Chapter 5

Chromium(III) Bidentate

Nitrogen / Phosphorus Mixed Ligand Chemistry

5.1 INTRODUCTION

Following the natural progression of the study of the novel complexes thus far, attention is now turned to the coordination of the bidentate ligands that encompass both phosphorus and nitrogen atoms within the same molecule. Such ligands possess the combination of donor atoms known to produce catalytically active species upon coordination to the $[CrCl_3(thf)_3]$ precursor [31]. One of the many intriguing properties of such ligands is that they combine both a soft phosphorus and a hard nitrogen donor atom. The fact that the phosphorus atom is a π–acceptor allows the stabilisation of a low oxidation state of a metal, while the σ–donor ability of the nitrogen is able to stabilise a higher oxidation state and the metal is therefore more susceptible to oxidative addition [116].

A variety of ligands were chosen and their coordination to the Cr(III) precursor allowed the formation and study of novel complexes with interesting properties. As well as steric and electronic differences, these ligands also differ in such a manner that they possess the ability to form chelate ring systems of various sizes once they have coordinated to the chromium centre via the respective P and N donor atoms.

A particularly intriguing aspect of the ligands with respect to chromium(III) chemistry was that to date no single crystal structures have been solved. A Cambridge Database search [117] was carried out in which chromium was selected first in any oxidation state and then specifically in the Cr^{3+} state. To encompass all possible structures, the bonds between the atoms, as well as the bridging atoms between the P and N donor atoms, were not specified. The structural frameworks that were searched are presented

in Figure 5.1. It is worth noting that regardless of the oxidation state of chromium, no complexes with PXN-type ligands have been solved to date.
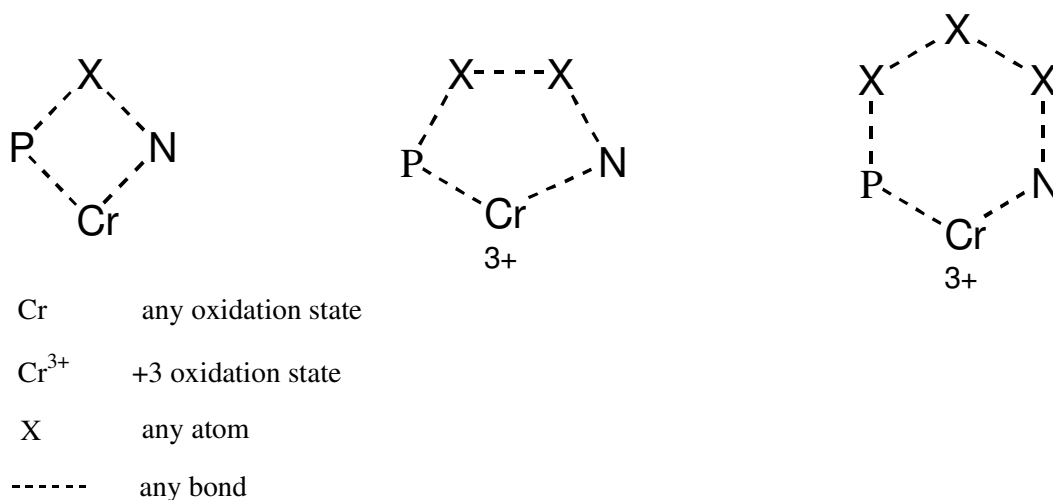

Cr	any oxidation state
Cr^{3+}	+3 oxidation state
X	any atom
------	any bond

Figure 5.1   **Results of structural framework searches using Cambridge Database [118]**

5.2   2-PYRIDYLDIPHENYLPHOSPHINE AND [CrCl$_3$(thf)$_3$]

The first ligand, 2–pyridyldiphenylphosphine (dpp), was a somewhat obvious choice as it combines the specific P and N ligand environments of the previous chapters, namely pyridine and diphenylphosphine. It was hoped that the presence of only one bridging atom between the P and N atoms would mimic the now highly regarded and catalytically active PNP ligand, which is known for its selectivity towards 1–octene catalysis. Of interest was whether a similar dimeric species formed upon coordination to [CrCl$_3$(thf)$_3$], as isolated by Bollmann [34] in their PNP investigations, with a strained four-membered chelate ring could be replicated, with the electronic and steric differences between the two systems thus allowing for comparative studies.

It must be duly noted, however, that according to the literature this particular ligand has the potential to coordinate via a number of modes [116, 118]. It can act as a bridging ligand in both homo and hetero binuclear compounds, as a chelating ligand which forms a rigid, strained four–membered ring with the metal centre, as well as P and N monodentate ligands. In the latter two modes, due to the P atom being a weaker σ–donor and stronger π–acceptor, this ligand usually coordinates preferentially via the P atom.

5.2.1   SYNTHESIS

A series of reactions involving 2–pyridyldiphenylphosphine and $[CrCl_3(thf)_3]$ was undertaken. The addition of one molar equivalent of dpp to $[CrCl_3(thf)_3]$ dissolved in thf and stirred overnight at room temperature was expected to yield either a chelating-ring-type compound or coordination to Cr via either the P or N atom, with the literature findings making P donation more likely [116]. Somewhat surprisingly, no reaction took place. The reaction was then allowed to reflux for a number of days, but this too proved fruitless. thf was then replaced with DCM as solvent yet, somewhat frustratingly, this also failed to result in the ligand substitution reaction.

5.3   2-DIPHENYLPHOSPHINOETHYLAMINE AND $[CrCl_3(thf)_3]$

In the second of these heterodifunctional unsymmetrical bidentate ligands, 2-diphenylphosphinoethylamine (dppea), the number of bridging carbon atoms between the P and N donors increased to two. This allowed the formation of more stable five–membered chelate rings similar to those in the previous chapters, with the addition of the various substituted pyridines also being possible.

One notable difference from the first PN ligand of this study is that the electronic and steric properties of the nitrogen atom have been altered. Reasons include a willingness to incorporate variety into the systems, as well as the fact that it was a readily available ligand. However, the main reason is that in many respects this is a novel ligand. It is true that a number of researchers have previously incorporated this ligand into their respective systems, including europium-induced NMR studies [119], iridium-based asymmetrical C=O hydrogenation [120] and palladium-based Suzuki-Miyaura coupling [121]. However, to date no one has studied this ligand with respect to the chemistry surrounding tri- and tetramerisation catalysis. Furthermore, characterisation of any dppea complex thus far has been limited to elemental analysis and NMR spectroscopy, with the sum total of any IR studies being the mere mention of NH_2 and Pd–Cl vibrations. These were all good reasons for undertaking novel IR, Raman, computational and crystallographic studies.

5.3.1 SYNTHESIS

The addition of dppea to the $[CrCl_3(thf)_3]$ precursor led to the immediate formation of blue-green solutions. Unlike with the previous classes of compounds, one was acutely aware of carrying out these reactions on a smaller scale than usual due to the high cost of the ligand.

A direct result of the novel nature of this ligand was that no density information was provided by the manufacturer (Sigma Aldrich). This led to the required masses of the ligand for each experiment having to be determined with the aid of a weighing balance.

As in the dppe compounds, the fact that the coordination of this PN ligand appeared to be immediate (colour change), and that it yielded solutions and not immediate precipitates, removed any ambiguity as to when the pyridine ligands should be added. However, to ensure completion the ligand–$[CrCl_3(thf)_3]$ mixture was stirred at room temperature for about 10 minutes before the pyridines were added.

5.3.2 INFRARED AND RAMAN SPECTROSCOPY

All the IR discussions thus far have included comparative studies between the respective free ligand spectra and those observed upon coordination to the metal centre since many band shifts are indicative of coordination. To date the respective free ligand spectra have all been readily available from previously published literature. This, however, is not the case for dppea as its limited characterisation thus far has resulted in the absence of any IR and Raman data. This is thus the first detailed vibrational study carried out on this ligand system, both free and complexed.

As has been illustrated with the previous classes of compounds, the isolation of sufficient amounts of single-crystal material (for IR/Raman and X–ray structure determination) of at least one of the compounds within each grouping has aided the interpretation. However, although no crystal structure was isolated for this particular class of compounds, the IR assignments were not made with any less confidence than for the previous classes. The reason was that enough vibrational similarities to those compounds have already been analysed in this study, which thus allows comparisons to be drawn. In addition, there is ample literature data – perhaps not in terms of the

PN ligand directly, but with regard to the individual vibrations that make up this ligand, as well as the various pyridine ligands.

5.3.2.1 Region 3380–2867 cm^{-1}

This is a region of notable significance as the compounds possess a variety of characteristic N–H and C–H ligand vibrations.

Present in the IR spectra of all the compounds are the N–H vibrations associated with the dppea ligand. Their absence to a large extent in the corresponding Raman spectra is a result of a small amount of fluorescence that has affected some of the weaker vibrations in this region. The bands are therefore not definable from the broadness that is observed.

Deserving particular attention is the compound [CrCl$_3$(dppea)(pyNH$_2$)] **(26)** as it possesses two different N–H environments. Although a degree of band superposition is expected, a closer examination shows the dominance of the pyNH$_2$ ligand environment as only two bands were observed – 3327 and 3198 cm^{-1}. This deduction resulted from comparative studies involving the pyNH$_2$-based compounds of the previous chapters [CrCl$_3$(pyNH$_2$)$_3$], [CrCl$_3$bipy(pyNH$_2$)] and [CrCl$_3$(dppe)(pyNH$_2$)], as well as its dppea counterparts which included the free dppea ligand.

