. A complex was reported that consist of a $\text{ReCp}(\text{NO})(\text{PPh}_3)$ and a $\text{Re}(\text{CO})_4\text{Br}$ unit, spanned by a malonyl ligand. Neither metal fragment has a hydride ligand. The introduction of a proton led to the formation of a hydroxycarbene complex⁴⁰ (Scheme 1.15). The stability of the fragments generated in the cleavage reactions is reported by the authors to be a driving force for the reaction.

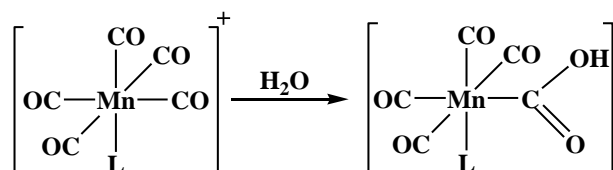


Scheme 1.15: Formation of hydroxycarbene complex from acyl complex

The carbonyl oxygen atom of a cationic manganese complex may be exchanged for the

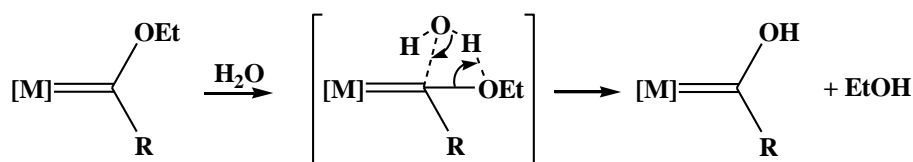
⁴⁰ J. M. O'Connor, R. Uhrhammer, R. K. Chadha, B. Tsu, A. L. Rheingold; *J. Organomet. Chem.*, **1993**, 455, 143–156 and references therein.

oxygen atom of water (Scheme 1.16)⁴¹. The intermediate acyl species that forms is interesting for its relationship to a hydroxycarbene complex. Elimination of CO₂ could afford the metal hydride through β-hydrogen transfer.



Scheme 1.16: Reaction of a manganese carbonyl cationic derivative with water

The formation of hydroxycarbene intermediates was observed in a kinetic study of the reaction of alkoxy carbene complexes with nucleophiles such as OH⁻ and H₂O (Schemes 1.17 and 1.18)⁴². Ylide formation, from reactions of nucleophiles with carbene complexes, has been documented for Group 6 metal carbene complexes⁴³. Attack of a hydroxide on an alkoxy carbene complex could lead to the formation of an anionic ylide intermediate, which could regenerate a hydroxycarbene ligand by elimination of ethanol, shown below:

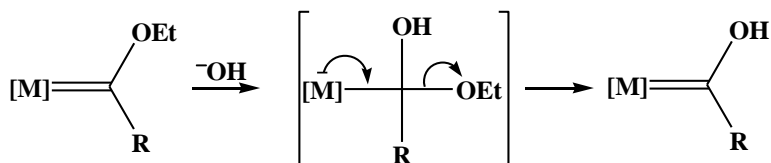


Scheme 1.17: Hydroxycarbene complexes via water-ethanol exchange

⁴¹ D. J. Darensbourg, J. A. Froelich; *J. Am. Chem. Soc.*; **1977**, *99*, 5940–5946

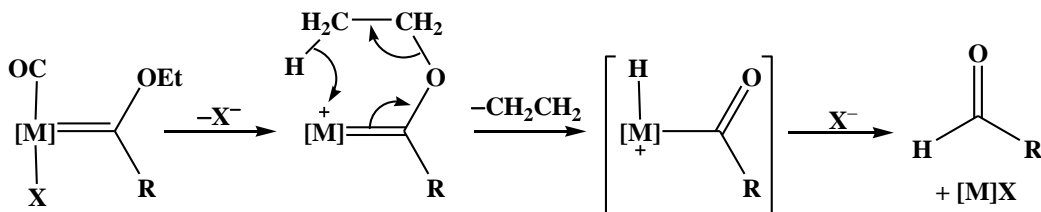
⁴² (a) C. F. Bernasconi; *Chem. Soc. Rev.*, **1997**, *26*, 299–307; (b) Aminolysis: M. Ali, S. Gangopadhyay, M. Mijanuddin; *J. Organomet. Chem.*, **2005**, *690*, 4878–4885

