Journal of Organometallic Chemistry, 113 (1976) C49—C52

Preliminary communication

UNSATURATED MACROCYCLIC PHOSPHINE COMPLEXES OF RHODIUM(I)

RONALD MASON*, GEOFFREY SCOLLARY**, BRIAN MOYLE, (in part) KENNETH I. HARDCASTLE***,
School of Molecular Sciences, University of Sussex (Great Britain)
BERNARD L. SHAW and CHRISTOPHER J. MOULTON
School of Chemistry, University of Leeds (Great Britain)
(Received April 2nd, 1976)

Summary

The syntheses and structures of *trans*-[RhCl(CO){t-Bu$_2$P(CH$_2$)$_4$C≡C(CH$_2$)$_4$P-t-Bu$_2$}] and [RhCl{t-Bu$_2$PCH$_2$CH$_2$CH=CHCH$_2$CH$_2$P-t-Bu$_2$}] are reported.

Long flexible chains carrying donor atoms in α- and ω-positions prefer to bridge metal atoms in open chain structures rather than to form chelate complexes. We have shown, however, that long chain α,ω-diphosphines of the type t-Bu$_2$P(CH$_2$)$_n$P-t-Bu$_2$ (n = 9, 10 or 12) form mono-, di- and tri-nuclear macrocyclic complexes with platinum metals in which the phosphorus donor atoms are *trans*-bonded [1, 2]. The unusual behaviour of these diphosphines has been interpreted in terms of favourable internal entropy and conformational effects [3]. One recognizes that entropy and conformational effects also operate in the formation of macrocycles containing acetylenes [4]: for example, an ethynyl (alkynyl) group seems to prefer a gauche-position [4, 5] i.e. a carbon atom α to the triple bond would prefer to be in a "corner" position. The diphosphine, t-Bu$_2$P(CH$_2$)$_4$C≡C(CH$_2$)$_4$P-t-Bu$_2$, was therefore synthesised to study its behaviour as a *trans*-bonding chelating ligand. Treatment of 1,10-dichlorodec-5-yne [6] with sodium iodide and di-t-butylphosphine and subsequent reaction of the diphosphonium salt with sodium hydroxide provides the diphosphine which, on heating with dirhodium tetracarbonyl dichloride in benzene, gives the mononuclear complex *trans*-[RhCl(CO){t-Bu$_2$P(CH$_2$)$_4$C≡C(CH$_2$)$_4$P-t-Bu$_2$}] in 85% yield. The reaction of the diphosphine, t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$, with dirhodium tetracarbonyl dichloride gives a mixture of products including a 25% yield of the mononuclear complex *trans*-[RhCl(CO){t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$}].

---

*To whom correspondence should be addressed.
**Permanent address: Melbourne State College, Melbourne, Australia.
***Permanent address: Department of Chemistry, California State University, Northridge, California 91324.

trans-[RhCl(CO){t-$Bu_2P(CH_2)_4C{\equiv}C(CH_2)_4P$-t-$Bu_2$}] was characterised by microanalytical methods and by IR and NMR spectroscopy. The ^{31}P NMR spectrum showed that two conformers of the complex exist in solution as a result of the restricted rotation about the rhodium—phosphorus bonds and the carbonyl or chloro ligands being gauche with respect to the four t-butyl substituent groups [2]. Crystals of the complex (from benzene) are orthorhombic with a = 21.991(2), b = 11.915(1), c = 11.890(1); space group $Pna2_1$; Z = 4. Integrated diffraction intensities of 1763 independent reflexions (Mo-K_α, automatic diffractometer, $I_{obs} > 3\sigma(I_{obs})$) provided for a straightforward structure determination and full matrix least squares refinement of atomic coordinates and anisotropic (Rh, P) and isotropic (C, O) thermal parameters has converged to R 0.097; as in our earlier work, there is configurational disorder of the carbonyl and chloro ligands and an inadequate model for this largely accounts for the relatively high unweighted discrepancy index.