A representation of these observations is highlighted in Figure 5.2 which compares [CrCl$_3$dppea(pyNH$_2$)] and [CrCl$_3$(pyNH$_2$)$_3$].
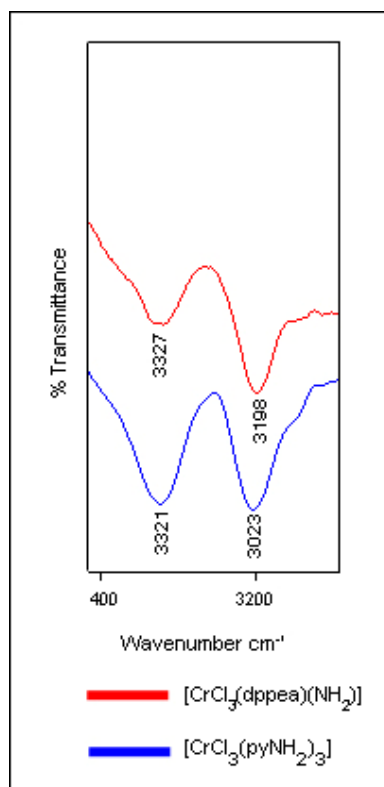
Figure 5.2   **IR spectra of N–H bands in [CrCl$_3$dppea(pyNH$_2$)] (red) and [CrCl$_3$(pyNH$_2$)$_3$] (blue)**

The C–H environments observed include C–H ring vibrations. CH$_2$ modes that bridge the P and N donor atoms, and tertiary butyl C–H's associated with the para-substituted pyridine ligand, pytb. Also of interest are C–H vibrations indicative of thf as their presence or absence allows mechanistic and structural insights to be proposed.

Four vibrations are common to all the complexes. The first is observed as a strong vibration in both the IR and Raman spectra at ~3050 cm^{-1}. The fact that it is also present in [CrCl$_3$(dppea)(thf)] **(24)** suggests it is an unshifted C–H stretch associated with the phenyl rings of dppea. However, as the same unshifted vibration is observed in the literature of other metal–pyridine studies [73, 74, 92, 96, 97], one cannot assign with complete certainty.

The second vibration is at ~3003 cm^{-1} and corresponds to a combination mode that Benial [114] assigned to the similar ligand, dppe. Also common to dppe is the CH$_2$ asymmetrical stretch vibration at ~2962 cm^{-1} which has shifted from a free ligand

position of 2934 cm^{-1} that is indicative of coordination. The fourth band is observed as an unshifted free dppea vibration at ~2903 cm^{-1}. Although it is not present in the Cr-dppe compounds of this study, other metal–dppe studies in the literature assign it to a combination mode [113]. The problem of band superposition arises once again as the bands at ~2962 and ~2903 cm^{-1} are also indicative of the CH_3 stretching modes expected in the compound [CrCl$_3$(dppea)(pytb)] **(27)**. Less ambiguous, however, are the other CH_3 symmetrical stretch vibrations that are observed at ~2928 cm^{-1} as a weak vibration (Raman spectrum only) and at 2868 cm^{-1} as a significantly stronger mode (both IR and Raman spectra). Both correlate with other metal–pytb vibrations, with the former at 2928 cm^{-1} having shifted from a free ligand position of 2920 cm^{-1} [92]. As all of the above vibrations are present in the IR and Raman spectra of [CrCl$_3$(dppea)(pytb)], they have thus been chosen as representative spectra of what is observed in all the complexes (except for the tertiary butyl vibrations) and are presented in Figure 5.3.
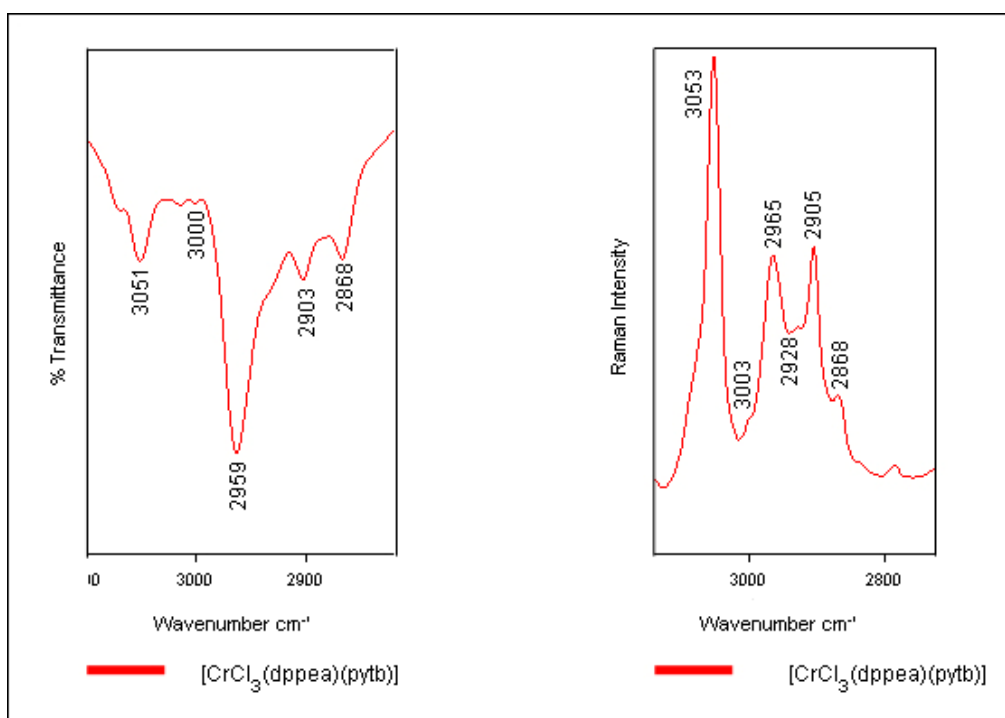

Figure 5.3   **IR and Raman spectra of [CrCl$_3$(dppea)(pytb)]**

Although not indicative of a specific substituent, the strong IR band at 3092 cm^{-1} is present only in [CrCl$_3$(dppea)(pyNH$_2$)] and is associated with the C–H stretch vibration of pyNH$_2$, in correlation with the literature [96].

A further matter to be discussed with regard to this region is the presence or absence of thf C–H modes. They are expected on $[CrCl_3(dppea)(thf)]$ only if direct ligand substitution has taken place. From comparative studies with $[CrCl_3(bipy)(thf)]$ (which shows strong evidence of coordinated thf throughout its spectrum), it is clear that in this region there is no evidence of such vibrations. It is therefore duly noted that this is an early indication that this compound may in fact be a dimeric species.

Finally, as to the question of the presence of bands indicative of a pyridinium environment resulting from asymmetrical dimeric cleavage, the answer is negative with the absence of characteristic pyH vibrations at 2800 cm^{-1} [94], as well as the absence of those additional modes observed in the spectrum of $[Hpyphenyl][CrCl_4(dppe)]$. Although the literature-assigned pyH vibration at ~3200 cm^{-1} is observed in the spectra of all the compounds except for $[CrCl_3(dppea)(thf)]$, it is deemed rather to be associated with N–H as throughout the rest of the spectra there is no further evidence of pyridinium formation.

5.3.2.2   Region 1652–1117 cm^{-1}

This is a region largely characteristic of C–H and C=C ring vibrations, with a relatively small degree of band superposition between the phenyl and pyridine environments observed. Also present in this region are bands associated with the para pyridine substituents, in particular CH$_3$ (tertiary butyl) and N–H (amino).

An expected phenomenon in line with similar vibrations in the dppe class is the distinct lack of shifting of the dppea ligand vibrations upon coordination, while the pyridine modes follow the same shift trends exhibited in all the previous chapters.

Furthermore, if any of the compounds have resulted from asymmetrical cleavage of a dimeric intermediate species, then characteristic pyridinium vibrations should be visible.

The majority of the dppea vibrations include C=C stretches, C–H twists and deformations, as well as ring breathing modes. Their assignments are relatively straightforward but special mention must be made of the two bands associated with C=C phenyl ring stretches at 1583 and 1568 cm^{-1} as the problematic overlap with

similar pyridine vibrations can to a certain extent be solved. Upon coordination to the chromium centre the former remains unshifted, while the latter shifts to a frequency of 1574 cm^{-1} [113]. These bands are visible in all the compounds in both the IR and Raman spectra, with that at 1583 cm^{-1} being noticeably stronger in the Raman. As has been observed in Chapter 4, both of these bands are observed in free pyridine. However, the opposite of the dppea band shifts is expected as upon coordination to the metal, 1583 cm^{-1} shifts to higher frequencies above 1600 cm^{-1}, while 1572 cm^{-1} remains unshifted [73, 74]. This is precisely what is seen in these novel compounds, which implies the coordination of the pyridine ligands to the metal. In terms of characterisation, the band at 1585 cm^{-1} is confidently assigned to a solely dppea ligand (C=C) [113], although ambiguity still surrounds the band at 1574 cm^{-1} (dppea/py). Table 5.1 presents the IR vibrations associated with coordinated pyridine while Figure 5.4 shows the IR and Raman spectra of [CrCl$_3$(dppea)(py)] **(25)**.

Table 5.1   **IR vibrations associated with coordinated pyridine**

Free py	[CrCl$_3$(dppea)(py)] / cm^{-1}	[CrCl$_3$(dppea)(pyNH$_2$)] / cm^{-1}	[CrCl$_3$(dppea)(pytb)] / cm^{-1}	[CrCl$_3$(dppea)(pyphenyl)] / cm^{-1}
1599	1606	1618	1616	1615

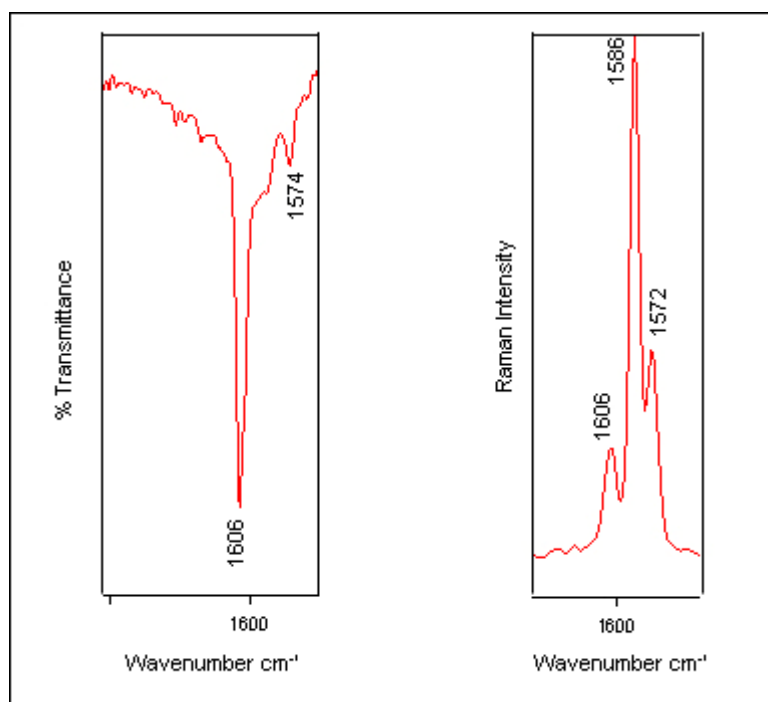**Figure 5.4**   **IR and Raman spectra of [CrCl$_3$(dppea)(py)]**

Also worthy of mention is the fact that three vibrations are present in the IR and Raman spectra of all the compounds and notably absent in the dppe compounds. They are observed at 1461, 1379 and 1229 cm^{-1}. They are assumed to be dppea-specific vibrations which, in the light of the other types of vibration that surround them, are more than likely C–H modes.