⁴³ (a) F. R. Kreissl, E. O. Fischer; *Chem. Ber.*, **1973**, *107*, 183–188; (b) E. O. Fischer, G. Kreis, F. R. Kreissl, C. G. Kreiter, J. Müller; *Chem. Ber.*, **1973**, *106*, 3910–3919



Scheme 1.18: Hydroxycarbene complexes via ylide intermediates

A different scenario can be proposed for going from an ethoxycarbene complex to a metal complex containing an acyl and hydride ligand. Scheme 1.19 shows a potential reaction based on C–H activation of a terminal methyl group. This is a less likely, but interesting alternative process which is, as far as we are aware, without a precedent in literature. It also represents a modification of $ZL \rightarrow X_2$ ligands according to the Green classification method and could be initiated by carbonyl loss and a remote agostic H–interaction.



Scheme 1.19: Metal hydrides from ethoxycarbene complexes

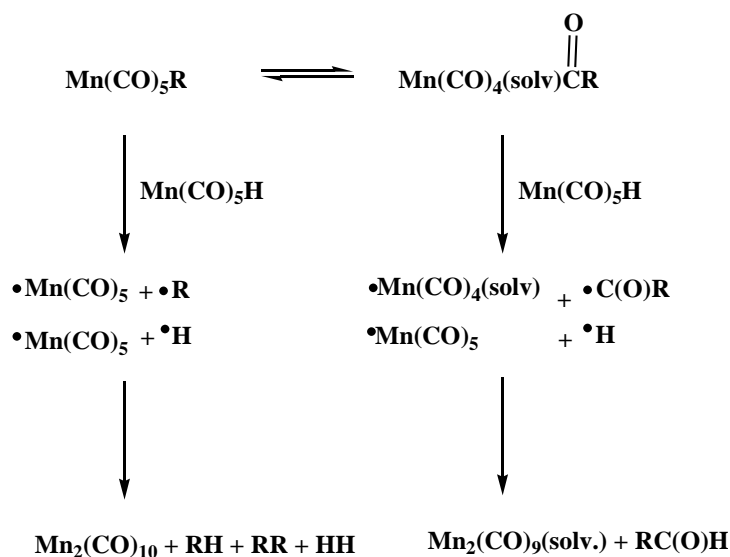
1.7 Mechanism for decomplexation of X–type ligands of Group 7 metals

Decomplexation reactions of alkyl and acyl ligands have been studied by Halpern (manganese complexes)⁴⁴, and Norton (rhenium complexes)⁴⁵. By examining the reaction kinetics, they ascribed specific mechanisms to the reactions.

⁴⁴ (a) M. J. Nappa, R. Santi, J. Halpern; *Organometallics*, **1985**, *4*, 34–41; (b) R. L. Sweany, J. Halpern; *J. Am. Chem. Soc.*, **1977**, *99*, 8335–8337

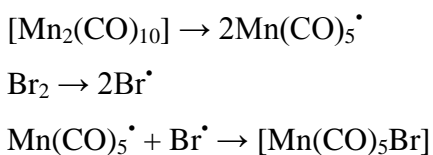
⁴⁵ B. D. Martin, K. E. Warner, J. R. Norton; *J. Am. Chem. Soc.*, **1986**, *108*, 33–39

Halpern found that the decomplexation reactions of manganese complexes proceeded via a radical mechanism, as is illustrated in Scheme 1.20. Upon addition of $[\text{Mn}(\text{CO})_5\text{H}]$, dimanganese complexes were obtained and in addition, organic products. The bond between the metal and the X-type ligand was cleaved homolytically and the formed radicals recombined to yield the new products.

