Large-ring Complexes Formed from Diacetylene Diphosphines of the Type $\mathrm{Bu^t{}_2PC{\equiv}C[CH_2]_nC{\equiv}CPBu^t{}_2}$ ($n = 4$ or 5); *X*-Ray Structure of $\mathrm{[IrCl(CO)\{Bu^t{}_2PC{\equiv}C[CH_2]_5C{\equiv}CPBu^t{}_2\}]}$

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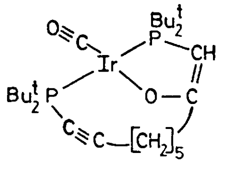
Summary Diacetylene diphosphines of the type $\mathrm{Bu^t{}_2PC{\equiv}C[CH_2]_nC{\equiv}CPBu^t{}_2}$ ($n = 4$ or 5) give, with iridium halogeno-carbonyls, large-ring mono- or bi-nuclear species and the *X*-ray structure of *trans*-$\mathrm{[IrCl(CO)\{Bu^t{}_2PC{\equiv}C[CH_2]_5C{\equiv}CPBu^t{}_2\}]}$ is reported; with platinum or palladium halides very large-ring polynuclear species are formed, *e.g.* a 72-atom ring in $\mathrm{[PtCl_2\{Bu^t{}_2PC{\equiv}C[CH_2]_5C{\equiv}CPBu^t{}_2\}]_6}$.

We have shown that long-chain diphosphines of the type $\mathrm{Bu^t{}_2P[CH_2]_nPBu^t{}_2}$ ($n = 9$, 10, or 12) give large chelate rings (12- to 45-membered) with some platinum metal chlorides.[1] The stability of these large rings relative to open-chain structures has been explained in terms of favourable conformational and entropy effects.[2] It is now well established that acetylenic groups promote the formation of large rings; for example good yields of cyclic non-conjugated diynes and tetraynes have been prepared from $\alpha\omega$-diynes and $\alpha\omega$-dibromoalkanes without using dilution techniques,[3] and $\alpha\omega$-diynes couple (dioxygen and copper) to give large-ring poly-ynes.[4] The effect of acetylenic groupings in promoting large ring formation has also been explained in terms of conformational and entropy effects and one could expect therefore that diacetylenic diphosphines of the type $\mathrm{Bu^t{}_2PC{\vdots}C[CH_2]_nC{:}CPBu^t{}_2}$ would form large chelate rings with metals. This chemistry is now described.



(I)

The diphosphines were prepared by treating $\mathrm{LiC{\equiv}C[CH_2]_nC{\equiv}CLi}$ ($n = 4$ or 5) with $\mathrm{Bu^t{}_2PCl}$. Addition of $\mathrm{Bu^t{}_2PC{\equiv}C[CH_2]_5C{\equiv}CPBu^t{}_2}$ (L) to a solution formed by treating sodium chloroiridate with carbon monoxide in boiling ethanol gave the mononuclear hydriocarbonyl complex $\mathrm{[IrHCl_2(CO)L]}$. This, when treated with triethylamine in ethanol, gave the mononuclear *trans*-$\mathrm{[IrCl(CO)L]}$. Crystals suitable for an *X*-ray analysis were grown from ethanol and are orthorhombic with $a = 15{\cdot}297(6)$, $b = 30{\cdot}72(1)$, $c = 12{\cdot}309(4)$ Å; $Z = 8$; space group *Pbca*; 3085 independent reflections [Mo-K_α four-circle diffractometry: $2\theta \leqslant 52°$; $I_{\mathrm{obs}} > 3\sigma(I_{\mathrm{obs}})$; intensities corrected for Lorentz and polarisation effects and for absorption] formed the basis of the *X*-ray structure analysis. The positional parameters of all the non-hydrogen atoms were determined by Patterson and difference Fourier synthesis and refined with the anisotropic thermal parameters by full-matrix least-squares methods. Atom C(6) in the macrocyclic ring is disordered, and was allowed fractional occupancy in two alternative positions; occupancies were determined as 0·7-[C(6A)] and 0·3[C(6B)] from a terminal difference synthesis. The positions of hydrogen atoms were found from a difference synthesis and their contributions were included in the structure factor calculations but their positions were not refined. Refinement converged to $R = 0{\cdot}026$ (weighted $R = 0{\cdot}026$). The molecular structure is shown in the Figure.†