The individual compounds are further discussed below, with the emphasis on the various pyridine-specific vibrations.

[CrCl$_3$(dppea)(py)]

The band observed as a strong IR vibration at 1447 cm^{-1} in [CrCl$_3$(dppea)(py)], and which is absent in the corresponding Raman spectrum, is a ring vibration that is characteristic of coordinated unsubstituted pyridine [73, 74]. It has shifted from a free ligand position of 1439 cm^{-1} and is unsurprisingly absent in the other compounds. Figure 5.5 compares [CrCl$_3$(dppea)(py)], [CrCl$_3$(dppea)(thf)] and free dppea to illustrate this additional band at 1447 cm^{-1}.
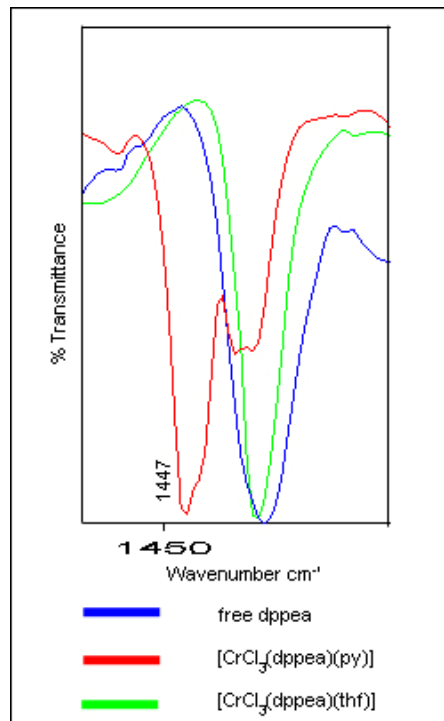

Figure 5.5   **Pyridine-specific vibration absent in [CrCl$_3$(dppea)(thf)] (green) and free dppea (blue)**

The only other vibration indicative of unsubstituted pyridine is that at 1221 cm^{-1} (C-H). However, it is not as specific as the previous band as it is also visible in [CrCl$_3$(dppea)(pyNH$_2$)].

[CrCl$_3$(dppea)(pyNH$_2$)]

As well as the shared C–H vibration with [CrCl$_3$(dppea)(py)], [CrCl$_3$(dppea)(pyNH$_2$)] possesses two vibrations that are specific to the pyNH$_2$ ligand. They are both indicative of ring vibrations and, in direct correlation with aminopyridine literature [96], coordination is implied due to the free ligand shifts. Table 5.2 documents these shifts.

Table 5.2 **IR vibrations associated with coordinated pyNH$_2$**

Free pyNH$_2$ / cm^{-1}	[CrCl$_3$(dppea)(pyNH$_2$)] / cm^{-1}	Shift / cm^{-1}
1508	1530	22
1333	1364	31

As one would expect, this compound also possesses bands that are characteristic of the amino substituent. These are present at 1652 cm^{-1} (N–H shifted from 1648 cm^{-1}) and 1281 cm^{-1} (C–NH$_2$ shifted from 1268 cm^{-1}) [96].

These IR vibrations are shown in Figure 5.6; the Raman spectrum is not shown as although the vibrations are present, the majority are weak and not as pronounced as their IR equivalents.
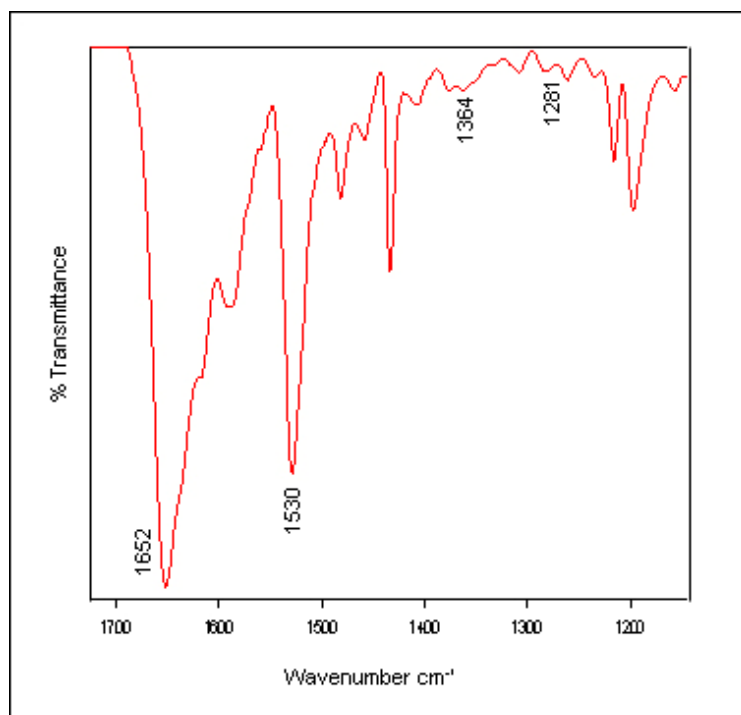
Figure 5.6 **IR spectrum of pyNH$_2$ vibrations observed in [CrCl$_3$(dppea)(pyNH$_2$)]**

[CrCl$_3$(dppea)(pytb)]

As well as the expected C–H and ring vibrations associated with the aromatic ring system, [CrCl$_3$(dppea)(pytb)] also possesses a number of tertiary butyl-specific vibrations. These additional bands in the spectrum increase the likelihood of band superposition with the dppea ligand, which complicates their assignments.

The ring vibrations are observed at 1543 and 1501 cm^{-1}, with only the former being associated solely with pytb as the latter is also present in the spectrum of [CrCl$_3$(dppea)(pyphenyl)] **(28)**. The latter has, however, shifted from a free ligand position of 1494 cm^{-1}, thus inferring coordination. Unfortunately, both the expected C–H specific vibrations are only tentatively assigned as they overlap with dppea vibrations. The same is true for the expected CH$_3$ asymmetrical and symmetrical deformations at 1462 (asym), 1368 (asym) and 1420 cm^{-1} (sym). The final weak band at 1201 cm^{-1} escaped ligand superposition and is confidently assigned to a C=C stretching mode that is specific to tb [92].

236

[CrCl$_3$(dppea)(pyphenyl)]

As was found in Chapter 4, it is rather difficult to differentiate between the phenyl rings attached to the phosphorus atoms and that which is substituted on the pyridine ring in the spectrum. Only the band at 1504 cm^{-1} is assignable and it is not pyphenyl-specific as it is also present in [CrCl$_3$(dppea)(pytb)].

Pyridinium vibrations

From a close inspection of all the spectra it is clear that there is a lack of evidence pertaining to pyridinium complex formation, a finding that is in agreement with the observations made in the region 3380 to 2861 cm^{-1}. Indeed, of the seven pyH vibrations that one would have expected to be present according to Mitchell [93], only three possibles are observed. These are 1480, 1158 and 1327 cm^{-1}. Apart from the fact that all three are present in the free dppea ligand and are assigned to C–H deformations, the band at 1327 cm^{-1} occurs at a weak intensity that is different from the strong intensity expected for pyH [94].

5.3.2.3   Region 1117–500 cm^{-1}

In direct correlation with the findings in the previous chapters, this particular region offers insights into the bond strengths and structural geometries that are, in addition to the fundamental assignments and coordinative shifts, common to all the regions.

Following the same trend as the previous region from 1652 to 1117 cm^{-1}, the majority of the bands that fall between these vibrational boundaries are ring and C–H vibrations. Overlap between the aromatic ligands is therefore unavoidable. However, a closer inspection of the nine vibrations that are common to the spectra of all the compounds shows that more than half are absent in the spectra of pyridine compounds, which signifies they are dppea phenyl ring-related vibrations. Furthermore, their lack of shifting upon coordination is not surprising, and indeed is expected, when comparisons are made with the findings in both the literature and the previous chapters of this thesis.