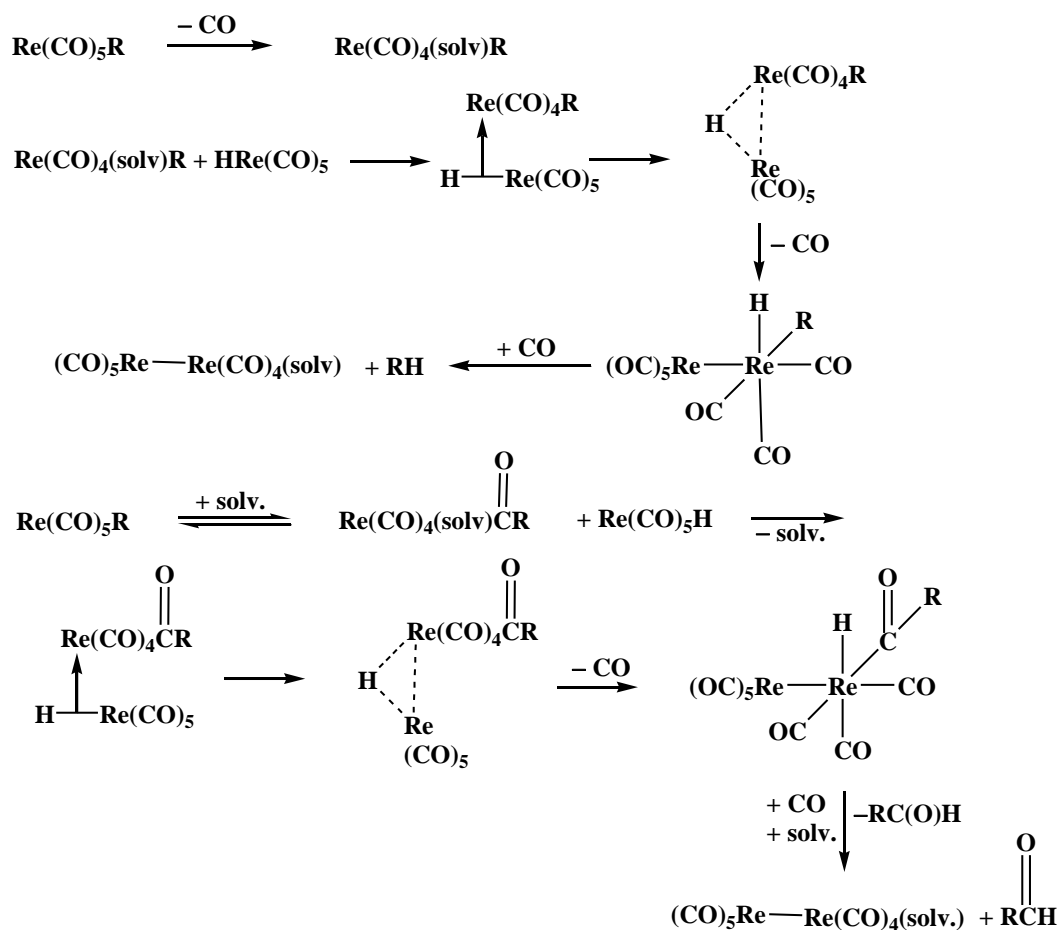


Scheme 1.20: Halpern's mechanism of Mn–ligand decomplexation

A similar radical mechanism was also proposed for the cleaving of $[\text{Mn}_2(\text{CO})_{10}]$ by halogens:



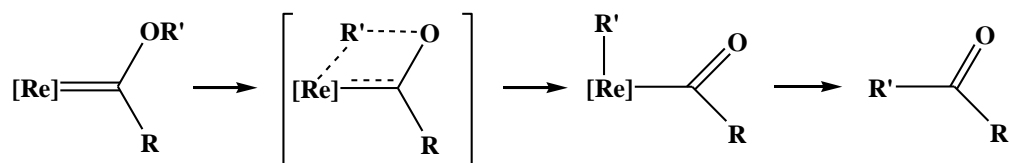
Norton and co-workers found that the analogous reaction with $[\text{Re}(\text{CO})_5\text{R}]^{37}$ and $[\text{Re}(\text{CO})_5\text{H}]$ proceeded differently and that a radical mechanism was not operative. They postulated a dinuclear intermediate (Scheme 1.21). In this case bond-formation occurred between Re–H (through the electrons in the Re–H bond of $[\text{Re}(\text{CO})_5\text{H}]$) and the rhenium atom of $[\text{Re}(\text{CO})_5\text{R}]$, as is shown below:



Scheme 1.21: Elimination of RH or RC(O)H from a rhenium complex

In the mechanism a 3-centered, 2-electron bond is formed between the two Re atoms and the H atom. The elimination of RH or RC(O)H can be described as a reductive elimination reaction. In this study the bridging hydrogen plays an important role in the transfer of a hydrogen atom from one Re to the other.

