Journal of Organometallic Chemistry, 338 (1988) C31–C34
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A functionalised diphosphine as a (P–N)-binucleating ligand: X-ray structure of the 'double A-frame' complex $[\{RhCl(BTPE)\}_2][RhCl_4(BTPE)]_2 \cdot xCHCl_3$ $(BTPE = (C_7H_4NS)_2PCH_2CH_2P(C_7H_4NS)_2)$

Mohammad F.M. Al-Dulaymmi, Peter B. Hitchcock, and Raymond L. Richards
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ (Great Britain)

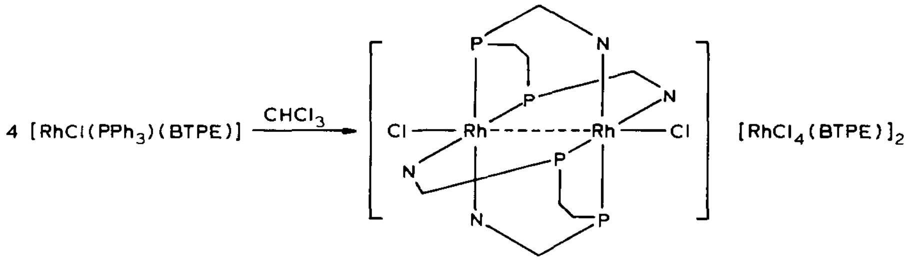
(Received October 1st, 1987)

Abstract

Treatment of $[RhCl(PPh_3)_3]$ with $(C_7H_4NS)_2PCH_2CH_2P(C_7H_4NS)_2$ (BTPE) in tetrahydrofuran gives the complex $[RhCl(PPh_3)(BTPE)]$ which oxidises in the presence of $CHCl_3$ to form $[\{RhCl(BTPE)\}_2][RhCl_4(BTPE)]_2$, whose X-ray structure shows the cation to have the BTPE spanning two rhodiums by P–N ligation.

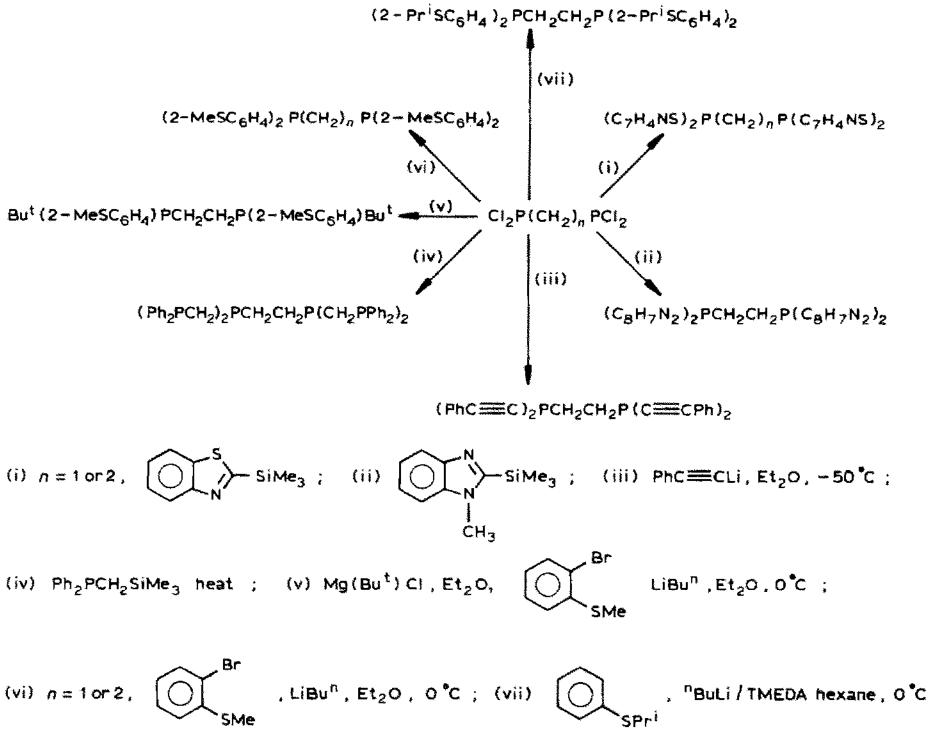
In continuation of our interest in the use of chelating phosphine ligands as a means of stabilising compounds containing ligands of catalytic interest, such as dinitrogen, hydrides etc. [1], we have prepared a range of diphosphine ligands substituted at phosphorus by potentially ligating groups, as shown in Scheme 1, thereby hoping to introduce heteroatom chelation at single metal centres and to be able to obtain multi-metallic compounds. We report here results for complexes involving rhodium and the benzothiazoyl-containing ligand $(C_7H_4NS)_2PCH_2CH_2P(C_7H_4NS)_2$(BTPE) that illustrate the potential of these ligands for producing unusual chemistry.