Bands absent in pyridine spectra:

- 1098 cm^{-1} ring breathing
- 999 cm^{-1} trigonal ring breathing
- 916 cm^{-1} C–H
- 508 cm^{-1} out of plane quadrant ring def

Bands present in pyridine spectra and thus indistinguishable:

- 1069 cm^{-1} in plane C–H def
- 739 cm^{-1} in plane out of phase C–H / ring
- 694 cm^{-1} CH$_2$ rock / ring

Figure 5.7 illustrates the presence and absence of these vibrations by comparing the IR spectra of the free ligands of pyridine, dppe and dppea.
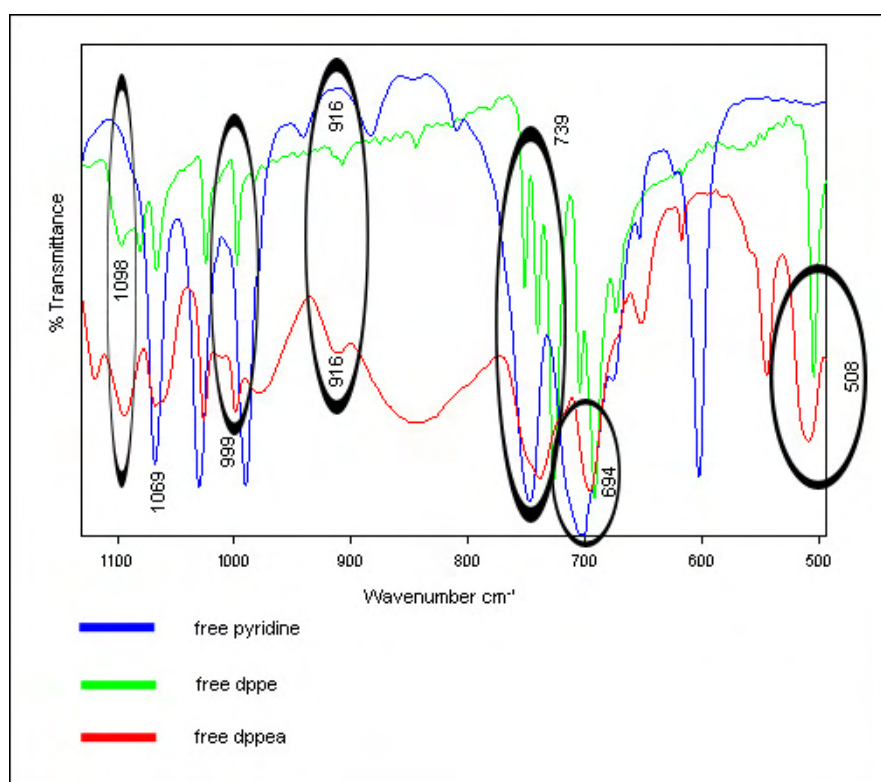

Figure 5.7   **IR spectra of free pyridine (blue), free dppe (green) and free dppea (red)**

An additional dppea-related vibration that deserves particular mention is that observed at ~666 cm^{-1} in all the compounds which, according to Benial [113], are indicative of a P–C stretching vibration resulting from the formation of the five-membered chelate

238

ring upon coordination. It is plausible that in these dppea compounds it has shifted from a free ligand position of 653 cm^{-1}.

In addition to these bands, there are a number of other vibrations that are present in the respective compounds which are indicative of the various pyridine derivatives. The shifts, and at times lack of shifts, relative to the free ligands compare very favourably with those in the literature and in previous chapters of this thesis.

The presence of strong IR bands at 757 and 641 cm^{-1} in [CrCl$_3$(dppea)(py)] is indicative of coordinated pyridine ring vibrations that have shifted from free ligand values of 749 and 604 cm^{-1} respectively (Table 5.3 and Figure 5.8). The latter, in particular, has been common throughout the previously discussed unsubstituted pyridine compounds [73, 74].

Table 5.3   IR vibrations associated with coordinated pyridine

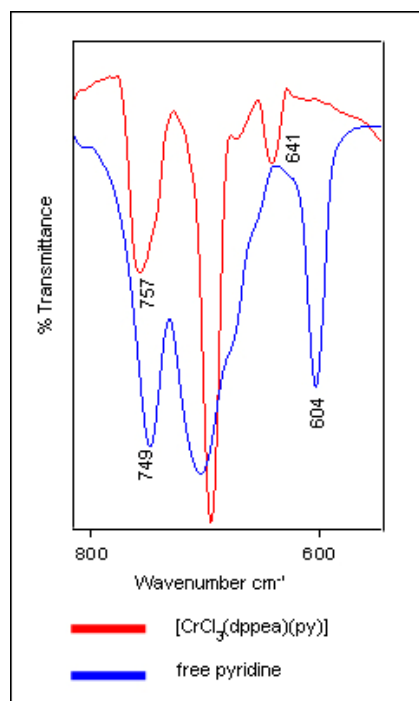| Free pyridine / cm^{-1}	[CrCl$_3$(dppea)(py)] / cm^{-1}	Shift / cm^{-1}
749	757	8
604	641	37

Figure 5.8   IR spectra comparison between [CrCl$_3$(dppea)(py)] (red) and free pyridine (blue)

239

[CrCl$_3$(dppea)(pytb)] possesses two tertiary butyl-specific bands that are observed in the spectra as strong IR vibrations and weak Raman vibrations at 572 and 547 cm^{-1} (Table 5.4 and Figure 5.9). They are assigned to a skeletal stretch and a rocking mode respectively and according to the literature, a notable coordinative shift is observed only for the latter [92].

Table 5.4   **IR vibrations associated with coordinated pytb**

Free pytb / cm^{-1}	[CrCl$_3$(dppea)(pytb)] / cm^{-1}	Shift / cm^{-1}
569	572	3
534	547	13
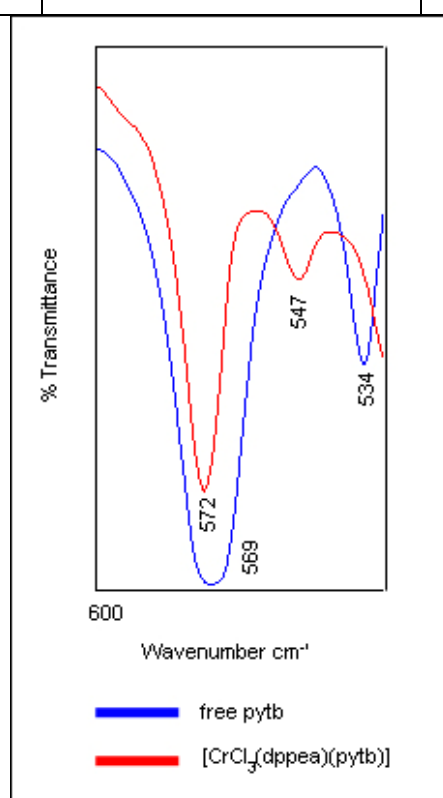
Figure 5.9   **IR spectra comparison between [CrCl$_3$(dppea)(pytb)] (red) and free pytb (blue)**

The compound [CrCl$_3$(dppea)(pyphenyl)] possesses ring vibrations that are indicative of the phenyl ring coordinated to the para-position of the pyridine (Table 5.5 and Figure 5.10) . Although one might expect these same bands in all the compounds due to the phenyl rings of the dppea ligand, this is not the case and their absence reinforces their py-phenyl assignments [97].

240

Table 5.5   **IR vibrations associated with coordinated pyphenyl**

Free pyphenyl / cm^{-1}	[CrCl$_3$(dppea)(pyphenyl)] / cm^{-1}	Shift / cm^{-1}
762	765	3
561	561	0
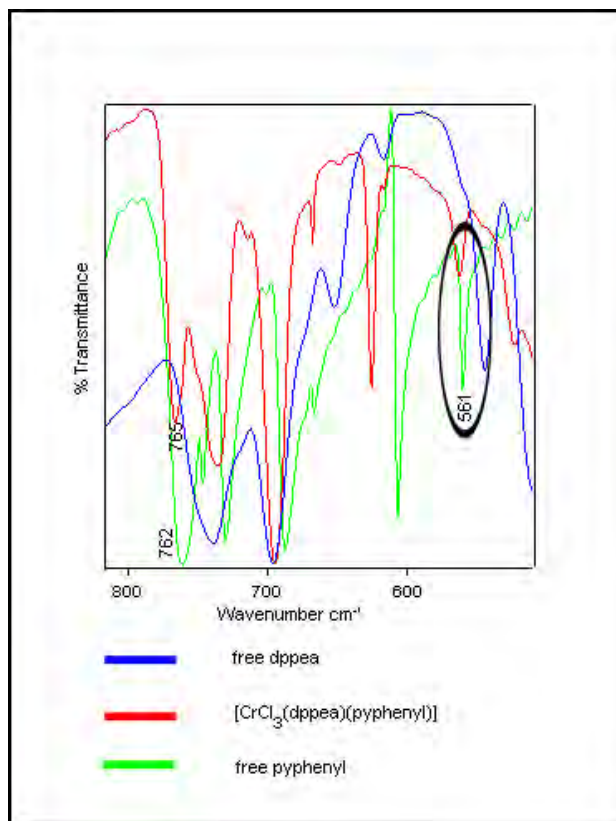
Figure 5.10   **IR spectra comparison between [CrCl$_3$(dppea)(pyphenyl)] (red) and free pyphenyl (green)**

It should be noted that due to band superposition, it was not possible to assign any pyNH$_2$-specific vibrations with any degree of confidence.

Perhaps the most significant of all the bands indicating the coordination of pyridine and its substituted derivatives to the metal centre is that observed at 992 cm^{-1} in the free ligands, the reason being that the degrees of shifting are relative to the particular substituents [75].

The detailed theory surrounding these shifts has been documented in Chapter 2, yet what is more intriguing is that the shifts observed here are virtually identical to those of the previous chapters (Table 5.6 and Figure 5.11). This is significant in itself as the

coordination of some of these pyridine ligands was confirmed by crystal structure determinations.

Table 5.6 **Shifting of the characteristic ring breathing vibration in [CrCl₃(dppea)(py)], [CrCl₃(dppea)(pyNH₂)], [CrCl₃(dppea)(pytb)] and [CrCl₃(dppea)(pyphenyl)]**

Pyridine / cm^{-1}	[CrCl$_3$(dppea)(py)] / cm^{-1}	Shift / cm^{-1}
990	1016	26

pyNH$_2$ / cm^{-1}	[CrCl$_3$(dppea)(pyNH$_2$)] / cm^{-1}	Shift / cm^{-1}
991	1023	32

Pytb / cm^{-1}	[CrCl$_3$(dppea)(pytb)] / cm^{-1}	Shift / cm^{-1}
995	1027	32

Pyphenyl / cm^{-1}	[CrCl$_3$(dppea)(pyphenyl)] / cm^{-1}	Shift / cm^{-1}
1001	1012	11

