Journal of Organometallic Chemistry, 94 (1975) 251—257

THE REACTIVITY OF *trans*-$[IrCl(CO)L_2]$ (L = TERTIARY PHOSPHINE) AND RELATED COMPOUNDS*

BERNARD L. SHAW
School of Chemistry, The University, Leeds LS2 9JT (Great Britain)

Summary

An example of anchimeric assistance in an oxidative addition reaction is discussed. Stable large ring (12- to 45-membered) complexes have been prepared from diphosphines $t\text{-}Bu_2P(CH_2)_nP\text{-}t\text{-}Bu_2$ ($n = 9, 10$ or 12). Some unusual iridium chemistry, including an iridium(II) compound, has been generated from ligands such as di-t-butyl-2-methoxyphenylphosphine.

There have been many studies on oxidative addition reactions of compounds of the type *trans*-$[IrCl(CO)L_2]$ (L = tertiary phosphine or tertiary arsine) [1-3]:

$$[Ir^{I}Cl(CO)L_2] + A\text{—}B \rightarrow [Ir^{III}Cl(A)(B)(CO)L_2]$$

Three mechanisms for such an addition have been established.

(1) Nucleophilic attack by the metal

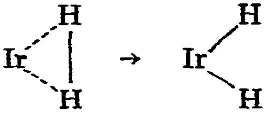
This is exemplified by the addition of methyl iodide. Kinetic studies [4] show that the addition involves a polar transition state:

$$Ir^{\delta+} \longrightarrow CH_3\text{—}I^{\delta-}$$

with a large negative $\Delta S^{\ddagger}$. Addition is promoted by polar solvents.

(2) Concerted addition

The addition of dihydrogen is thought to be concerted. It involves a



much less polar transition state than in *1* and is less affected by changing the solvent.

---

* Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.

(3) Radical chain

Recently some oxidative addition reactions involving sterically hindered organic halides have been shown to involve free radicals [5]. They require an initiator such as dioxygen. An iridium(II) intermediate has been postulated:

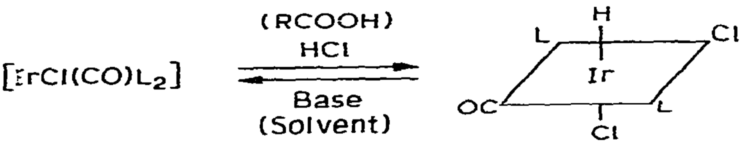
$Ir^{I} + Q\cdot \rightarrow Ir^{II}\text{—}Q$ (Q = initiator)

The tendency for *trans*-[IrCl(CO)L_2] to undergo oxidative addition depends on the electronic and steric effects of L but it is frequently very difficult to assess their relative importance. We have shown that the realtive tendencies of acids such as HCl, CH_3COOH or PhCOOH to add to [IrCl(CO)L_2] can be readily studied spectrophotometrically [6,7]. One can therefore arrange ligands, L, in order of decreasing stability of the adduct (Table 1). As can be seen there is an excellent correlation between this ligand order and values of ν(Ir—H) for the adducts. It is suggested that steric effects are more important than electronic effects in determining the above order and that these steric effects govern the strength of the bonding of the chlorine ligand *trans* to hydride, which in turn influences the value of ν(Ir—H).

Steric and electronic effects also control the rates of oxidative addition reactions. The electronic effect has been studied for the addition of methyl iodide to *trans*-[MCl(CO){P(4-$ZC_6H_4)_3\}_2$] (M = Ir or Rh). The steric effects of 4-substituted triphenylphosphines are assumed to be the same. The relative rates of CH_3I addition were (M = Ir) Z = OMe > Me > H > Cl [8]; (M = Rh) Z = OMe > H > F [9]; i.e. the rate is increased by electron donation in agreement with the metal acting as a nucleophile. However the effect is small e.g. for Ir the *tris*-(4-methoxyphenyl)phosphine complex reacts only about 10 times faster than the triphenylphosphine complex.

