Structural Chemistries and X-Ray Crystal Structures of Some Macrocyclic Tertiary Phosphine Complexes of d^8 Metal Ions: $[\mathrm{IrCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]$, $[\mathrm{PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}}]$, and $[\mathrm{RhCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]_2$

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Summary The structural characterizations of $[\mathrm{IrCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]$, $[\mathrm{PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}}]$, and $[\mathrm{RhCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]_2$ are summarized with emphasis on the observed conformations of the macrocycles and preferred stereochemistries at the metals.

The synthesis[1] of large ring co-ordination complexes with *trans*-bonding tertiary phosphine ligands offers the opportunity of examining the chelate effect in relation to ring size and of providing previously inaccessible conformational parameters of medium and large heterocyclic rings. The remarkable effect of di-t-butyl substituents in promoting large chelate ring formation has been interpreted in terms of a favourable conformational effect and internal entropy changes.[2] We report here the main structural features of three of these large-ring chelate compounds, two mononuclear species with 13- and 15-atom rings and a binuclear species with a 26-atom ring.

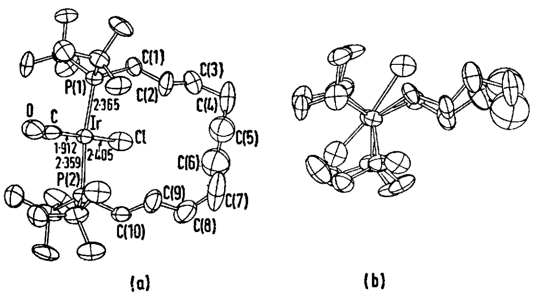

Figure 1. Structure of $[\mathrm{IrCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]$. (a) Perpendicular to the 13-atom ring; (b) looking along the P–P vector.

$[\mathrm{IrCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]$ crystallizes in the orthorhombic space group *Pbca* the unit cell dimensions being $a = 12{\cdot}370(2)$, $b = 34{\cdot}154(4)$, $c = 15{\cdot}272(2)$ Å; $Z = 8$ (the corresponding rhodium complex is strictly isomorphous). The diffraction analysis has been based on 2040 independent reflections [Mo-K_α automatic diffractometry; $I_{\mathrm{obs}} \geqslant 3\sigma\ (I_{\mathrm{obs}})$] with least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms, except for those of atoms C(5) and C(6) which are disordered and whose positions were estimated from difference electron density syntheses, somewhat constraining the positions to provide acceptable bond lengths and bond angles. The unweighted converged discrepancy index, R, is 0·043. The molecular structure is represented in Figure 1, average e.s.d.'s in the bond lengths being 0·003 (Ir–P and Ir–Cl) and 0·009 Å (Ir–C); the latter is misleadingly low in view of some conformational disorder (*vide infra*).

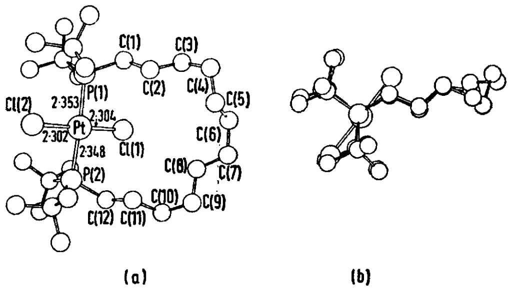

Figure 2. Structure of $[\mathrm{PtCl_2\{Bu_2P(CH_2)_{12}PBu^t_2\}}]$. (a) Perpendicular to the 15-atom ring; (b) looking along the P–P vector.

$[\mathrm{PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}}]$ crystallizes in the monoclinic system, space group $I2/a$ with $a = 25{\cdot}639(3)$, $b = 16{\cdot}836(2)$, $c = 16{\cdot}285(2)$ Å, $\beta = 92{\cdot}99(1)°$, $Z = 8$. The data collection routine and refinement analysis were identical to those for the iridium complex, the converged discrepancy index, R,

Table

Torsion angles[a] (degrees) in macrocyclic tertiary phosphine complexes

Angle	$[\mathrm{IrCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]$	$[\mathrm{PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}}]$	$[\mathrm{RhCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}}]_2$
A	−59	−61	−60
B	160	170	169
C	177	174	176
D	40[b]	63	75
E	79[b]	78	176
F	172[b]	190	183
G	—	81	—
F′	—	190	—
E′	140[b]	190	183
D′	−94[b]	−68	−101
C′	168	158	166
B′	−167	−170	−205
A′	56	58	59

[a] Torsion angles A ··· A′ refer to the sequence: $\mathrm{M} \text{———} \mathrm{P(1)} \overset{A}{\text{———}} \mathrm{C(1)} \overset{B}{\text{———}} \mathrm{C(2)} \text{———} \cdots\cdots \mathrm{C(2')} \overset{B'}{\text{———}} \mathrm{C(1')} \overset{A'}{\text{———}} \mathrm{P(2)} \text{———} \mathrm{M}$.

