COMMUNICATION

ChemComm
www.rsc.org/chemcomm

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

Edward J. Farrington,[a] Eloisa Martinez Viviente,[a] B. Scott Williams,[b] Gerard van Koten*[b] and John M. Brown*[a]

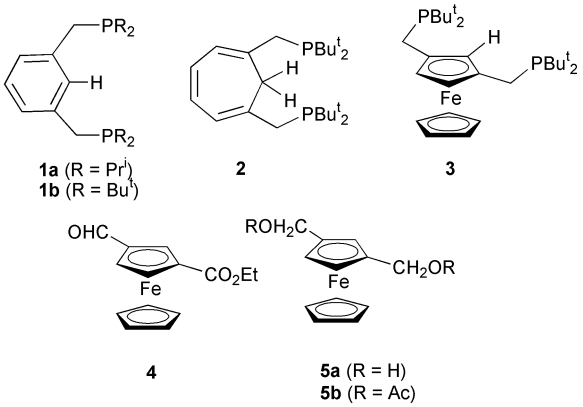
[a] *Dyson Perrins Laboratory, South Parks Road, Oxford, UK OX1 3QY. E-mail: bjm@herald.ox.ac.uk*

[b] *Dept. of Metal-Mediated Synthesis, Utrecht University, Padualaan 8 3584 CH. Utrecht, The Netherlands. E-mail: g.vankoten@chem.uu.nl*

Received (in Cambridge, UK) 25th September 2001, Accepted 12th December 2001
First published as an Advance Article on the web 21st January 2002

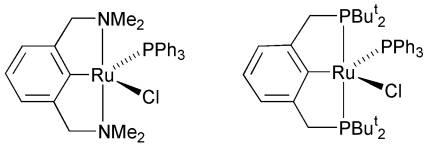
The 1,3-bis(diphosphinomethyl)ferrocene 3 readily reacts with $[(C_2H_4)_2RhCl]_2$ to form an equilibrating pair of diastereomers 8a and 8b by C–H insertion into the ferrocene.

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 n-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.



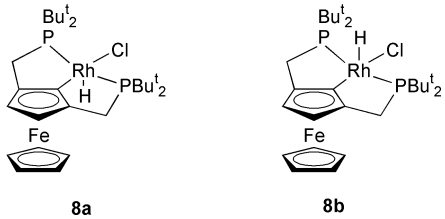
General methods for the preparation of 1,3-disubstituted ferrocenes are severely lacking.[4] In order to synthesise a suitable precursor, we prepared compound **4** according to published procedures, involving the photochemical displacement of *p*-xylene from CpFe[*p*-xylene]$^+BF_4^-$ in the presence 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.

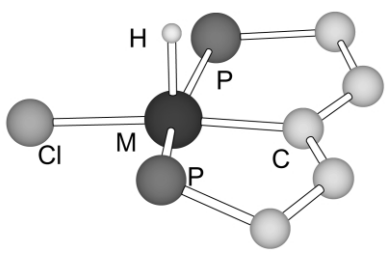


When ligand **3** was reacted with $[(C_2H_4)_2RhCl]_2$ in CD_2Cl_2 at ambient temperature a clean transformation occurred within minutes, the product being characterised by NMR and MS.† Initially, two sets of resonances were observed in the ^1H NMR spectrum, in particular two distinct Rh–H signals at *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



C-M-Cl = 162-180° ; P-M-P = 167-169°

Fig. 1 Geometry of MHCl pincer complexes.

DOI: 10.1039/b108585a

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.

We thank EPSRC and Johnson-Matthey for a CASE Studentship (to E. J. F.). The Seneca Foundation is acknowledged for support of a visit to Oxford by E. M. V.; B. S. W. thanks NATO for a Fellowship. Johnson-Matthey contributed a loan of precious metal salts.

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.

1 M. Rietveld, D. M. Grove and G. van Koten, *New J. Chem*., 1997, **21**, 751; D. Morales-Morales, R. Redon, C. Yung and C. M. Jensen, *Chem. Commun*., 2000, 1619; R. B. Bedford, S. M. Draper, P. N. Scully and S. L. Welch, *New J. Chem*., 2000, **24**, 745; M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed*., 2001, **40**, 3750; C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans*., 1976, 1020.

2 M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun*., 1996, 2083; F. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, *J. Am. Chem. Soc*., 1999, **121**, 4086; F. Liu and A. S. Goldman, *Chem. Commun*., 1999, 655; C. M. Jensen, *Chem. Commun*., 1999, 2443.

3 S. Nemeh, R. J. Flesher, K. Gierling, C. Maichle-Mossmer, H. A. Mayer and W. C. Kaska, *Organometallics*, 1998, **17**, 2003.

4 A. N. Nesmeyanov, E. V. Leonova, N. S. Kochetkova, A. I. Malkova and A. G. Makarovskaya, *J. Organomet. Chem*., 1975, **96**, 275; and references therein.

5 W. E. Lindsell and L. Xinxin, *J. Chem. Research (S)*, 1998, 62; W. E. Lindsell and L. Xinxin, *J. Chem Research (M)*, 1998, 0423; P. Bickert, B. Hildebrandt and K. Hafner, *Organometallics*, 1984, **3**, 653.

6 A. N. Nesmeyanov, N. A. Vol'kenau and I. N. Bolesova, *Tetrahedron Lett*., 1963, **4**, 1725.

7 K. Pagel, A. Werner and W. Friedrichsen, *J. Organomet. Chem*., 1994, **481**, 109; S. Kaluz and S. Toma, *Collect. Czech. Chem. Commun*., 1987, **52**, 2717; C. Zou and M. S. Wrighton, *J. Am. Chem. Soc*., 1990, **112**, 7578; B. Misterkiewicz, R. Dabard and H. Patin, *Tetrahedron*, 1985, **41**, 1685.

8 C. S. Combs, C. I. Ashmore, A. F. Bridges, C. R. Swanson and W. D. Stephens, *J. Org. Chem*., 1968, **33**, 4301.

9 H. Abbenhuis, U. Burckhardt, V. Gramlich, A. Togni, A. Albinati and B. Muller, *Organometallics*, 1994, **13**, 4481.

10 P. Dani, T. Karlen, R. A. Gossage, S. Gladiali and G. van Koten, *Angew. Chem., Int. Ed*., 2000, **39**, 743.

11 (*a*) J. C. Grimm, C. Nachtigal, H.-G. Mack, W. C. Kaska and H. A. Mayer, *Inorg. Chem. Comm*., 2000, **3**, 511; (*b*) S. Nemeh, C. Jensen, E. Binamira-Soriaga and W. C. Kaska, *Organometallics*, 1983, **2**, 1442; (*c*) R. J. Errington, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans*., 1982, 1829; (*d*) C. Crocker, H. D. Empsall, R. J. Errington, E. M. Hyde, W. S. McDonald, R. Markham, M. C. Norton, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans*., 1982, 1217; (*e*) C. Crocker, R. J. Errington, W. S. McDonald, K. J. Odell, B. L. Shaw and R. Goodfellow, *Chem Commun*., 1979, 498.