A third possible reaction to consider, not investigated in the Norton mechanism, is shown in Scheme 1.22. It represents an alkyl or hydrogen transfer from a carbene precursor to the rhenium centre. Elimination of a ketone (R = alkyl) or aldehyde (R = H) proceeds by reductive elimination.



Scheme 1.22: Reductive elimination can produce aldehydes or ketones ($R' = R, H$)

1.8 Shvo catalyst

The useful and versatile Shvo diruthenium catalyst⁴⁶ contains a protonic hydrogen atom between two oxygen atoms and a hydridic hydrogen atom, situated between the ruthenium atoms. The Shvo catalyst is a keto–enol/hydride complex.

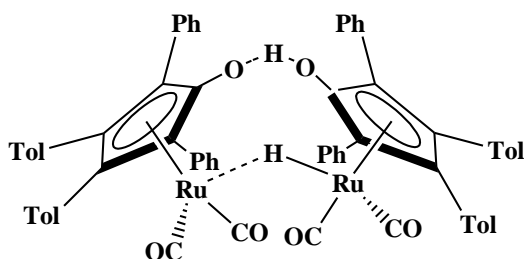


Figure 1.4: The Shvo catalyst

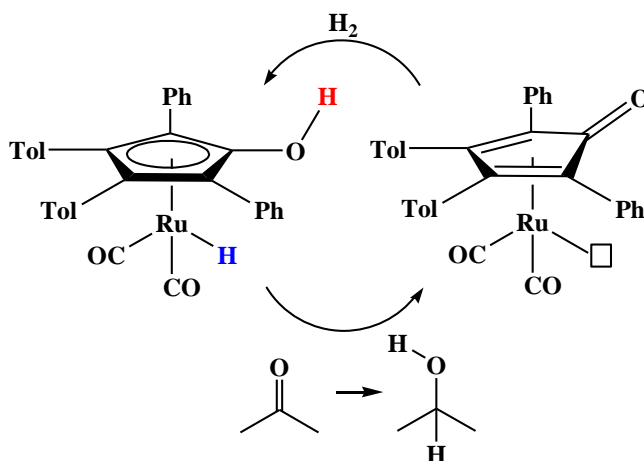
Two features of the Shvo complex are specifically of interest and relevant to this study – they are the bridging hydride atom and the pendant oxygen atoms with a protonic hydrogen between them. The formation of hydride species was expected to occur during the reactions planned for this study.

Karvembu *et al*⁴⁷ explains that the dissociation of a ligand of the catalyst is an important reason for catalytic activity. The Shvo catalyst dissociates into a 16–electron (Ru(0)) and

⁴⁶ (a) Y. Shvo, D. Czarkie, Y. Rahamim; *J. Am. Chem. Soc.*, **1986**, *108*, 7400–7402; (b) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana; *J. Am. Chem. Soc.*, **2001**, *123*, 1090–1100; (c) R. M. Bullock; *Chem. Eur. J.*, **2004**, *10*, 2366–2374

⁴⁷ R. Karvembu, R. Prabhakaran, K. Natarajan; *Coord. Chem. Rev.*, **2005**, *249*, 911–918

an 18–electron (Ru(II)) species and has found application in redox reactions, hydrogenation reactions and racemization reactions. Its hydrogenation activity of a polar double bond is shown below. Hydrogen transfer to ketones, following a hydridic route, has been suggested to go through an “inner–sphere” or “outer–sphere” pathway. In both, the hydride migrates to the carbon atom of the ketone, but in the former the substrate coordinates to the catalyst and in the latter not⁴⁸.



Scheme 1.23: Shvo catalyst: ketone hydrogenation

The Shvo catalyst was the first ligand–metal bifunctional (metal has a hydridic hydrogen, ligand has a protonic hydrogen) hydrogenation catalyst to be developed and was found to make inefficient use of Ru, because much of it is present as the diruthenium species (not active in reduction)⁴⁹. Only the hydride mononuclear species can be obtained if the Shvo catalyst is reacted with H₂ or formic acid⁵⁰.