Treatment of $[RhCl(PPh_3)_3]$ with BTPE in tetrahydrofuran (thf) gave an orange crystalline complex which was identified by analysis and spectroscopy (^{31}P ABX spectrum) as $[RhCl(PPh_3)(BTPE)]$. On dissolution in $CHCl_3$ it oxidises to give, in good yield, red crystals of the complex $[\{RhCl(BTPE)\}_2][RhCl_4(BTPE)]_2$ (eq. 1).



(1)

0022-328X/88/$03.50 © 1988 Elsevier Sequoia S.A.



Scheme 1.

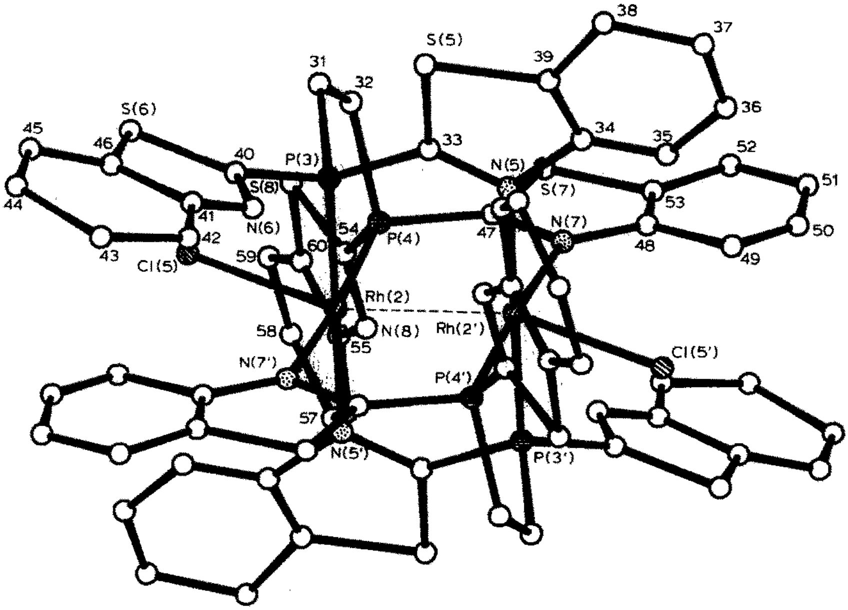


Fig. 1. Structure of $[\{RhCl(BTPE)\}_2]^{2+}$. Selected bond distances (Å) and angles (°) are: Rh(2)–Cl(5), 2.54(2); Rh(2)–N(5)′, 2.16(5); Rh(2)–N(7)′, 2.25(5); Rh(2)–P(3), 2.21(2); Rh(2)–P(4), 2.22(2); Rh(2)–Rh(2)′, 2.723(8); Rh(2)′–Rh(2)–Cl(5), 160.3(5); Rh(2)′–Rh(2)–P(4), 86.6(5); Rh(2)′–Rh(2)–N(7)′, 94(1); Rh(2′)–Rh(1)–P(3) 86.6(5); Rh(2)′–Rh(2)–N(5)′, 94(1); Cl(5)–Rh(2)–P(3), 83.4(7); Cl(5)–Rh(2)–N(5)′, 96(1).