The spectra of the complexes are given in Figure 5.23.
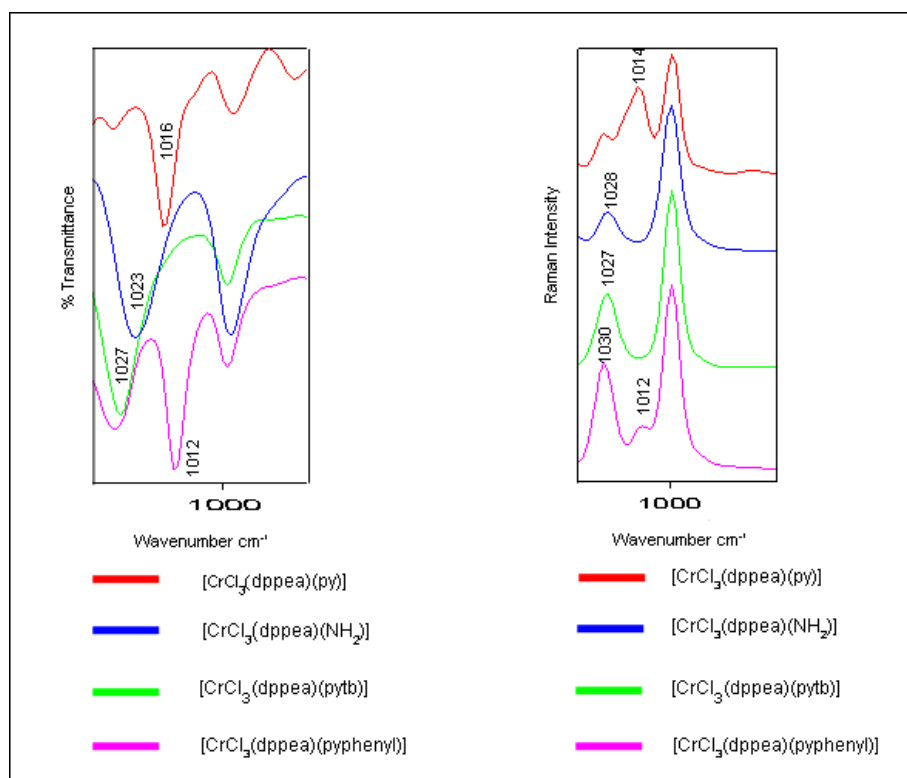
Figure 5.11 **IR and Raman spectra of [CrCl₃(dppeay)(py)] (red), [CrCl₃(dppea)(pyNH₂)] (blue), [CrCl₃(dppea)(pytb)] (green) and [CrCl₃(dppea)(pyphenyl)] (purple) showing shifting of the characteristic ring breathing vibration**

242

Up to this point this regional IR study has focused mainly on the presence of bands, yet their absence can be just as informative. This is indeed the case for the [CrCl$_3$(dppea)(thf)] complex. The absence of the band at around 856 cm^{-1}, which is indicative of coordinated thf [77, 78], leads one to believe that this is in fact a dimeric species as opposed to the monomeric product resulting from direct ligand substitution. This is actually in accordance with the observation made regarding the region 3380 to 2861 cm^{-1} in which no thf C–H modes were found. When one then couples this finding with all the other analyses of these compounds, it is logical to assume that in each case the dimeric intermediate species is cleaved symmetrically by the addition of the amine ligand to yield monomeric products. This idea is supported by the absence of pyH vibrations which one would have expected if asymmetrical cleavage had taken place. As was the case in the previous region, those bands that could be related to pyH (1040 and 1000 cm^{-1}) are visible in the free dppea spectrum and are too intense to correlate with the literature expectations [93, 94].

5.3.2.4   Region 500–200 cm^{-1}

An FIR spectrum of the free dppea ligand was not obtainable due to the incompatibility between the need for instrumentation operated under vacuum and the liquid state of the sample since evaporation of sample would be problematic. This, however, did not hinder the analysis of the respective compounds' spectra to any great extent. Reasons include the fact that this is a region primarily synonymous with only metal–ligand vibrations, and that the spectrum of free dppe (which possesses many similar vibrational modes) was available. It should be noted that the MIR spectrum of the free dppea ligand extended to around 450 cm^{-1} so the higher frequency bands of the FIR spectra did permit free ligand comparisons.

The two vibrations at ~470 and ~450 cm^{-1} that are present in all the complexes are absent in the free ligand MIR spectrum. They are also notably absent in the free dppe spectrum. Thus, as assigned by Benial [113], it is logical to assume they are indicative of five–membered ring deformations that have resulted from P and N coordination to the chromium.

A final indication of unsubstituted pyridine coordination is also found in this region with the characteristic free pyridine vibration at 404 cm^{-1} having shifted to the expected coordination frequency of 438 cm^{-1} [73, 74].

The band at ~423 cm^{-1} in all the complexes is tentatively assigned to the Cr–P vibration, based on the similar assignment in the dppe class of compounds. While the corresponding dppe assignments could have been an out of plane quadrant ring deformation shifting from a value of 401 cm^{-1}, this is not the case for this dppea class as it possesses the band at 401 cm^{-1} in addition to that at 423 cm^{-1}.

With regard to bands associated with Cr–Cl vibrations, [CrCl$_3$(dppea)(py)], [CrCl$_3$(dppea)(pytb)] and [CrCl$_3$(dppea)(pyphenyl)] appear to possess the three bands indicative of the monomeric *mer* arrangement [80]. This leaves [CrCl$_3$(dppea)(thf)] and [CrCl$_3$(dppea)(pyNH$_2$)] in which only two bands are observed. What this implies is one of two possibilities: either the *cis* arrangement or dimer formation. On the basis of all the previous evidence from the other regions for these two compounds, it is logical to suggest that [CrCl$_3$(dppea)(pyNH$_2$)] adopts the *cis* orientation and that the [CrCl$_3$(dppea)(thf)] is in fact a dimeric species.

Of the remaining bands, those at ~284 and 269 cm^{-1} are assumed to be dppea-related vibrations as they are absent in dppe as well as in pyridine and its derivatives.

The band at 243 cm^{-1} in all the complexes is assigned to the Cr–N vibration resulting from the coordinating dppea ligand. This is based on the absence of such a band in free dppe and indeed in its Cr-based complexes, but perhaps more important is that a similar assignment was made for the Cr–N (bipy) mode of the bipyridine compounds in Chapter 3 [79].

Unfortunately, the Cr–N (py) band at around 220 cm^{-1} was affected by band superposition as the Ph–P–Ph vibration of the dppea ligand occurs at around the same frequency. Unlike with the dppe compounds, differentiation between the two could not be made as even in the [CrCl$_3$(dppea)(thf)] compound the band was split to give values of 218 and 214 cm^{-1}.

The IR and Raman spectra of [CrCl$_3$(dppea)(py)] (Figure 5.12) were chosen as representative spectra of all the compounds to illustrate the vibrations that are common to all. In addition, this particular IR spectrum also shows the vibration associated with unsubstituted pyridine coordination at 438 cm^{-1}.
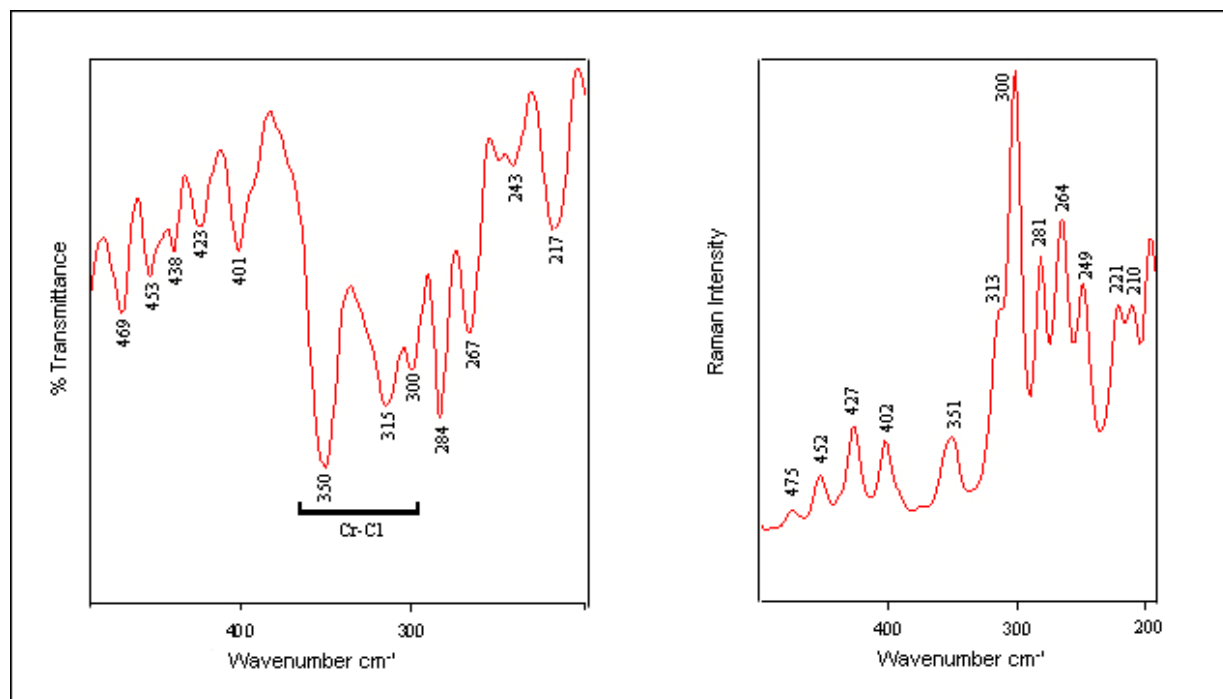

Figure 5.12   **FIR and Raman spectra of [CrCl$_3$(dppea)(py)]**

Table 5.7 **Vibrational assignments of [CrCl$_3$(dppea)(thf)] (24), [CrCl$_3$(dppea)(py)] (25), [CrCl$_3$(dppea)(pyNH$_2$)] (26), [CrCl$_3$(dppea)(pytb)] (27) and**

[CrCl$_3$(dppea)(pyphenyl)] (28)

