# Chapter 6

# Future work and Conclusions

## 6.1 FUTURE WORK

Future work could be directed towards the synthesis, isolation and investigation of the C–C coupling reactions of dimeric (chloro-bridged) Cr(III) complexes and cation Cr(III) complexes with labile ligands. Such studies would aid the greater understanding of oligomerisation reactions with Cr(III) catalysts.

From the wide variety of ligands that could be employed, it may be of interest to consider those that would lead to bimetallic complexes upon coordination to [$CrCl_3(thf)_3$]. An example of such a ligand is ((RP)–1–[(1S)–1–aminoethyl)–2–(diphenylphosphino)ferrocene) which would lead to a Fe–Cr system. This would also be a direct progression from the ligands of this study with respect to the $Ph_2P$ and $NH_2$ donor environments, with the added interest of incorporating a six–membered chelate ring.

From an extensive literature search only one reference was found to this specific ligand, with the focus on the Ru(II)-catalysed asymmetrical hydrogenation of ketones [122] (Figure 6.1). This therefore opens the door to structural and spectroscopic studies similar to those carried out in this study, as well as to investigations into catalytic activity. The literature also revealed that although novel, the formation of the six-membered chelate ring with chromium is a plausible expectation as such systems have been solved crystallographically with similar ligands and metals, including tungsten, palladium and ruthenium [123, 124, 125].

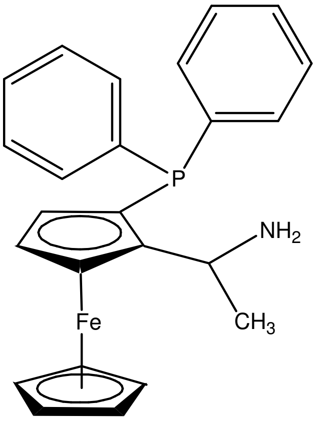

**Figure 6.1** ((RP)–1–[(1S)–1–aminoethyl)–2–(diphenylphosphino)ferrocene)

## 6.2 CONCLUSION

This project succeeded in fulfilling its core objective which was to enhance the fundamental knowledge of Cr(III) compounds via detailed structural and spectroscopic techniques. It is, however, noted that further analytical techniques must be applied before the structures are defined with absolute certainty. What proved to be particularly interesting was that all the techniques used complemented each other extremely well and thus the findings of an individual technique could assist or add weight to the findings of another.

IR and Raman spectroscopy proved to be extremely useful as analytical tools for providing evidence of ligand coordination. Furthermore, they offered insights into both the molecular geometry of the compounds and the synthetic routes via which the products were formed. Ligand coordination was based on vibrational shifts relative to the respective free ligands and these shifts correlated very well indeed with similar vibrations found in the literature. Additional evidence of ligand coordination was found in the FIR region where metal–ligand vibrations were observed. Once again the previous literature assisted in these assignments. The FIR region also led to deductions regarding the molecular geometry of the compounds, whereby the number of Cr–Cl vibrations related to either the *cis* or *mer* arrangements. Synthetic route deductions were based principally on the crystallographic findings of this study. However, by studying the IR and Raman spectra of these structures it was possible to add weight to these pathway proposals even when structures were not available.

A direct complement to the IR and Raman spectroscopic analysis was the generation of the corresponding theoretical spectra by means of DFT calculations. This proved to be highly successful as excellent correlations between the experimental and calculated spectra were observed. The generation of HOMO and LUMO orbitals of the compounds by computational means also proved successful as sites of potential electrophilic and nucleophilic attack were determined. Of interest was that while electrophilic attack consistently occurred at the *mer* arranged chlorine atoms, regardless of the ligand environment, sites of nucleophilic attack were determined by geometry-related factors. These were particularly prevalent in the monodentate pyridine complexes of Chapter 2, in which nucleophilic attack was expected only at the pyridine ring system *trans* to a chlorine atom. A further conclusion drawn from the generation of these frontier orbitals was that the sterically and electronically different substituted pyridine ligands did not play a role in altering the region of nucleophilic attack.

The use of NMR spectroscopy to study paramagnetic systems is ordinarily avoided. However, this study proved that information associated with ligand coordination and the determination of reaction times can be obtained from such a practice. Regardless of the inability to conduct kinetic studies, for reasons discussed in this study, NMR spectroscopy was successfully incorporated into this study of paramagnetic systems.

The number of single crystal structures that were determined was a considerable achievement considering that the isolated precipitates were so highly insoluble. All eight structures provided novel insights with regard to bond lengths, bond angles, packing arrangements, etc. They were also instrumental in the proposal of synthetic routes to compound formation as it was clear that dimeric intermediates existed which offered alternative pathways to the initially expected route of direct ligand substitution.

The results of the FAB-MS provided additional confirmation of compound identities by way of identifiable fragmentation patterns. In addition the presence of chlorine atoms in the compounds allowed for the successful comparison of isotopic distribution patterns between the experimental results and those generated theoretically.

With regard the proposed synthetic pathways to product formation discussed throughout the thesis, one is able to conclude that based on the information available in literature as well as the vibrational and structural data presented in this study, product formation via dimerisation is plausible.