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Synthesis and reactivity of a ferrocene-derived PCP-pincer ligand

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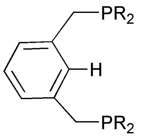
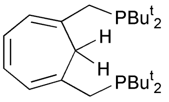
The 1,3-bis(diphosphinomethyl)ferrocene 3 readily reacts with $[(C_2H_4)_2RhCl]_2$ to form an equilibrating pair of diastereomers 8a and 8b by C–H insertion into the ferrocene.

Pincer-type ligands have played a significant role in homogeneous catalysis.[1] With the recent development of effective catalysts for dehydrogenation that involve Rh, or more especially Ir, complexes related to compound **1**, interest in their application has been heightened.[2] Among the factors that contribute to their reactivity in the critical C–H activation step will be the chelate bite angle and the electronic character of both the σ- and π-bonding entities. Synthesis and complexation chemistry of a higher homologue **2** based on cycloheptatriene has already been reported.[3] For these reasons we are interested in the synthesis of the ferrocene analogue **3**, and report its successful completion together with some preliminary reactions that demonstrate the access to pincer-type ligation.



1a (R = Pr^i)
1b (R = Bu^t)



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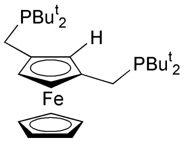

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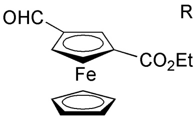

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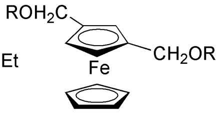
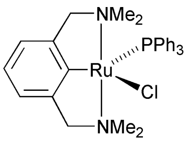


5a (R = H)
5b (R = Ac)

General methods for the preparation of 1,3-disubstituted ferrocenes are severely lacking.[4] In order to synthesise a suitable precursor, we prepared compound **4** according to published procedures, involving the photochemical displacement of *p*-xylene from CpFe[*p*-xylene]$^+BF_4^-$ in the presence of 3-methoxycarbonyl-6-dimethylaminofulvene.[5,6] This was cleanly reduced by $LiAlH_4$ in refluxing THF to the primary diol **5a** in 89% yield.[7] Attempts to form the diacetate **5b** by conventional means (Ac_2O, py, DMAP) were unsuccessful, but it was demonstrated that direct S_N1 reaction in AcOH at 80 °C proceeded cleanly, according to precedent.[8] Rather than isolate the diacetate according to conventional phosphination procedures,[9] diol **5a** was converted directly into the desired diphosphine **3** by heating with $HPBu^t_2$ (2 equiv.) in AcOH (80 °C, 1 h), isolating the product† in 62% yield by precipitation from MeOH.

The new ligand was surveyed for its reactivity towards simple unsaturated metal complexes under mild conditions. A model reaction was first established, using ligand **1b**. By NMR (C_6D_6, 65 °C, 30 min), displacement of the pincer diamine ligand[10] in **6** by the diphosphine was observed. The formation of complex **7** was inferred,‡ although it was not isolated. Repeating this reaction with ligand **3** gave no evidence of complexation, however. Reaction of the ferrocene-derived ligand **3** with $(PPh_3)_3RuCl_2$ or $(MeCN)_2PdCl_2$ likewise failed to give characterisable products.



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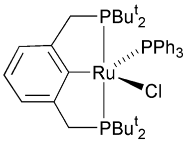

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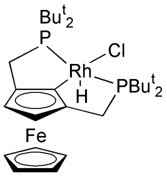
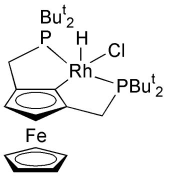
When ligand **3** was reacted with $[(C_2H_4)_2RhCl]_2$ in CD_2Cl_2 at ambient temperature a clean transformation occurred within minutes, the product being characterised by NMR and MS.† Initially, two sets of resonances were observed in the ^1H NMR spectrum, in particular two distinct Rh–H signals at *ca.* −27 ppm. Equilibration occurred over 4 h so that the lower field signal, initially the minor component, became strongly predominant. The equilibration could also be followed by ^{31}P NMR, it being observed that the signal at 87.5 ppm, decreases monotonically over 3 h as the signal at 93.5 ppm increases. The structures of several (PCP)RhHCl complexes or Ir analogues have been determined, and exhibit common geometric features.[11] The ligand and M–Cl form a distorted square plane with the M–H in orthogonal relationship (Fig. 1).