There are many similarities between the stereochemical features of the present complex (Fig. 1) and those of [IrCl(CO){t-$Bu_2P(CH_2)_{10}P$-t-Bu_2}] (Table 1) but the conformation of the unsaturated chelate is better defined due to the absence

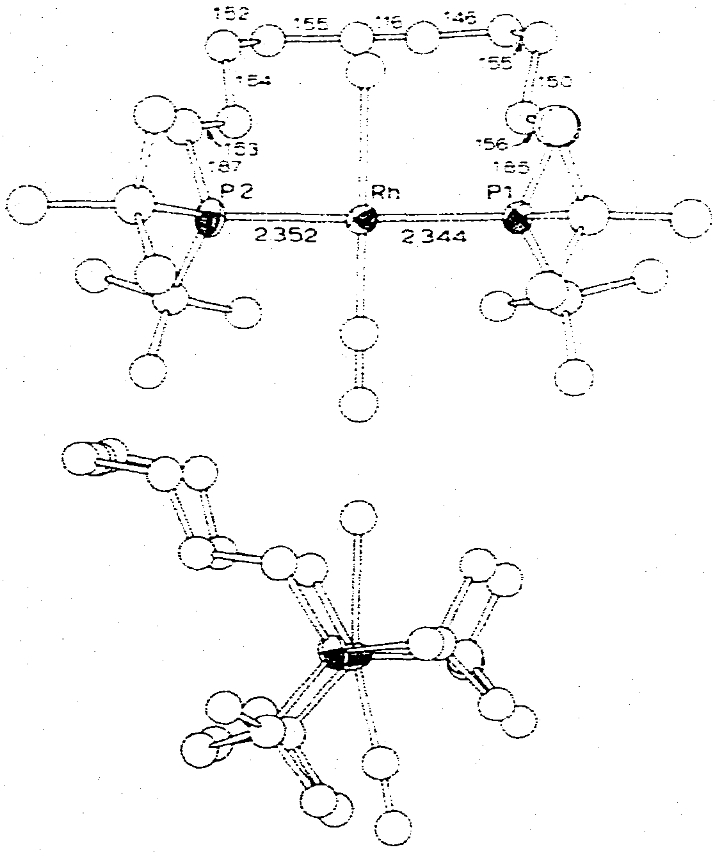

Fig. 1. The general stereochemistry and important bond lengths in *trans*-[RhCl(CO){t-$Bu_2P(CH_2)_4C{\equiv}C$-$(CH_2)_4P$-t-Bu_2}] and the molecular conformation as shown by viewing along the phosphorus—phosphorus bond. Standard deviations in the bond lengths average 0.004 Å (M—P), 0.01 Å (P—C) and 0.02 Å (C—C).

TABLE 1

TORSION ANGLES^a (degrees) IN [RhCl(CO){t-Bu$_2$P(CH$_2$)$_4$C≡C(CH$_2$)$_4$P-t-Bu$_2$}]

A	−58	*A*′	57
B	163	*B*′	−168
C	180	*C*′	180
D	67	*D*′	−69
E	54^b	*E*′	157^b

^{a}Torsion angles *A*····*A*′ refer to the sequence $\mathrm{Rh{-}P(1)\overset{A}{-}C(1)\overset{B}{-}C(2)-\cdots\cdots-C(9)\overset{B'}{-}C(10)\overset{A'}{-}P(2)-Rh}$.
^{b}Bonds adjacent to acetylene group.

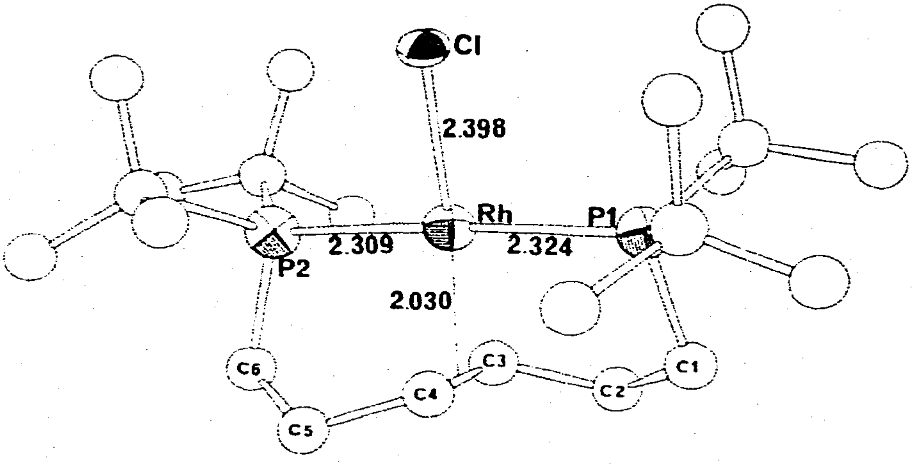

Fig. 2. The geometry of [RhCl{t-Bu$_2$PCH$_2$CH$_2$CH=CHCH$_2$CH$_2$P-t-Bu$_2$}]. Standard deviations in the metal—phosphorus and metal—chlorine bond lengths are 0.004 and 0.01$_2$ Å for the metal—carbon bond.