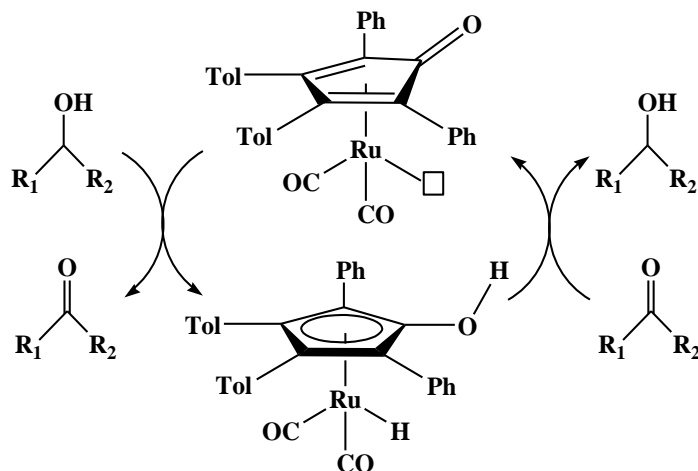
A cycle has been developed whereby the catalytic species are regenerated and it acts as

⁴⁸ A. Comas–Vives, G. Ujaque, A. Lledos; *Organometallics*, **2007**, 26, 4135–4144

⁴⁹ (a) C. P. Casey, S. E. Beetner, J. B. Johnson; *J. Am. Chem. Soc.*, **2008**, 130, 2285–2295; (b) A more efficient phosphine–substituted Ru catalyst has been developed by Casey’s group for the hydrogenation of aldehydes: C. P. Casey, N. A. Strotman, S. E. Beetner, J. B. Johnson, D. C. Priebe, T. E. Vos, B. Khodavandi, I. A. Guzei; *Organometallics*, **2006**, 25, 1230–1235

⁵⁰ C. P. Casey, S. W. Singer, D. R. Powell; *Can. J. Chem.*, **2001**, 79, 1002–1011

an oxidation catalyst. Here the 16-electron species is the active species. Alcohols are dehydrogenated by the Shvo catalyst⁵¹. Hydrogen atoms that are abstracted may be transferred to quinone. The hydroquinone that formed is reoxidized by air with a Co-salen complex's aid. A part of the cycle is given below.



Scheme 1.24: Part of catalytic cycle of the Shvo catalyst

1.9. Aims of project

Carbene to acyl and acyl to carbene ligand conversions featured prominently as a central theme and this capability was taken into consideration in setting goals for this study.

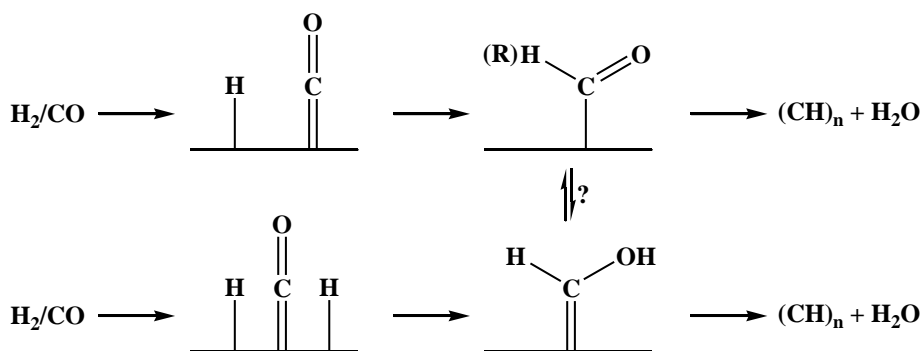
1.9.1 Introduction

A basic aim of this study was to investigate aspects of the synthesis and chemistry of rhenium carbene complexes with thienyl substituents. With rhenium having an uneven number of valence electrons there are interesting possibilities for synthesizing complexes with unique characteristics. The factors affecting carbene or acyl formation is not clearly understood in literature and rhenium carbene chemistry has not attracted nearly the same amount of attention than Group 6 Fischer carbene complexes. The possibility of

⁵¹ J. B. Johnson, J.-E. Bäckvall; *J. Org. Chem.*, **2003**, 68, 7681–7684

preparing stable hydroxycarbene complexes from protonation instead of alkylation of acylmetalates or from hydride transfer processes was an interesting possibility.