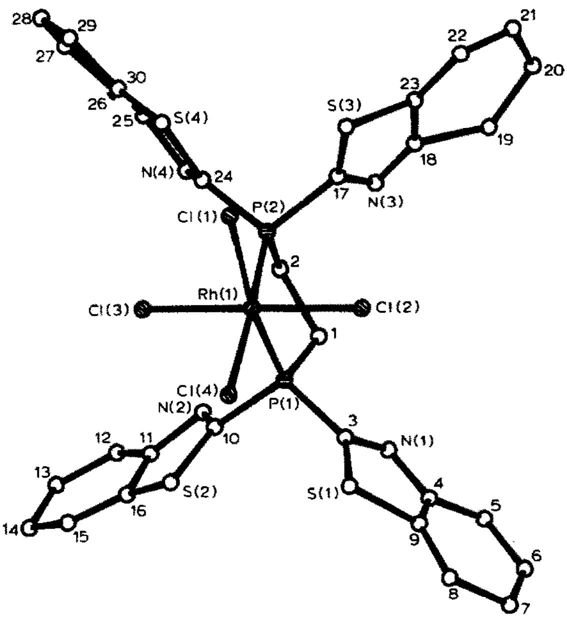


Fig. 2. Structure of $[RhCl_4(BTPE)]^-$. Selected bond distances (Å) and angles (°) are: Rh(1)–Cl(1), 2.45(2); Rh(1)–Cl(2), 2.33(2); Rh(1)–Cl(3), 2.36(2); Rh(1)–Cl(4), 2.39(2); Rh(1)–P(1), 2.22(2); Rh(1)–P(2), 2.18(2); Cl(1)–Rh(1)–Cl(2), 91.0(6); Cl(1)–Rh(1)–Cl(3), 92.1(6), Cl(1)–Rh(1)–Cl(4), 96.7(6); Cl(1)–Rh(1)–P(1), 169.9(7); Cl(1)–Rh(1)–P(2), 85.6(7).

The X-ray structure * of this salt shows it to contain a novel binuclear cation (Fig. 1), with the BTPE ligand spanning two metals; the two identical anions contain rhodium involved in classical diphosphine chelation by BTPE (Fig. 2).

In the cation, each rhodium carries a BTPE ligand chelating through the phosphorus atoms, and a benzothiazoyl group from each phosphorus ligates the second rhodium through nitrogen, to give a 'Double-A-Frame' geometry such as is observed in carboxylate complexes [2]. The Rh–Rh distance of 2.723(8) Å is within the range associated with a Rh–Rh single-bond [3]. The formally rhodium(III) anions have unexceptional coordination.

The ligands which we describe here, possessing potentially 'hard' and 'soft' ligation, promise a rich coordination chemistry. We find, as expected, that they form complexes with a wide range of metals, e.g. $[\{M(CO)_3\}_2\text{-}\mu\text{-}\{(2\text{-}MeSC_6H_4)_2PCH_2CH_2P(C_6H_4SMe\text{-}2)_2\}]$ (M = Mo or W) and $[\{RhCl(CO)\text{-}\mu\text{-}[(C_7H_4NS)_2PCH_2P(C_7H_4NS)_2]\}_2]$, which has a 'regular' A-frame structure. It is important to note that in these complexes there are a number of uncoordinated nitrogen or sulphur atoms

---

Crystal data. $C_{120}H_{80}Cl_{10}N_{16}P_8Rh_4S_{16} \cdot xCHCl_3$, $M = 3273.1$, triclinic, space group $P1$, a 13.684(3), b 16.764(5), c 19.977(4) Å^3, α 87.99(2), β 85.22(2), γ 77.08(2)°, U4450 Å^3, $Z = 1$. Data were collected on an Enraf–Nonius CAD4 diffractometer using Mo-K_α radiation and a crystal sealed in a capillary with some mother liquor. 2462 unique reflections with $I > \sigma(I)$ were used in the refinement giving $R = 0.14$, $R' = 0.18$. There are several disordered molecules of $CHCl_3$ solvent in the unit cell. Tables of atomic coordinates and a full list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

which have the potential for ligation to other metal species and thus for building up polynuclear compounds containing a variety of metals.

References

1 H. Dadkhah, J.R. Dilworth, K. Fairman, D.L. Hughes, C.T. Kan, and R.L. Richards, J. Chem. Soc. Dalton Trans., (1985) 1523 and ref. therein.

2 F.A. Cotton and R.A. Walton, Multiple Bonds between Metal Atoms, Wiley, New York, 1982.

3 M. Cowie and S.K. Dwight, Inorg. Chem., 19 (1980) 209 and 2500.