We have looked for and found another type of electronic effect in oxidative addition reactions. Since the addition of CH_3I to *trans*-[IrCl(CO)L_2] in-

TABLE 1



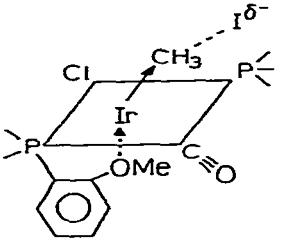
L		ν(Ir—H) (cm^{-1})
PMe_3	Decreasing stability of adduct Increasing acidity of H	2169
PMe_2Ph		2191
PMe_2-t-Bu		2208
$PMePh_2$		2217
PEt_2-t-Bu		2227
PPh_3		2237
P-n-Pr_2-t-Bu		2242
P-n-Bu_2-t-Bu		2244
PMe-t-Bu_2		2254
PEt-t-Bu_2		2300
PPh-t-Bu_2		2300

TABLE 2

RATE DATA FOR THE ADDITION OF CH_3I TO *trans*-$[IrCl(CO)L_2]$ IN TOLUENE AT 298.3 K

L	10^2k (l mol^{-1}s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1}mol^{-1})
PMe_2Ph	4.7 ± 0.15	46.4 ± 0.8	—114 ± 3
$PMe_2(2\text{-}MeOC_6H_4)$	530 ± 25	27.6 ± 0.8	—133 ± 3
$PMe_2(4\text{-}MeOC_6H_4)$	6.75 ± 0.2	38.1 ± 7.5	—138 ± 25

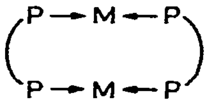
volves a polar transition state there is the possibility of neighbouring group participation (anchimeric assistance or intramolecular catalysis) at the rate determining step. We therefore studied the kinetics of addition of CH_3I to *trans*-$[IrCl(CO)L_2]$ with L = PMe_2Ph, dimethyl-2-methoxyphenyl- or dimethyl-4-methoxyphenyl-phosphine anticipating some anchimeric assistance by the 2-methoxyl group. The additions are first order in $[CH_3I]$ and in [complex] (Table 2 gives the rate data). The dimethyl-2-methoxyphenylphosphine complex reacts much (ca. 100 times) faster than the other two, the rate enhancement being due mainly to a very small enthalpy of activation (ca. 6 kcal). We interpret this rate enhancement as a direct MeO ··· Ir interaction in the transition state I [10]. Clearly such an effect (intramolecular catalysis) might be of use in increasing the rates of some of the important Pd—PPh_3 catalysed reactions developed by Heck and coworkers [13,14]. Thus by using say diphenyl-2-methoxyphenylphosphine instead of PPh_3 one might be able to use aryl or vinyl bromides or even chlorides instead of the more expensive iodides.



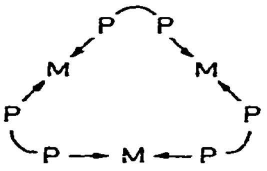
(I)

The second part of this paper is concerned with some large ring compounds formed from long chain diphosphines of the type t-$Bu_2P(CH_2)_nP$-t-Bu_2 (n = 9, 10 or 12). We have found that these diphosphines with bulky end groups give *trans*-bonding mononuclear (II), binuclear (III) and trinuclear (IV) complexes with from 12- to 45-membered rings. (M = metal atom) [11]. Thus on treating $IrCl_6^{3-}$.with carbon monoxide and then adding t-$Bu_2P(CH_2)_{10}P$-t-Bu_2 a mixture of iridium(I) carbonyl complexes *trans*-$[IrCl(CO)\{t\text{-}Bu_2P(CH_2)_{10}P\text{-}t\text{-}Bu_2\}]_x$ (x = 1 or 2) is formed. The mononuclear complex (13-atom ring) sublimes slowly (ca. 180°C/1 atm) into beautiful yellow needles. Its structure has been determined by X-ray diffraction (R. Mason and F.C. March) and is shown in Figs. 1 and 2. The carbonyl group lies in a *gauche* position with respect to the four t-butyl groups. The ^{31}P NMR spectrum at 25°C in deuteriochloroform shows two resonances probably due to the two rotamers with either CO or Cl in the

(II)



(III)