24		25		26		27		28		
IR / cm^{-1}	R / cm^{-1}	IR / cm^{-1}	R / cm^{-1}	IR / cm^{-1}	R / cm^{-1}	IR / cm^{-1}	R / cm^{-1}	IR / cm^{-1}	R / cm^{-1}	Assignment
3365s	-	-	-	-	-	3372s,	-	3380s	-	ν (NH) asym (dppea) (76)
-	-	-	-	3327s	-	-	-	-	-	ν(NH) asym (pyNH$_2$) (76, 96)
3291s/sh	-	-	-	-	-	-	-	3298w	-	ν(NH) (dppea) sym (dppea) (76)
-	-	3242s	3243w	-	-	3236sh	-	-	-	ν(NH) (dppea)
-	-	3211s	3210w	3198s	-	3202w	-	3195sh	-	ν(NH) sym (76) / overtone / pyH
-	3169w	-	-	-	3168w	-	3168w	-	3166w	ν(NH) sym (76) / Overtone (113)
-	3140w	3134s	3135m	-	3139w	-	3141w	-	3138w	Overtone (113)
-	-	-	-	-	-	-	-	3114s	-	unassigned
-	-	-	-	3092s	3089sh	-	-	-	-	ν (CH) (pyNH$_2$) (96)
-	-	3075s	3071s	-	-	3067sh	-	3069sh	-	ν (CH) (dppe) (113) / (py) (73)
3051s	3054s	3050s	3056s	3047sh	3054s	3051s,	3053s	3047s	3055s	ν (CH) (dppe) (113) / (py) (73, 74, 92, 96, 97)
-	3001w	3002w	3002w	-	3003w	3000w	3003msh	-	3004w	Combination (113)
-	-	2974m	2987w	-	-	-	-	-	-	unassigned
2964s	2959m	2962sh, 2951w	2962m, 2945m	2965s	2957m	2959s	2965s	2959sh	2961m	ν (CH$_2$) asym (113)/ ν (CH$_3$) asym (92)
-	-	-	-	-	-	-	2928s, 2924s	-	-	ν (CH$_3$) sym (92)
2900ssh	2909m	-	2910m	-	2909m	2903s	-	2907sh	2911m	Combination (113)/ ν (CH$_3$) sym (92)
-	-	2889w	2888m	-	-	-	-	-	-	unassigned
-	-	-	-	-	-	2868s	2867m	-	-	ν (CH$_3$) sym (92)
-	-	-	-	1652s	1644m	-	-	-	-	δ (NH$_2$) (96)
-	-	1606s	1606m	1618s/sh	1616w	1616s	1618m	1615s	1615s	ν$_{ring}$ (py) (73, 74, 92, 96,

24		25		26		27		28		
										97)
-	-	-	-	-	-	-	-	-	1598s	ν_{ring} (py) (97)
1583m	1585s	1588w	1586s	1590m	1585s	1585m/sh	1585s	1585m	1587s	ν_{ring} (dppe) (113)
1574m	1573msh	1572w	1572m	1572sh	1572msh	1570sh	1572msh	-	1573msh	ν_{ring} (dppe) (113) / ν_{ring} (py) (73, 74, 92, 96, 97)
-	-	-	-	-	-	1543w	1547vw	-	-	ν_{ring} (pytb) (92)
-	-	-	-	1530s	1533m	-	-	-	-	ν_{ring} (96)
-	-	-	-	-	-	1501m	1499vw	1504w	1513m	ν_{ring} (py) (92) (97)
1481s	1484w	1485m	1486w	1482m	1485vw	1482m	1483w	1482s	1485vw	CH def + ν(semicircle) (113)
1461m	1461w	1459w	1458w	1458w	1460vw	1462m	1463m	1462w	1462vw	Dppea vib / CH$_3$ asym def (92)
-	-	1447s	-	-	-	-	-	-	-	Py ring (73, 74)
1432s	1435w	1435s	1437w	1434m	1435w	1434s	1443m	1432s	1432vw	CH def + ν(semicircle) (113)
1410w	1411w	1408w	1407vw	1408w	1414w	1420s	1396vw	1416s	1416vw	Overtone(113) / CH$_3$ sym def (92) / ν_{ring} (97)
1379w	1379w	-	-	1376w	1375vw	1368m	1375vw	1378w	1379w	Dppea vib
-	-	-	-	1364w	-	-	-	-	-	ν_{ring} (96)
1329w	1331w	1338w	1335vw			1330w	1331w	1332w	1332w	δ (CH) def (113)
1309w	1308w	1316w	1316w	1308w	1308vw	1307w	1306w	1308w	1293s	CH$_2$ twist(113)
-	-	1278w	1281w	1281w	-	-	-	-	-	unassigned
1260w	1273w	-	-	1261w	1269w	1272m	1274w	1260w	-	unassigned
1229w	1232w	1237m	-	1233w		1230m	1232m	1226s	1229m	Dppea vib
	-	1221m	1220m	1215m	1217w	-	-	-	-	δ (CH) (73, 74, 92)
-	-	-	-	-	-	1201w	1201m	-	-	ν (CC) (pytb) (92)
1186w	1188m	1187w	1188m	1197m	1189w	1188w	1188m	1188w	1188m	δ (CH) def (113)
1158w	1159m	1155w	1157m	1157w	1159w	1157w	1156m	1156w	1159m	δ (CH) def (113)
1117m	-	1127m	1129w	1123w	1128vw	1125m	1126m	1118m	1130w	ν (P-C(C$_6$H$_5$)) (113)
1098s	1099m	1104m	1101m	1099	1098m	1096m	1097m	1100m	1099m	Ring breathing (113)
1069m	1071vw	1068s	1069w	1071vw	-	1067s	1069m	1070s	1072m	δ (CH) def (113)
1043m	-	1046m	1046m	1055w	1047m	-	-	-	-	ν_{ring} (63, 64, 113))

24		25		26		27		28		
1026m	1027s	1030w	1029s	-	-	-	-	1030m	1030s	δ (CH) def (113)
-	-	1016m	1014s	1023m	1028m	1027s	1027s	1012m	1012m	Ring breathing (pyX) (73-75, 92, 96, 97)
1000m	999s	998w	999s	999m	999s	998m	999s	998m	999s	Trigonal ring breathing (113)
957w	956vw	962m	962w	957w	-	958m	954w	956m	-	Dppea vib
916w	920w	923w	920w	919w	924vw	925w	929m	920m	919w	Dppea vib
-	-	-	-	-	848s	843m	844w	837m	843w	ν_{ring} breathing (py) (92) / X-sens (96) / δ_{ring} (97)
819sh/m	824vw	823m	822w	827m	-	831s	-	-	-	In phase γ(CH) def (92, 96, 113)
803m	795vw	-	-	807sh/m	-	-	-	-	-	unassigned
-	-	784s	-	-	-	-	-	-	-	Py vib
-	-	-	-	-	-	-	-	765s	762m	$\delta_{ring} + \nu_{ring}$ (97)
-	-	757s	756w	-	-	-	-	-	-	γ (CH) (73, 74)
739s	741w	746s	-	743s	750vw	739s	732m	735s	734vw	In phase γ(CH) (dppe) (113)
694s	685m	695s	693w	697s	684w	697s	684m	693s	684m	CH$_2$ rock (113)
-	673sh	668w	666m	-	667w	668w	668m	667w	667m	ν (PC) (5 membered ring) (113)
-	-	-	650m	-	-	-	-	-	-	δ_{ring} (73, 74)
-	-	641m	641vw	-	-	-	-	-	-	ν_{ring} (py) (73, 74)
-	617m	617w	617m	-	617m	616w	617m	625s	618m	δ (quadrant ring) def (dppea) (113)
-	-	-	-	-	-	572s	570w	-	-	Skeletal str (tb) (92)
-	-	-	-	-	-	-	-	561m	563w	δ_{ring} (97)
-	-	-	-	-	-	547m	549w	-	-	Rock (tb) (92)
522s	523w	522s	524w	524s	527m	524m	526w	523s	524w	δ (quadrant ring) def (dppea) (113)
508s	506vw	505s	506vw	500s	505w	509s	505w	505s	504vw	γ (quadrant ring) def (113)
471w	471w	469w	475w	473w	471vw	474w	465w	471w	470vw	5 membered ring def
449w	446w	453w	452w	453w	446vw	449w	-	448w	446w	5 membered ring def

24		25		26		27		28		
-	-	438w	-	-		-	-	-	-	γ_{ring} (py)(73, 74)
421w	419w	423w	427w	421w	415m	427w	432w	422w	431vw	Cr-P ? (114, 115)
400w	397w	401w	402w	402w	-	400w	396w	397w	405m	γ (quadrant ring) str (113)
339w	357w	350w	351w	350w	350w	373w	358br	360w	362w	Cr-Cl (80)
313w	314w	315w	313msh	316w	313sh	350w	336br	336w	-	Cr-Cl (80)
-	-	300w	300s	-	-	319w	320m	315w	319m	Cr-Cl (80)
287w	293m	284w	281m	287w	296m	295w	297m	283w	293m	Dppea specific
269w	260m	267w	264m	269w	275msh	273w	271m	271w	263m	Dppea specific
243w	br (fluor)	242w	249m	243w	254m	243w	258m	240w	-	Cr-N (NH_2) (79)
218w	br (fluor)	217w	221m	218w	-	220w	-	221w	-	Ph-P-Ph (114) / Cr-N (41, 80, 81)
214w	br (fluor)	-	210m	214w	208msh	215w	207m	-	-	Ph-P-Ph (114) / Cr-N (py) (41, 80, 81)

ν = stretching, δ = in-plane bending, γ = out-of-plane bending, def = deformation, asym = asymmetrical, sym = symmetrical vs = very strong, s = strong, m= medium,

w = weak, vw = very weak, br (fluor) = broad due to fluorescence

5.3.3 COMPUTATIONAL STUDY

In keeping with the selection of [CrCl$_3$(dppe)(pytb)] in Chapter 4, the analogous dppea complex, [CrCl$_3$(dppea)(pytb)], was also selected as being representative of the other complexes in its class.

As has been the case throughout this study, excellent correlation between the experimental and calculated spectra, which are presented in Figures 5.13 and 5.14, is again observed. However, unlike [CrCl$_3$(dppe)(pytb)], and in common with all the other computationally studied complexes, no FIR spectrum is shown owing to the problems associated with solid-state effects that limit the number of distinct Cr–Cl modes observed in the actual spectrum.

A selection of important vibrations, which through their experimental-calculated correlations confirm previous experimental indications of coordination, is presented in Tables 5.8 and 5.9.

Also to be found in the table is an example of vibrations that, on the basis of a combination of comparative and literature studies, have been loosely assigned as dppea-specific vibrations. However, the successful correlation of the calculated results has allowed these bands to be assigned to specific vibrations as in the case of the mode at ~950 cm^{-1} which is a CH$_2$–NH$_2$ vibration.