This structural arrangement gives rise to a single magnetic environment for the hydride as defined by the high-field signal in the ^1H NMR spectrum, with one reported exception.§ In the present case there are two distinct structural isomers possible for the insertion products **8a** and **8b** in which the $(C_5H_5)Fe$ moiety is respectively *cis*- (**8a**) or *trans*- (**8b**) to the hydride. The hydride resonance of the more stable isomer formed on standing the solution in CD_2Cl_2 for several hours shows a lack of NOE communication with the C_5H_5 ring, but an intense NOE to one



8a



8b

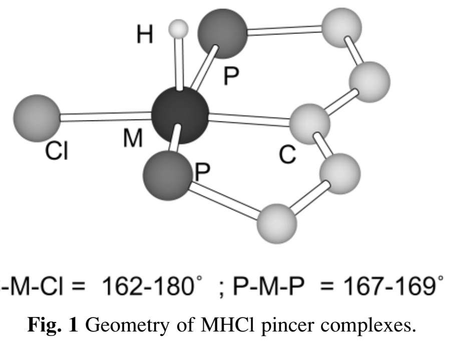


Fig. 1 Geometry of MHCl pincer complexes.

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pair of *tert*-butyl groups. On this basis the assignment of *cis*- or *trans*- to the preferred initial and final products of insertion is as defined in the spectroscopic data.† The results are consistent with initial intramolecular C–H insertion from the less hindered *exo*-face of the ferrocene to give complex **8a**. Equilibration of complexes **8a** and **8b** may occur through reversal of that step, or phosphine dissociation and recombination.

The reactivity of ligand **3** towards C–H insertion in a simple Rh complex demonstrates that the relevant bis-chelate can be readily formed, despite the additional strain energy engendered by the smaller template ring of ferrocene *vs.* arene. The catalytic chemistry of **3** and its relatives will be explored in future work.

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Notes and references

† For **3**: Mp 157–158 °C (decomp.). δ_H ($CDCl_3$): 4.35 (brs, 1H), 4.15 (d, J_{HP} 1 Hz, 2H), 4.06 (s, 5H), 2.59 (d, J_{HP} 2 Hz, 4H, CH_2), 1.11 (2 × d, J_{HP} 11 Hz, 18H, 18H, diastereotopic Bu^t). δ_C ($CDCl_3$): 87.6 (d, J_{CP} 20 Hz, 2C), 70.3 (s, 1 CH), 70.1 (s, 5 CH), 68.9 (d, J_{CP} 6 Hz, 2 CH), 31.8 (2d, J_{CP} 22 Hz, J_{CP} 7 Hz, 4 C), 30.1 (2d, J_{CP} 13 Hz, J_{CP} 3 Hz, 12 Me), 22.7 (d, J_{CP} 23 Hz, 2 CH_2). δ_P ($CDCl_3$): 34.1 (s). MS AP+ 502.2601 (Calc. for $C_{28}H_{48}P_2Fe$ 502.2581. For **8a**: δ_H (CD_2Cl_2): −27.55 (dt, 1H Rh–H, J_{RhH} 47 Hz, $^2J_{PH}$ 12.5 Hz), 1.23 (9H, virtual q, J 6.5 Hz), 1.52 (9H, virtual q, $J =$ 6.5 Hz), 2.67 (1H, brq), 3.00 (1H, brq), 3.96 (s, 5H), 4.34 (s, 2H). δ_P (CD_2Cl_2): 88.45 (d, J_{RhP} 114Hz). For **8b**: δ_H (CD_2Cl_2): −27.45 (dt, 1H Rh–H, J_{RhH} 47 Hz, $^2J_{PH}$ 13 Hz), 1.20 (9H, virtual q, J 6.5 Hz), 1.57 (9H, virtual q, J 6.5 Hz), 2.54 (1H, brq), 2.90 (1H, brq), 3.91 (5H, s), 4.42 (2H, s). δ_P (CD_2Cl_2): 93.5 (d, J_{RhP} 115 Hz). ES MS (**8a** + **8b**): 605.1634 ($M^+ - Cl$) (Calc. for $C_{28}H_{48}FeP_2Rh$ 605.1636); 604.1575 ($M^+ - HCl$) (Calc. for $C_{28}H_{47}FeP_2Rh$ 604.1557).

‡ For **7**: δ_P (C_6D_6): 46, 50 (ABq, J 5 Hz), 61 (s).

§ In ref. 11*b* the HRhCl pincer complex derived from ligand **1a** has been reported as giving rise to two distinct high-field ^{1}H NMR signals considered to be conformational isomers. This observation was confirmed by us when the synthesis was repeated starting with the ligand·$(HBr)_2$ salt. We suspected that a mixture of HRhCl and HRhBr complexes was responsible, however. Further work has confirmed that the pure HRhCl complex, unambiguously synthesised, gives only a single high-field resonance δ_H −27.8 ppm, J_{RhH} 52Hz, $^2J_{PH}$ 12 Hz.

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