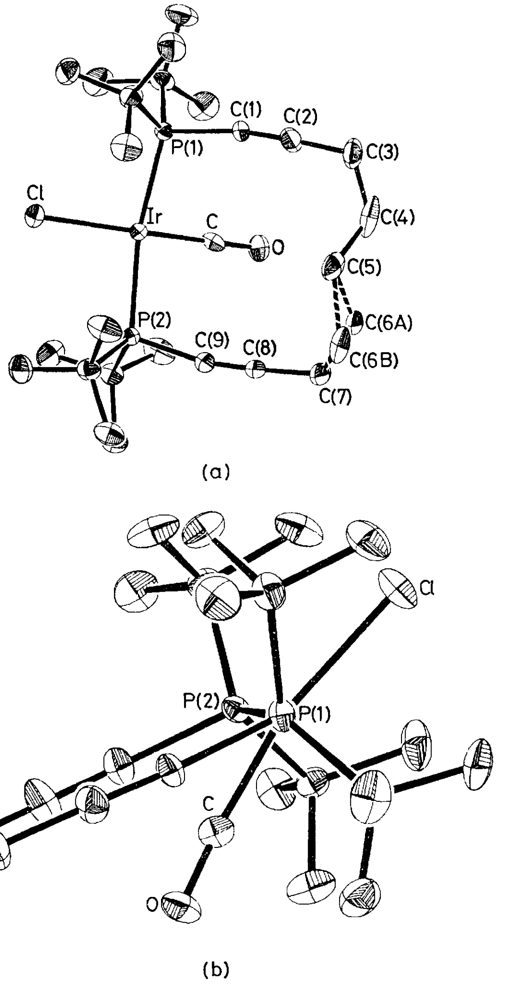


FIGURE. Structure of $[\text{IrCl(CO)}\{\text{Bu}^t_2\text{PC}{\equiv}\text{C}[\text{CH}_2]_5\text{C}{\equiv}\text{CPBu}^t_2\}]$ (a) perpendicular to the 12-atom ring; (b) looking *exactly* along the P(1)–iridium vector [partial atom C(6B) has been omitted for clarity and the iridium atom is hidden behind P(1)]. Some important bond lengths and bond angles are Ir–Cl, 2·366(2); Ir–P(1), 2·332(2); Ir–P(2), 2·337(2); Ir–C, 1·808(7); C–O, 1·140(8) Å; Cl–Ir–C, 167·6(2)°; P(1)–Ir–P(2), 164·15(6)°; Ir–C–O, 175·1(7)°.

The *X*-ray and ^{31}P n.m.r. data for *trans*-$[\text{IrCl(CO)}\{\text{Bu}^t_2\text{P}[\text{CH}_2]_{10}\text{PBu}^t_2\}]$ show the presence of two rotamers, one with the CO in the *gauche* position with respect to the four t-butyl groups and the other with the Cl *gauche* to the t-butyl groups. In contrast only one rotamer can be detected in the ^{31}P n.m.r. spectrum of [IrCl(CO)L]; this is presumably the rotamer with the Cl *gauche* to the t-butyl group and is presumably stabilized by having adjacent C≡O and C≡C groups as in the Figure. Similarly we find that of the three possible rotamers of complexes of the type *trans*-$[\text{MCl(CO)}(\text{Bu}^t_2\text{PC}{\equiv}\text{CR})_2]$ one rotamer is much preferred and one is present in only very low abundance. Treatment of sodium bromoiridate with carbon monoxide followed by the diphosphine (L) gives only the binuclear species $[\text{IrHBr}_2(\text{CO})\text{L}]_2$; no mononuclear species could be detected. Treatment with triethylamine then gives the binuclear $[\text{IrBr(CO)L}]_2$ with a 24-membered ring. Presumably the bromide ligand is sufficiently large to prevent the diphosphine spanning *trans*-positions in the mononuclear complex. When [IrCl(CO)L] is heated with sodium isopropoxide in propan-2-ol for 16 h the extremely stable complex $[\overline{\text{IrCO}\}\text{Bu}^t_2\text{PCH}{=}\text{C(O)}}\overline{[\text{CH}_2]_5\text{C}{\equiv}\text{CPBu}^t_2}\}]$ (I) containing 11- and 5-membered chelate rings is formed (possibly traces of water are involved in this reaction). This formulation is based on microanalytical, molecular weight, and i.r., n.m.r. (^{31}P and ^{1}H), and mass spectral data.