While the Cr–P vibration is confirmed at a slightly higher frequency than its dppe counterpart, the remaining metal ligand vibrations are for the most part difficult to correlate due to the mixing modes.
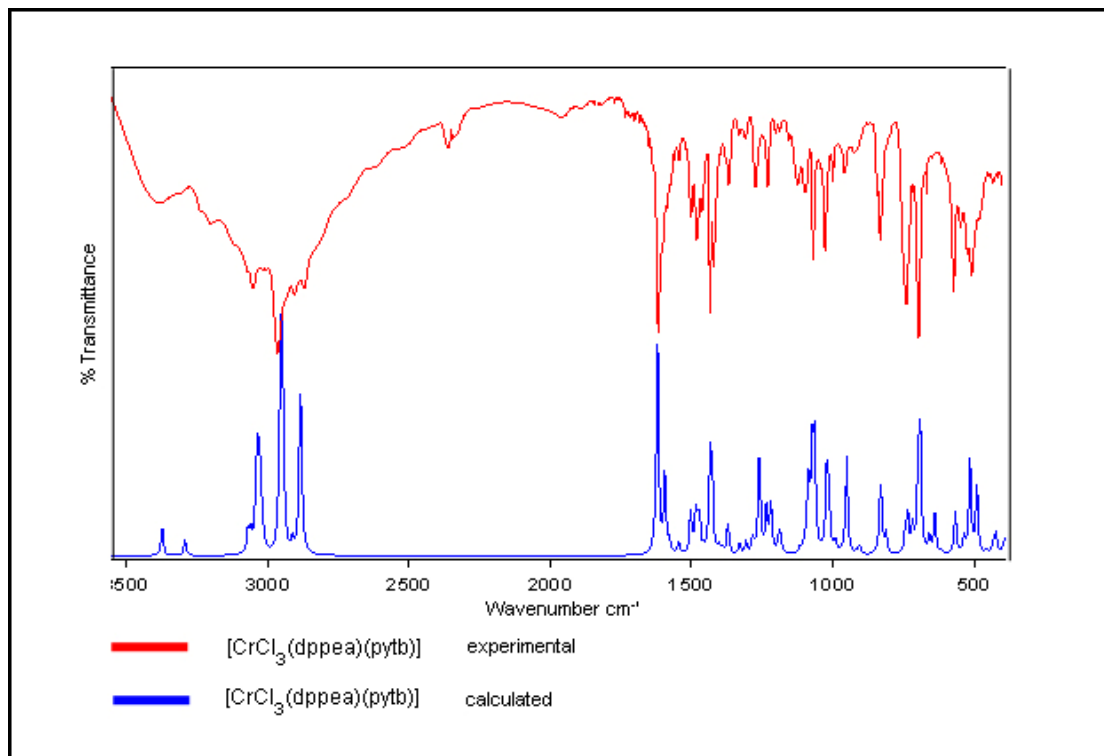
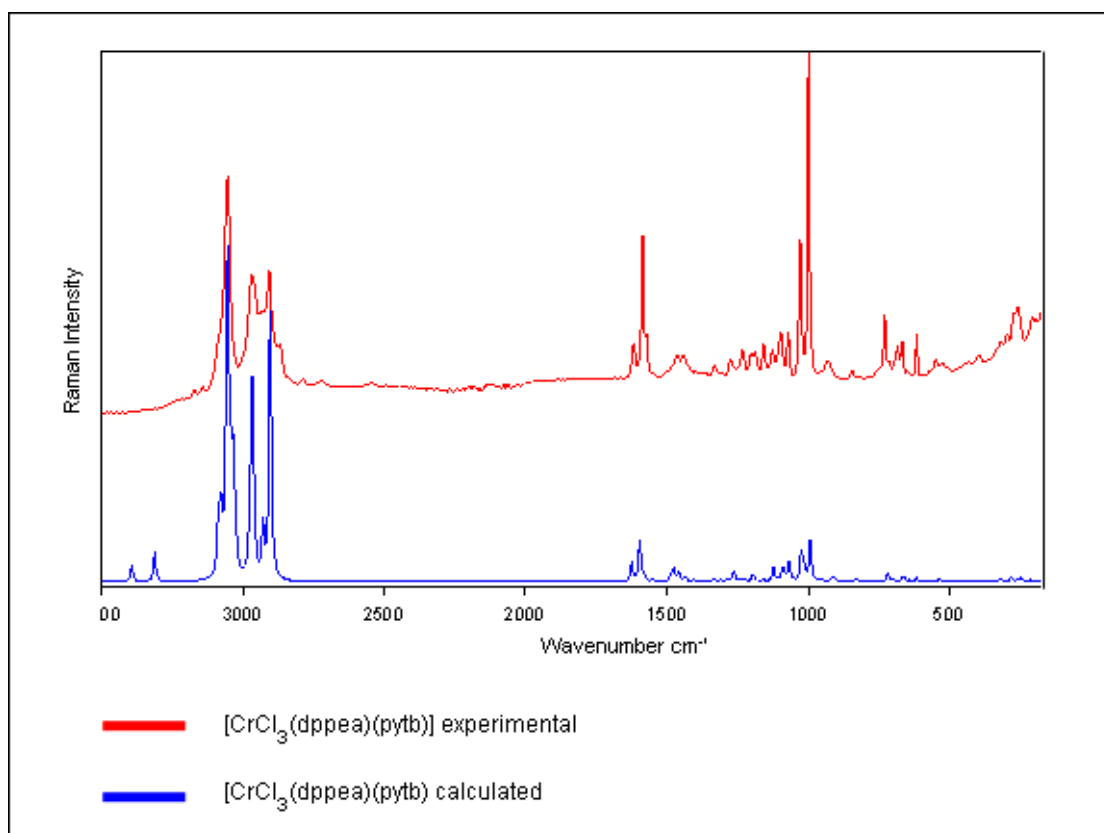**Figure 5.13**   **Experimental (red) and calculated (blue) MIR spectra of [CrCl₃(dppea)(pytb)]**

Figure 5.14   **Experimental (red) and calculated (blue) Raman spectra of [CrCl₃(dppea)(pytb)]**

Table 5.8　　　**Selected experimental and calculated IR and Raman band assignments for**
[CrCl$_3$(dppea)(pytb)]

[CrCl$_3$(dppea)(pytb)] IR / cm^{-1}		[CrCl$_3$(dppea)(pytb)] Raman / cm^{-1}		Assignment	
Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
3372	3371	-	3391	ν (NH) asym	ν (NH) asym
1616	1618	1618	1624	ν_{ring} (py)	ν_{ring} (py)
1585	1592	1585	1596	ν_{ring} (dppea)	ν_{ring} (dppea)
1027	1018	1027	1021	Ring breathing (pytb)	Ring breathing (pytb)
998	993	999	993	Trigonal ring breathing (dppea)	Trigonal ring breathing (dppea)
958	952	954	953	dppea specific	CH$_2$–NH$_2$ (dppea)
668	674	668	659	ν (PC) (5-membered ring)	ν (PC) (5- membered ring)
427	432	432	433	Cr–P	Cr–P
-	422		423	-	Cr–N (NH$_2$) + P-C(C$_6$H$_5$)
373, 350, 319	380, 369, 336, 315	358, 336, 320	380, 370, 337, 315	Cr–Cl	Cr–Cl + Cr–N (NH$_2$)/ pytb rock
-	259		260	-	Cr–N (py) + CH$_3$ twist
243	243	258	244	Cr–N (NH$_2$)	Cr–Cl + Cr–N (NH$_2$)
220, 215	-	207	-	Ph–P–Ph / Cr–N (py)	-

Table 5.9   Scaling factors determined for [CrCl$_3$(dppea)(pytb)]

Region / cm^{-1}	IR	Raman
0 – 1860	0.975824	0.978314
2827 – 3745	0.951054	0.956602

The HOMO and LUMO orbitals that were generated by computational means (Figure 5.15) illustrate that while attack by electrophiles is likely to take place around the chlorine atoms only, nucleophilic attack is possible at the trans chlorine atoms as well as at the pyrindine and phenyl rings that are trans to each other.

HOMO   **LUMO**
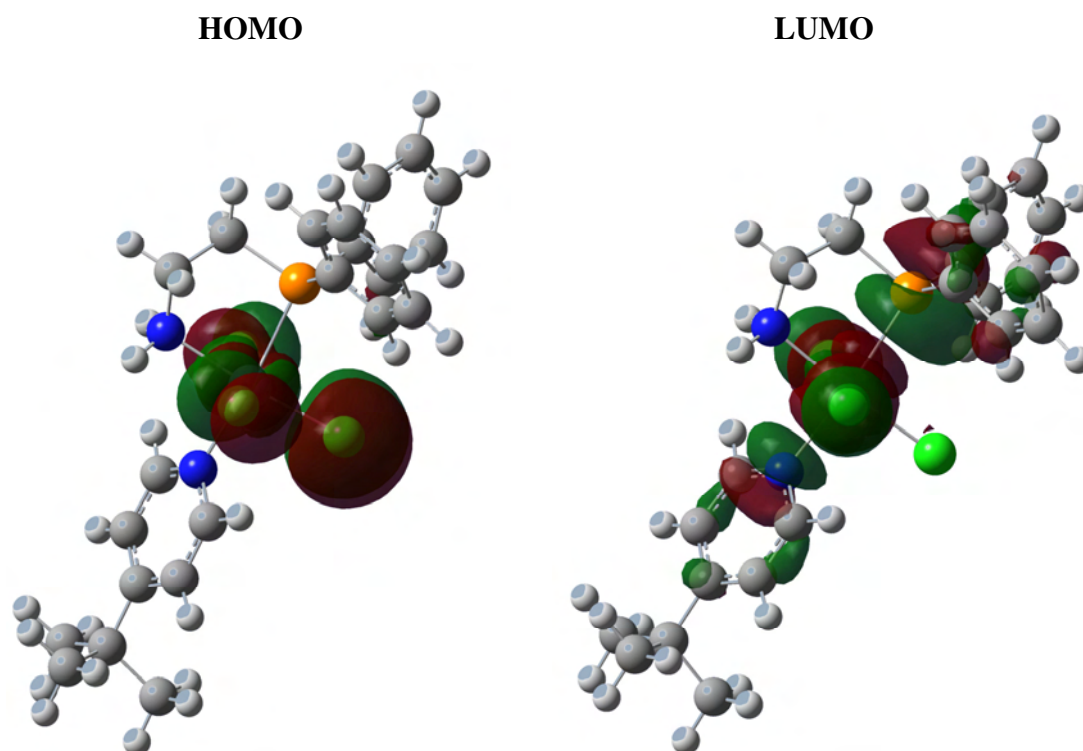
Figure 5.15   HOMO and LUMO orbitals of [CrCl$_3$(dppea)(pytb)]]