In the important Fischer–Tropsch synthesis⁵², mechanisms for the heterogeneous catalysis of the reaction of syngas (H_2/CO) to give hydrocarbons and water have been proposed⁵³. The carbide mechanism was the first suggested mechanism and it was proposed by Fischer and Tropsch⁵⁴. The hydroxycarbene mechanism was suggested by Anderson and Emmett and the acyl–mechanism by Pichler and Shultz. The possible interchange between hydroxycarbene and acyl–hydride complexes could be of interest with respect to the mechanisms shown below (Scheme 1.25). These proposed mechanisms are shown below.



Scheme 1.25: Acyl mechanism (top) and hydroxycarbene mechanism (bottom)

1.9.2 Thiophene derivatives

Thiophene derivatives are aromatic, flat, electron excessive, and display double bond delocalization. This makes them versatile reagents and substituents in carbene chemistry.

⁵² (a) P. M. Maitlis; *J. Organomet. Chem.*, **2004**, 689, 4366–4374; (b) W. A. Herrmann, *Applied Homogenous Catalysis With Organometallic Compounds*, Vol. 2; Editors: B Cornils, W.A. Herrmann; VCH Weinheim, **1996**, 747

⁵³ R. C. Brady III, R. Pettit; *J. Am. Chem. Soc.*, **1981**, 103, 1287–1289

⁵⁴ F. Fischer, H. Tropsch; *Chem. Ber.*, **1926**, 59, 830–831

The heteroaromatic rings are activated at the carbon atom α to the sulfur atom⁵⁵ by proton abstraction with a strong base like *n*-BuLi.

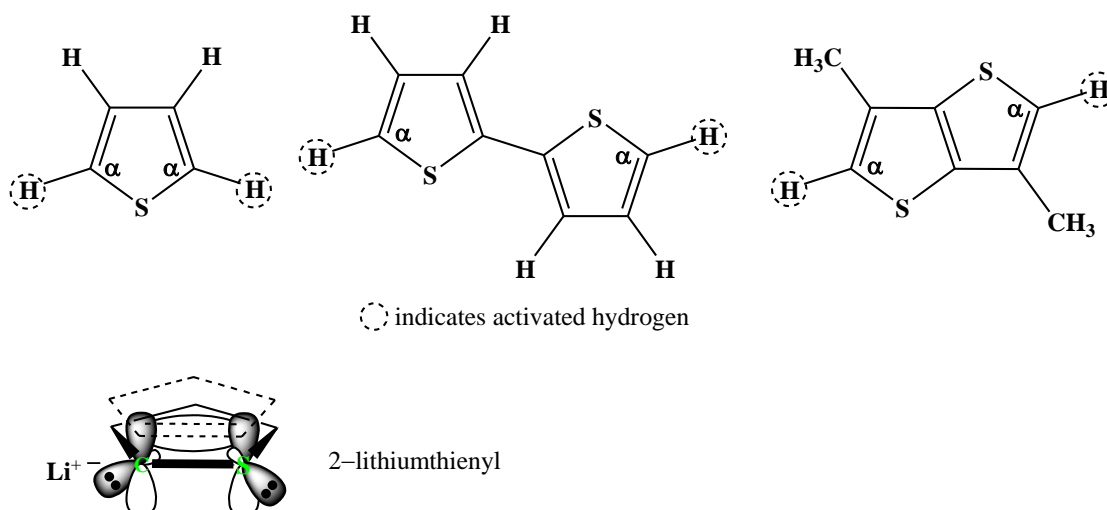


Figure 1.5: Thiophene, thiophene derivatives and 2-lithiumthienyl

If rings have hetero-atoms that can coordinate to the metal (like pyridine or pyrrole substrates) there may also be bonding through the hetero-atom. The sulfur atom also has two electron pairs in two non-bonding orbitals, but because of the ring aromaticity does not strongly feature as a Lewis base to transition metals. In fact, coordination to transition metals is mostly through the π -system and η^5 - and η^2 -coordination are common. However, the carbon atom with the negative charge is the more reactive nucleophile. 2-Lithiumthienyl can be directly attached to rhenium, if there is a vacant coordination site on the metal⁵⁶.