(IV)

gauche position with respect to the four t-butyl groups. Recently the X-ray structures of the two binuclear complexes have been determined, *trans*-[RhCl(CO){t-$Bu_2P(CH_2P(CH_2)_{10}P$-t-Bu_2}]$_2$ (R. Mason and F.C. March) and *trans*-[$PdCl_2${t-$Bu_2P(CH_2)_{10}P$-t-Bu_2}]$_2$ (W.S. McDonald and M.C. Norton); both have 26-membered rings. The structure of the palladium complex is shown in Fig. 3. Clearly these very large ring compounds, of which *trans*-[IrCl(CO){t-Bu_2P-$(CH_2)_{12}P$-t-Bu_2}]$_3$ with a 45-membered ring is the largest, should show some interesting conformational and chemical properties.

The last part of my paper is concerned with some unusual iridium chemistry generated from complexes with di(t-butylphosphine)phenoxide ligands. This is

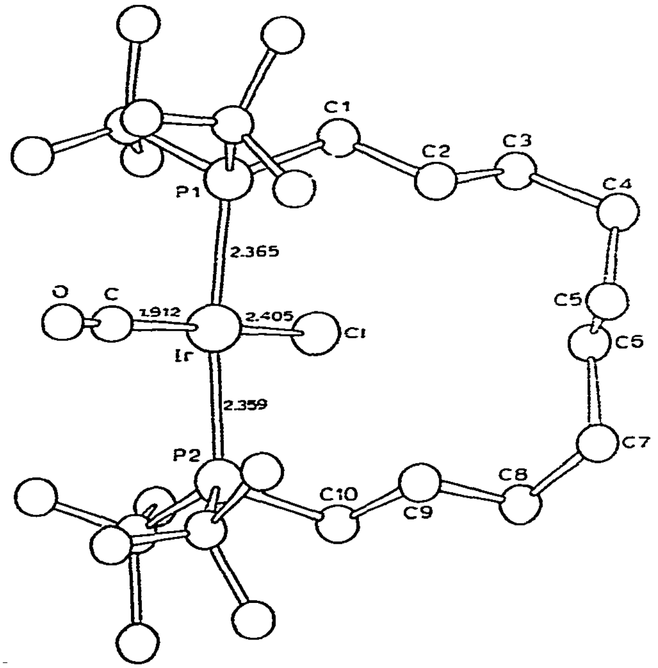


Fig. 1. The structure of *trans*-[IrCl(CO){t-$Bu_2P(CH_2)_{10}P$-t-Bu_2}] showing the 13-atom ring.