of intra-ring disorder. With the distance of the metal from the centre of the acetylenic function being 5.25 Å, there is clearly no need to invoke any bonding interactions. Unsaturated fragments of a macrocycle can only react to the electronic needs of the metal when the ring size is contracted. Thus a simple structural model shows that a shorter chain diphosphine such as t-Bu$_2$P(CH$_2$)$_6$P-t-Bu$_2$ cannot span *trans*-coordination positions and would give di- or poly-nuclear species unless the metal ion modifies the polymethylene chain. When a refluxing ethanol or 2-propanol solution of rhodium trichloride was treated with t-Bu$_2$P-(CH$_2$)$_6$P-t-Bu$_2$ (1.5—2.0 mol per rhodium atom), the mononuclear complex [RhCl{t-Bu$_2$PCH$_2$CH$_2$CH=CHCH$_2$CH$_2$P-t-Bu$_2$}] was formed in 50% yield and sublimes in vacuo to give large needles suitable for X-ray diffraction. The crystals are monoclinic with *a* 20.783(12), *b* 8.580(4), *c* 14.799(9) Å, and *β* 100.70(2)°; space group $P2_1/c$, $Z = 4$. Structure determination and refinement were essentially as before (1417 independent reflexion intensities; *R* 0.071) and the molecular stereochemistry is depicted in Fig. 2.

The structure corresponds to a *transoid* arrangement around the coordinated alkene fragment but in solution (CDCl$_3$ or C$_6$D$_5$) ^{31}P NMR spectroscopy shows that a minor component (ca. 8%) is present which we take to correspond to a *cisoid* arrangement, in both isomers the phosphorus spectrum is a doublet with ^{1}J(Rh—P) 127 Hz. The metal—carbon bond lengths average 2.15(1) Å, are very similar to those in other, more simple, rhodium-ethylene complexes [7], and we can reasonably deduce that ring strain effects are small. The general ring conformation provides for the carbon—carbon (olefin) vector to be oriented at 76° with respect to the phosphorus—phosphorus vector although, as expected, the plane containing the olefin fragment is orthogonal to that containing the rhodium, phosphorus and chlorine atoms; the alkyne fragment, by contrast, has its carbon—carbon vector oriented within one degree of that of the phosphorus—phosphorus vector.

The mean Rh^{I}—P bond lengths in the thirteen- and nine-membered rings are significantly different at 2.348(3) and 2.316(3) Å respectively; the equivalent P—Rh—P bond angles are 171.6° and 176.0° with the latter reflecting the olefin fragment moving into the coordination sphere. The Rh—P bond length of 2.365 Å in the 26-atom chelate ring complex $[RhCl(CO)\text{-t-}Bu_2P(CH_2)_{10}P\text{-t-}Bu_2]_2$ [2] establishes the limits in metal—phosphorus bond lengths, due to steric effects in the varying chelate rings and the *cis*-influences of the remaining ligands, as 0.05 Å; given our early observations and comments [8] on the stereochemistries of $(Ph_3P)_3RhCl$ and $(Ph_3P)_2(C_2F_4)RhCl$, the variations in the metal—phosphorus bonds seem best associated with intra-annular strain phenomena.

We are grateful to the Science Research Council for support of these studies. G.S. and K.I.H. thank Melbourne State College and California State University, Northridge for study leave.

References

1 A.J. Pryde, B.L. Shaw and B. Weeks, Chem. Commun., (1973) 947.
2 F.C. March, R. Mason, K.M. Thomas and B.L. Shaw, Chem. Commun., (1975) 584.
3 B.L. Shaw, J. Amer. Chem. Soc., 97 (1975) 3856.
4 J. Dale, A.J. Hubert and G.S.D. King, J. Chem. Soc., (1963) 73.
5 N. Sheppard, Advan. Spectrosc., (1959) 288.
6 B.W. Baker, R.W. Kierstead, R.P. Linstead and B.C.L. Weedon, J. Chem. Soc., (1954) 1804.
7 R. Mason and D.M.P. Mingos in J.M. Robertson (Ed.), Int. Rev. of Sci. Chem. Cryst. Phys. Chem. Series 2, Butterworths, 1975, p. 121 (and ref. therein).
8 P.B. Hitchcock, M. McPartlin and R. Mason, Chem. Commun., (1969) 1367.