The behaviour of the ligands $\text{Bu}^t_2\text{PC}{\equiv}\text{C}[\text{CH}_2]_n\text{C}{\equiv}\text{CPBu}^t_2$ towards platinum or palladium dichlorides is quite different from that towards iridium: no mononuclear or binuclear species could be detected. When a solution of $[\text{PtCl}_2(\text{Bu}^t\text{CN})_2]$ in toluene was refluxed for several hours with 1 mol. equiv. of $\text{Bu}^t_2\text{PC}{\equiv}\text{C}[\text{CH}_2]_5\text{C}{\equiv}\text{CPBu}^t_2$, the toluene then evaporated off to low bulk, and the residue treated with methanol, a cream microcrystalline solid formed. Microanalysis and i.r., and ^{1}H-, ^{13}C-, and ^{31}P-n.m.r. spectroscopy showed the expected formulation $[\text{PtCl}_2\{\text{Bu}^t_2\text{PC}{\equiv}\text{C}[\text{CH}_2]_5\text{C}{\equiv}\text{CPBu}^t_2\}]_x$ with *trans*-phosphorus donors and *trans*-chlorines. However, molecular weight measurements (osmometrically in benzene or chloroform) showed a hexameric species, *i.e.* $x = 6$. This result was sufficiently surprising to cause us to repeat the preparation several times using concentrations of starting materials from 0·07 to 0·20M in toluene. In all cases a hexameric species was isolated in high yield (> 90%). The molecule is fluxional: at or below 300 K the ^{31}P n.m.r. spectrum shows the presence of approximately equal amounts of two conformers (rotamers) with δ 26·0 [^1J(PtP) 2601 Hz] and 33·0 p.p.m. (relative to H_3PO_4) [^1J(PtP) 2592 Hz]. On heating, these resonances broaden and coalesce reversibly; at 350 K a single sharp central peak with two satellites is observed at δ 31·9 [^1J(PtP) = 2622 Hz]. We suggest that the hexameric species has a 72-membered ring. This seems more likely than, say, a catenane with two interlocking 36-membered rings (although we have no evidence against such a formulation). Treatment of $[\text{PdCl}_2(\text{PhCN})_2]$ with $\text{Bu}^t_2\text{PC}{\equiv}\text{C}[\text{CH}_2]_5\text{C}{\equiv}\text{CPBu}^t_2$ in toluene gave what appears to be a heptameric species *trans*-$[\text{PdCl}_2\{\text{Bu}^t_2\text{PC}{\equiv}\text{C}[\text{CH}_2]_5\text{C}{\equiv}\text{CPBu}^t_2]_7$ (80%). $[\text{PdBr}_2(\text{PhCN})_2]$ gave a similar heptameric species. We suggest that chlorocarbonyliridium behaves differently from platinum or palladium chlorides because a nonvalence interaction between the carbonyl group and the acetylene holds the chain in a particular conformation which

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

promotes the formation of a monomeric species (or binuclear species in the case of the bromide).

We thank the S.R.C. for support, Johnson Matthey Ltd., for the generous loan of chemicals, and the University of Melbourne for a Travelling Scholarship (G.A.W.).

(*Received, 25th February* 1977; *Com.* 167.)

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