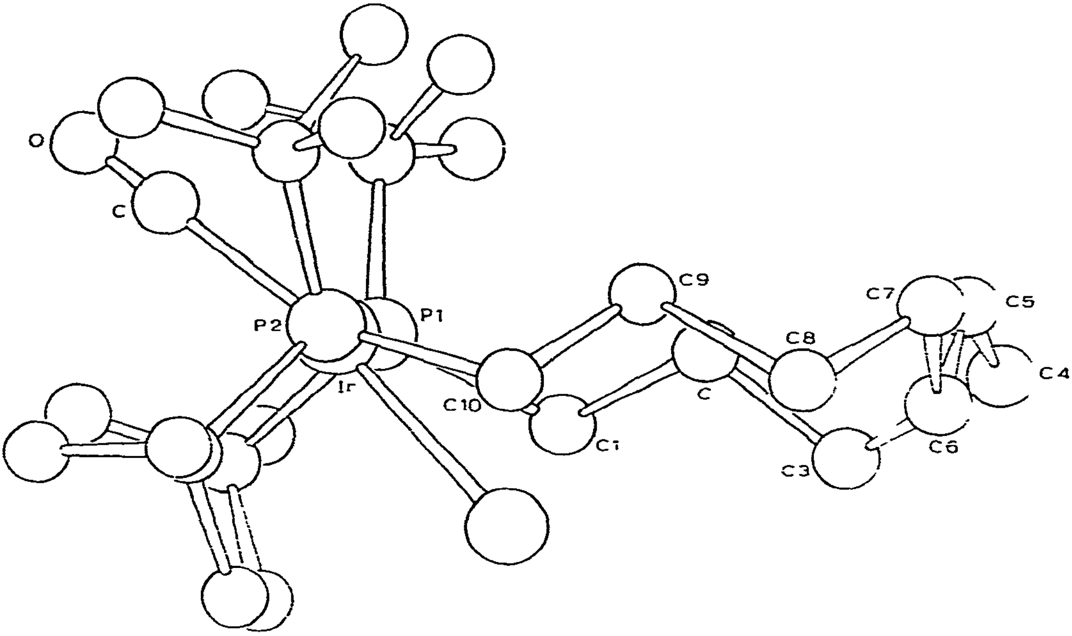


Fig. 2. *trans*-[IrCl(CO){t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$}]. View along the P—Ir—P bonding.

outlined in Scheme 1. When chloroiridic acid is treated with carbon monoxide and di-t-butyl (2-methoxyphenyl)phosphine in boiling 2-methoxyethanol, demethylation occurs and the yellow iridium(I) carbonyl species V is formed. A benzene solution of this compound is stable in the absence of air but in the presence of air it starts to go blood red on the surface and gives mainly the planar iridium(II) species VI together with the five-coordinate iridium(III) hydride VII, which is purple. This iridium(III) species is coordinatively unsaturated

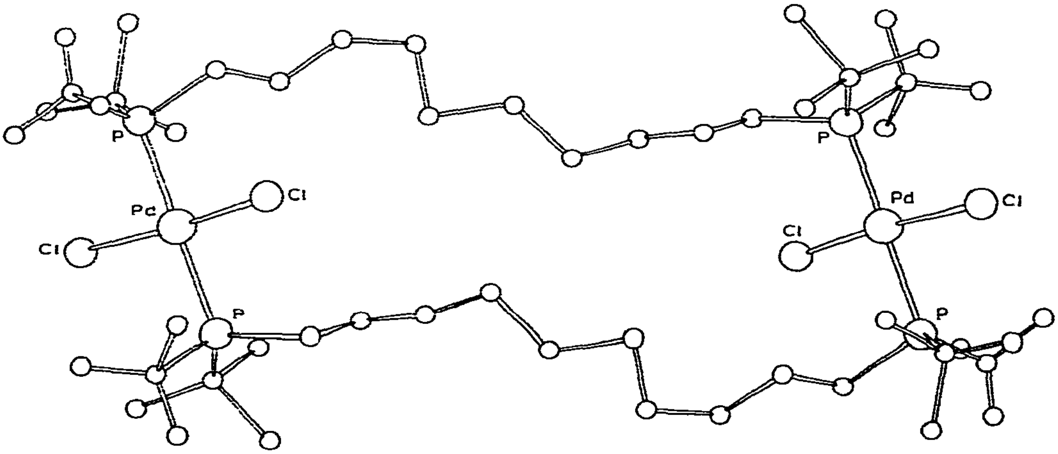
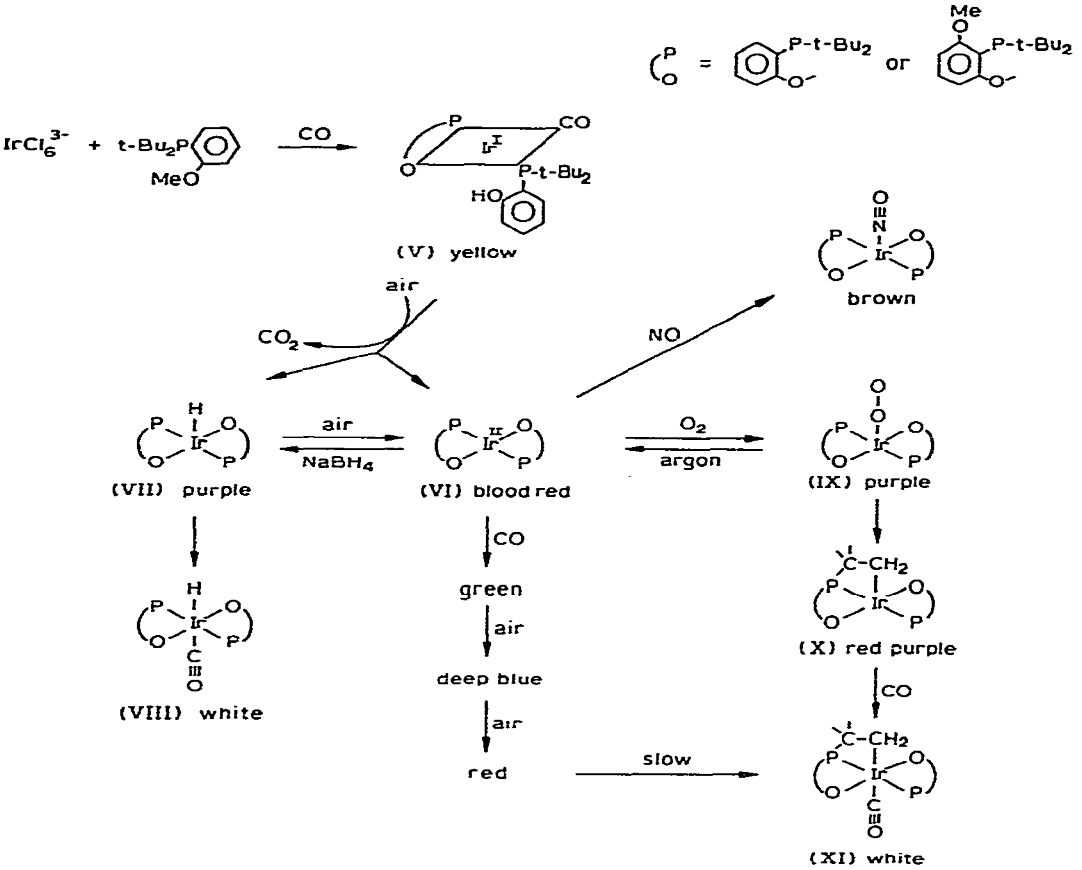