[b] Atoms defining these angles have not been subject to least squares refinement.

being 0·064 for 3303 observed reflections with all non-hydrogen atoms having refined isotropic Debye factors only. The essential geometry is shown in Figure 2, the e.s.d.'s in the metal–ligand bond lengths being 0·005 Å.

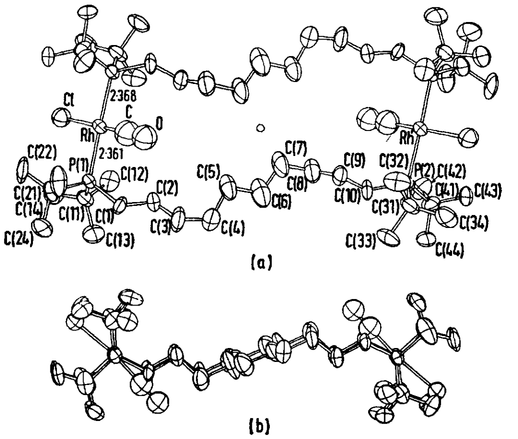

FIGURE 3. Structure of $[\mathrm{RhCl(CO)}\{\mathrm{Bu_2P(CH_2)_{10}PBu_2}\}]_2$. (a) Perpendicular to the 26-atom ring; (b) looking along the P–P vector.

The binuclear complex $[\mathrm{RhCl(CO)}\{\mathrm{Bu^t_2P(CH_2)_{10}PBu^t_2}\}]_2$ forms monoclinic crystals, space group $P2_1/c$, with $a = 8{\cdot}474(1)$, $b = 32{\cdot}651(4)$, $c = 12{\cdot}307(2)$ Å and $\beta = 112{\cdot}35(2)°$; $Z = 2$ and the molecule has precise $\bar{1}$ (C_i) symmetry in the crystal. 2071 reflections were assessed as being of significant intensity [Mo-K_α diffractometry; $I_{\mathrm{obs}} \geqslant 3\sigma(I_{\mathrm{obs}})$] and, apart from chlorine–carbon monoxide ligand disorder, the diffraction analysis was straightforward with convergence to $R_1 = 0{\cdot}079$. Nominal e.s.d.'s in the metal–ligand bond lengths (Figure 3) are 0·005 (Rh–Cl and Rh–P) and 0·01 Å (Rh–C).

The structures are identical in that either a chlorine or carbonyl ligand is *gauche* with respect to the sets of four t-butyl groups on *trans*-phosphorus atoms.[3] The four t-butyl groups are not symmetrically placed with respect to the co-ordination 'plane', the asymmetry being determined by interactions of the carbonyl- or chloro-ligands with the ring methylene hydrogen atoms. In the 26-atom ring dirhodium complex and in the 15-atom ring platinum complex, the t-butyl groups are quite accurately eclipsed but they are slightly rotated with respect to one another in the 13-atom ring complex. The carbonyl group is *gauche* with respect to the t-butyl groups in the iridium complex but there is some evidence, largely the poor refinement of the carbonyl ligand dimensions, of a small degree of carbonyl–chlorine disorder. In the binuclear dirhodium complex, adequate convergence of the *X*-ray data provides for a 60 : 40 distribution of isomers (rotamers) with the chloro-*gauche* form being predominant.

Most of the torsion angles (Table) are close to the 'normal' values of 180° or 60° but others demonstrate some degree of ring strain. In the 26-membered macrocycle, carbon atoms C(3)—C(8) are coplanar ($\pm$ 0·05 Å) and, because of the molecular symmetry, parallel to the plane containing C(3′)—C(8′); the planes are separated by a perpendicular distance of 0·52 Å. These central methylene fragments pack in a fashion which is reminiscent of the situation in linear alkanes and long-chain fatty acids. The unfavourable torsion angle of 101° around the bond C(8)—C(9) for the binuclear species is probably a consequence of the transannular van der Waals' interaction between the C(3)—C(8) and C(3′)—C(8′) methylene hydrogens.

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[1] A. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Chem. Comm.*, **1973**, 947.

[2] B. L. Shaw, *J. Amer. Chem. Soc.*, accepted for publication.

[3] The analogous palladium complex $[\mathrm{PdCl^t_2}\{\mathrm{Bu^t_2P(CH_2)_{10}PBu^t_2}\}]_2$ has $a = 8{\cdot}470(2)$, $b = 32{\cdot}428(7)$, $c = 12{\cdot}259(4)$ Å, $\beta = 112{\cdot}18(2)$, $Z = 2$. The analysis was hampered by decomposition of the crystals, but the structure has been shown to be very similar to this binuclear rhodium complex (M. C. Norton and W. S. McDonald, personal communication).