Thiophene is readily polymerized or oligomerized and its electrons can be transported, due to extended conjugation, as shown in Figure 1.6. Metals can be bound to these

⁵⁵ C. H. DePuy, S. R. Kass, G. P. Bean; *J. Org. Chem.*, **1988**, 53, 4427–4433

⁵⁶ T. B. Gunnoe, M. Sabat, W. D. Harman; *J. Am. Chem. Soc.*, **1998**, 120, 8747–8754

oligomers or polymers to furnish complexes with special characteristics. Examples include inorganic–organic hybrid materials⁵⁷ and chromophores⁵⁸.

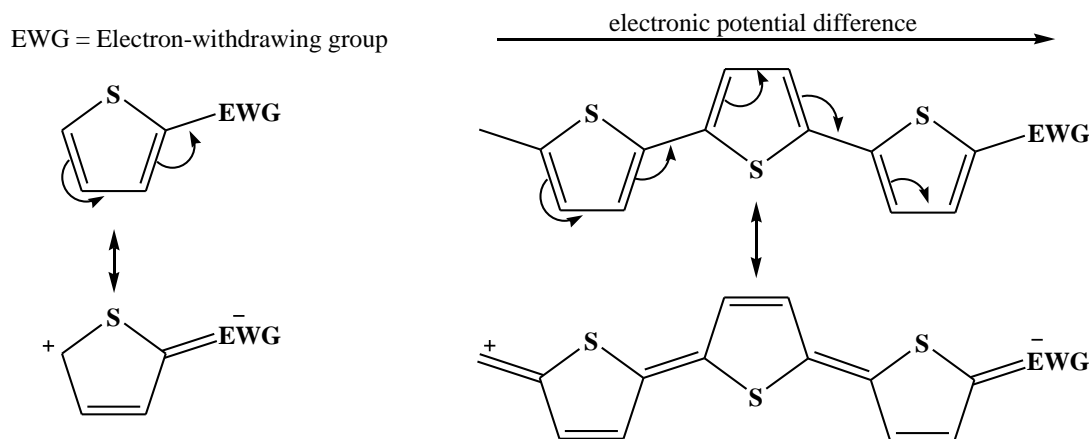


Figure 1.6: Electron conjugation over the thienyl ring system

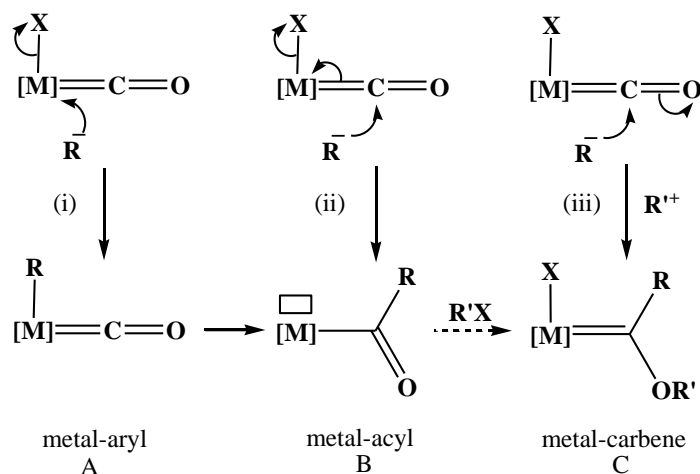
1.9.3 Reaction of organolithium agents with Group 7 metal carbonyls

Anionic reagents can react with group 7 metal carbonyls in many different ways, depending on electronic and steric properties, the nature of the transition metal and the properties of the lithiated substrate. Scheme 1.26 summarizes different possible reaction routes already observed, affording, if the substrate is an aryl, a metal–aryl, metal–acyl or metal–carbene complex. Earlier reference was made to all of these types of products. In Scheme 1.25 the following occurs: (i) attack of the aryl on the metal with the elimination of the halogen ligand (ii), attack of the aryl on a carbonyl carbon with the elimination of the halogen ligand and (iii) transformation of a carbonyl ligand into a carbene ligand with retention of the halogen ligand.

