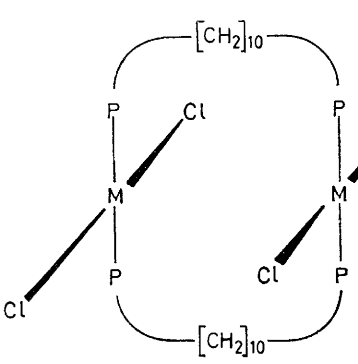
Large Ring Compounds Involving *trans*-Bonding Bidentate Ligands

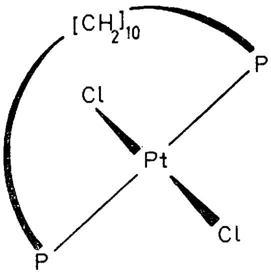
By ANTHONY J. PRYDE, BERNARD L. SHAW,* and BRIAN WEEKS
(*School of Chemistry, The University, Leeds* LS2 9JT)

Summary Large ring mononuclear compounds of platinum and iridium involving the *trans*-co-ordinating ligands $Bu^t_2P[CH_2]_xPBu^t_2$ (x = 9 or 10), and large ring binuclear complexes are described; it is suggested that mononuclear bidentate complexes with a large ring might be more stable than those with an intermediate size ring.

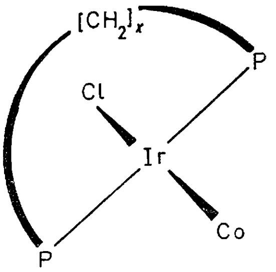
The effect of ring size on the stability of metal chelates has been much investigated and large chelate rings from flexible ligands are thought not to exist.[1] We now find that treatment of $[\mathrm{PtCl_2(PhCN)_2}]$ with $\mathrm{Bu^t_2P(CH_2)_{10}PBu^t_2}$† gives two crystalline isomers $[\mathrm{PtCl_2\{Bu^t_2P[CH_2]_{10}PBu^t_2\}}]_x$. The less soluble (21—32% yield) is binuclear (*M* osmometrically in $\mathrm{CHCl_3}$ = 1450, calc. 1393). It shows a well defined 1:2:1 t-butyl ^{1}H n.m.r. pattern, indicating *trans*-phosphorus nuclei[2] and has a very simple i.r. absorption spectrum (500—220 cm^{-1}), consisting of one very strong peak at 334 cm^{-1}, characteristic of a linear Cl–Pt–Cl system. Probably this compound has structure (**1**) with a 26-membered ring. The second and more soluble isomer is volatile, subliming slowly at 180—195° without decomposition into yellow prisms (yields 28—43%). This complex again shows a 1:2:1 triplet t-butyl ^{1}H n.m.r. pattern and one i.r. absorption band due to ν(Pt–Cl) (326vs cm^{-1}) and it is mononuclear in chloroform (*M* found = 678, 703, calc. 697). Moreover, it gives a mass spectrum with a well defined set of peaks for the parent ion in the expected intensity ratios; the most intense peak is at *m/e* 696, also as expected. This volatile complex clearly has structure (**2**) with the *trans*-coordinating ligand forming a 13-atom ring with the metal. We have also made volatile complexes of the type $[\mathrm{IrCl(CO)\{Bu^t_2P[CH_2]_{\mathit{x}}PBu^t_2\}}]$ which very probably have structure (**3**) (x = 9 or 10), by adding the biphosphine ligand to a solution formed by treating chloroiridic acid with carbon monoxide in boiling ethanol.[3] Other complexes which are probably binuclear and have large rings are also formed in this treatment. Some of the complexes are being investigated by *X*-ray diffraction.



(1)



(2)



(3)

The stability associated with chelation has long been regarded as an entropy or probability effect.[4] However, ring strain is likely to be less in large rings (12- or 13-atom) than in rings of intermediate size (*ca.* 8-membered), as in cycloalkanes,[5] and we suggest that large rings from flexible bidentate ligands might be generally more stable than rings of intermediate size. We have treated $[\mathrm{PtCl_2(PhCN)_2}]$ with $\mathrm{Bu^t_2P[CH_2]_5PBu^t_2}$ and, although we have not separated the product mixture into all its components we could find no evidence for a mononuclear species.

It has been reported that the diphosphine ligand spans *trans*-positions in $[\mathrm{NiCl_2\{(C_6H_{11})_2P[CH_2]_5P(C_6H_{11})_2\}}]$;[6] however, in order to accommodate reasonable bond angles and bond lengths the P–Ni–P angle in this complex must deviate considerably from 180°. An investigation of this compound by *X*-ray diffraction would be of great interest.

The bulky t-butyl groups on our ligands will hinder the phosphorus donor atoms from taking up mutual *cis*-positions but will not prevent them from taking up mutual *trans*-positions. We have also treated $[\mathrm{PtCl_2(PhCN)_2}]$ with $\mathrm{Ph_2P(CH_2)_{10}PPh_2}$ but obtain a mixture which we have not yet separated; it possibly contains *trans*-bonding bidentate, chelate, and polynuclear complexes.

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† Made by treating $\mathrm{PHBu^t_2}$ with $\mathrm{Br[CH_2]_{10}Br}$ and subsequent treatment of the product with sodium hydroxide.

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