5.3.4   MASS SPECTROMETRY

[CrCl$_3$(dppea)(pytb)] and [CrCl$_3$(dppea)(pyphenyl)] were selected for FAB-MS analysis. These structures were confirmed by the isotopic distribution pattern [M–Cl]$^+$ (m/z = 486), (m/z = 506) which was observed in the respective spectra and shown in Figures 5.16 and 5.17. Both patterns corresponded well with the theoretically generated equivalents.
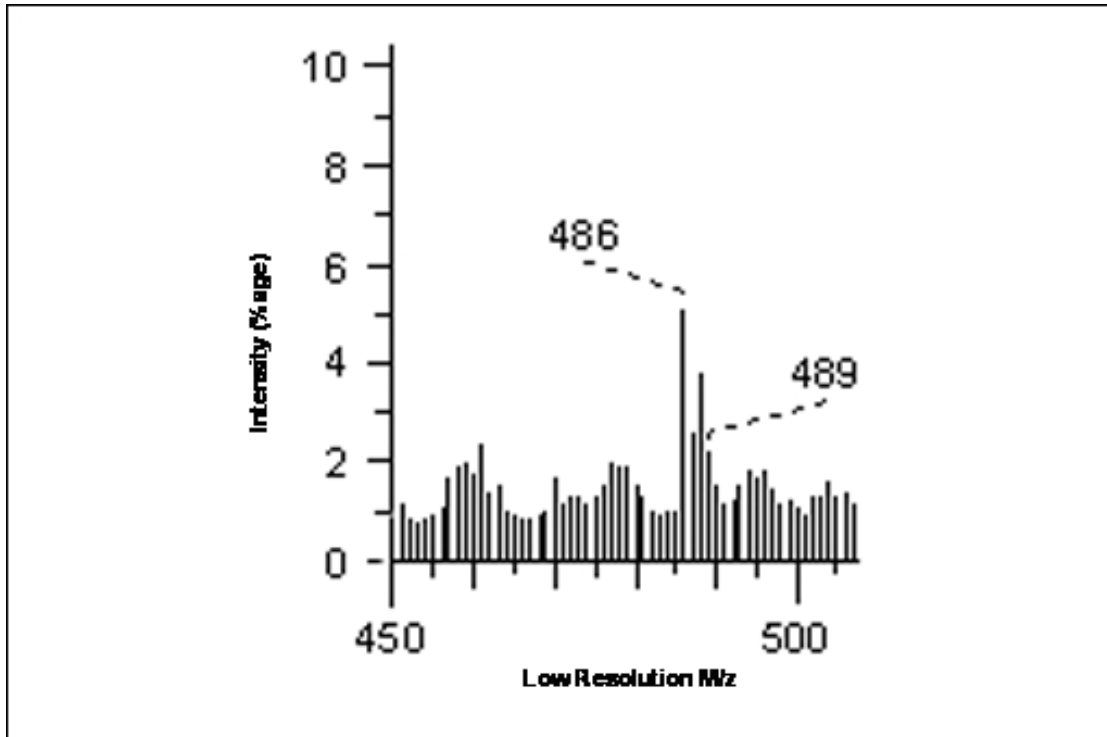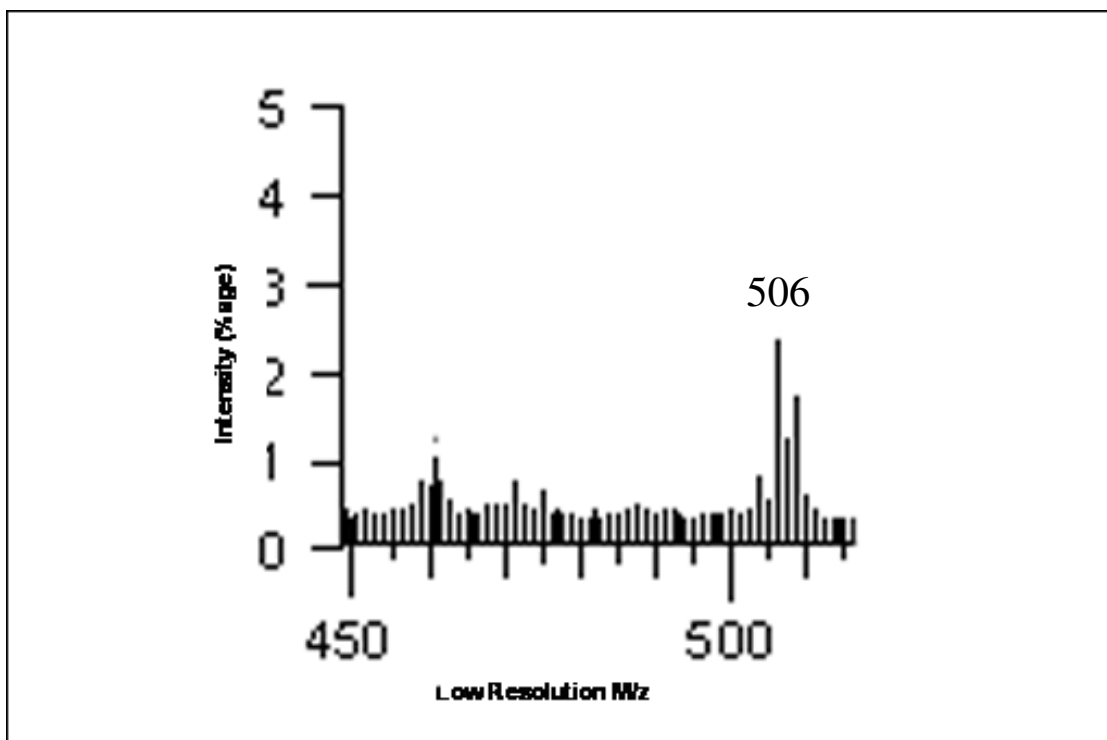
Figure 5.16   FAB-MS spectrum of [CrCl₃(dppea)(pytb)]

Figure 5.17   FAB-MS spectrum of [CrCl₃(dppea)(pyphenyl)]

5.4   EXPERIMENTAL

5.4.1   SYNTHESIS OF [CrCl$_3$(dppea)(thf)] / [Cr(dppea)Cl$_2$(μ-Cl)]$_2$ (24)

A Schlenk tube was charged with [CrCl$_3$(thf)$_3$] (0.1 g, 0.267 mmol) and thf (20 cm^3). The addition of dppea (0.06 g, 0.267 mmol) resulted in an immediate colour change with the reaction mixture being observed as a blue-green solution. To ensure completion it was allowed to stir overnight at room temperature. Following the reduction of volume and the addition of Et$_2$O (20 cm^3), a blue-green precipitate was visible. Removal of the supernatant via syringe and addition of Et$_2$O (3 x 20 cm^3) was then followed by drying of the residue under reduced pressure. After a period of 3 hours a blue-green precipitate (24) was isolated in good yield (monomer: 0.1 g, 81% / dimer: 0.1 g, 48%)

5.4.2   SYNTHESIS OF [CrCl$_3$(dppea)(py)] (25)

Following the charging of a Schlenk tube with [CrCl$_3$(thf)$_3$] (0.1 g, 0.267 mmol) and thf (20 cm^3), dppea was added, followed 10 minutes later by pyridine. The resulting blue-green solution was left to stir at room temperature overnight. The volume was then reduced and upon addition of Et$_2$O (20 cm^3) a blue precipitate was observed. The supernatant was removed via syringe and the residue washed with Et$_2$O (3 x 20 cm^3) and dried under reduced pressure to result in a light blue precipitate (25) isolated in good yield (0.9 g, 73%)

5.4.3   SYNTHESIS OF [CrCl$_3$(dppea)(pyNH$_2$)] (26)

A Schlenk tube was charged with [CrCl$_3$(thf)$_3$] (0.1 g, 0.267 mmol) and thf (20 cm^3). The blue-green solution resulting from the subsequent addition of dppea turned more of a light blue colour with the formation of a precipitate once pyNH$_2$ had been added after 10 minutes. After it had been stirred at room temperature overnight to ensure completion of the reaction, the supernatant was removed via syringe and the light blue residue washed with Et$_2$O (3 x 20 cm^3), followed by drying under reduced pressure. The result was a light blue precipitate (26) in good yield (0.11 g, 85%).

5.4.4 SYNTHESIS OF [CrCl$_3$(dppea)(pytb)] (27)

A Schlenk tube was charged with [CrCl$_3$(thf)$_3$] (0.1 g, 0.267 mmol) and thf (20 cm^3). Dppea was then added and the blue-green solution stirred at room temperature for 10 minutes. Following the addition of pytb, the solution remained blue-green and it was allowed to stir overnight at room temperature. Reduction of volume and addition of Et$_2$O (20 cm^3) resulted in a blue-green precipitate. Removal of the supernatant via syringe and addition of Et$_2$O (3 x 20 cm^3) allowed the residue to be dried under reduced pressure, resulting in the isolation of a blue-green precipitate (27) in good yield (0.11 g, 78%).

5.4.5 SYNTHESIS OF [CrCl$_3$(dppea)(pyphenyl)] (28)

Upon dissolution of [CrCl$_3$(thf)$_3$] (0.1 g, 0.267 mmol) in thf (20 cm^3) within a Schlenk tube, dppea was added, followed 10 minutes later by pyphenyl. To ensure completion of the reaction, the blue-green solution was stirred at room temperature overnight. The volume was then reduced and Et$_2$O (20 cm^3) added. The precipitate that resulted was washed with Et$_2$O (3 x 20 cm^3) and dried under reduced pressure for 3 hours. A blue-green precipitate (28) was isolated in good yield (0.12 g, 83%).