⁵⁷ M. H. Chisholm, A. J. Epstein, J. C. Gallucci, F. Feil, W. Pirkle; *Angew. Chem. Int. Ed.*, **2005**, *44*, 6537–6540

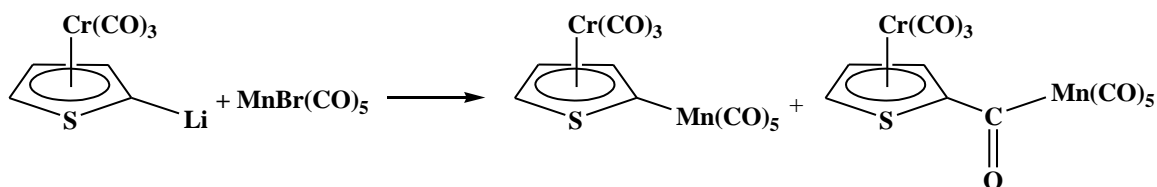
⁵⁸ S. Goeb, A. De Nicola, R. Ziessel, C. Sabatini, A. Barbieri, F. Barigelletti; *Inorg. Chem.*, **2006**, *45*, 1173–1183

R = aryl, X = halogen, R' = alkylating agent



Scheme 1.26: Aryl, acyl and alkoxy-carbene complexes

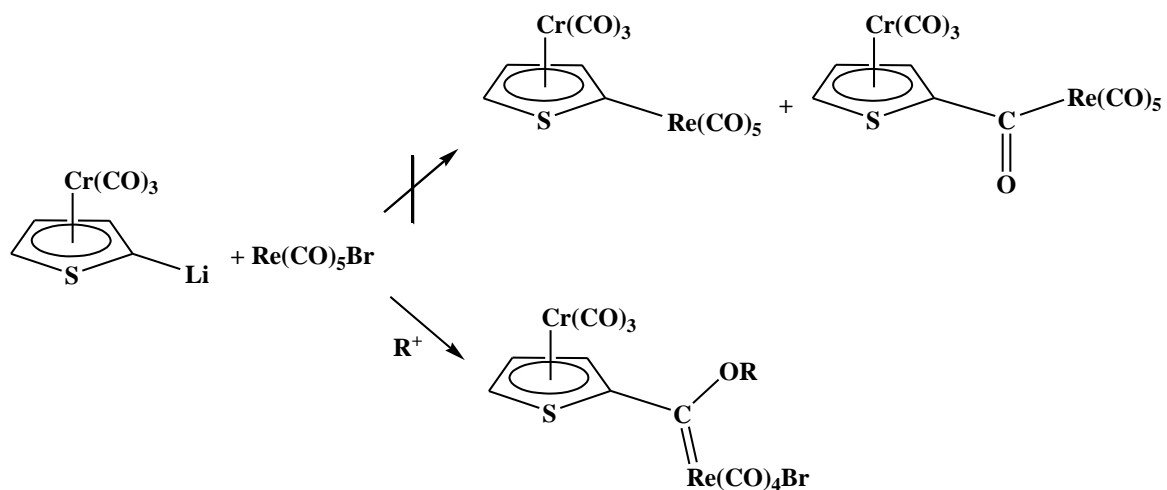
Previous studies with 2-lithiumthienyl π -bonded to chromium tricarbonyl in our laboratories revealed complexes of types A and B (Scheme 1.26). When reacted with $[\text{Mn}(\text{CO})_5\text{Br}]$ both products reveal reactions that proceed by Br^- elimination (Scheme 1.27)⁵⁹. By contrast, the reaction of 2-lithiumthienyl with $[\text{Mn}(\text{CO})_5\text{Br}]$ gave a deep red unstable compound.



Scheme 1.27: Reaction of a nucleophile with $[\text{Mn}(\text{CO})_5\text{Br}]$

$[\text{Re}(\text{CO})_5\text{Br}]$ reacted differently as shown in Scheme 1.28. The bromo-carbene complex was afforded after alkylation of the intermediate (type C).

⁵⁹ T. A. Waldbach, P. H. van Rooyen, S. Lotz; *Organometallics*, **1993**, *12*, 4250–4253



Scheme 1.28: Reaction of a π -coordinated thiophene with $[\text{Re}(\text{CO})_5\text{Br}]$

In this study the reactions of lithiated thiophene derivatives with $[\text{Re}(\text{CO})_5\text{X}]$ ($\text{X} = \text{Br}, \text{Re}(\text{CO})_5$) were going to be investigated. This study extends the above results by focusing on Re-carbene chemistry and anticipates the formation of hydroxycarbene intermediates.