Fig. 3. The structure of *trans*-[PdCl$_2${t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$}]$_2$ showing the 26-atom ring.

SCHEME 1
SOME UNUSUAL IRIDIUM CHEMISTRY-COMPLEXES WITH 2-(DI-t-BUTYLPHOSPHINO)PHENOXIDE LIGANDS



and reacts with carbon monoxide rapidly to give the white 6-coordinate hydridocarbonyl VIII. The red paramagnetic iridium(II) species VI with P—O = di(t-butylphosphino)6-methoxyphenoxide takes up dioxygen reversibly to give the purple dioxygen adduct IX. This dioxygen adduct gradually changes to the red-purple compound X which has one of the t-butyl methyls metallated. The red-purple metallated compound X is coordinatively unsaturated and reacts with carbon monoxide to give the iridium(III) carbonyl XI. The iridium(II) species also reacts with carbon monoxide to give a green compound, this immediately goes deep blue in air and gradually red and then colourless, giving XI. Other reactions are also mentioned in Scheme 1. Both the iridium(II) complexes with P—O either di(t-butylphosphino)phenoxide or di(t-butylphosphino)6-methoxyphenoxide have had their structures proved by X-ray diffraction studies [12].

I am extremely grateful to my coworkers listed in the references and to the organisers of this excellent symposium. I also offer my best wishes to Professor Hieber.

References

1 J.P. Collman, Accounts Chem. Res., 1 (1968) 136.
2 L. Vaska, Accounts Chem. Res., 1 (1968) 335.
3 J. Halpern, Accounts Chem. Res., 3 (1968) 386.
4 P.B. Chock and J. Halpern, J. Amer. Chem. Soc., 88 (1966) 3511.
5 J.S. Bradley, D.E. Connor, D. Dolphin, J.A. Linger and J.A. Osborn, J. Amer. Chem. Soc., 94 (1972) 4043.
6 B.L. Shaw and R.E. Stainbank, J. Chem. Soc. Dalton, (1972) 223.
7 B.L. Shaw and R.E. Stainbank, J. Chem. Soc. A, (1971) 3716.
8 R. Ugo, A. Pasini, A. Fusi and S. Cenini, J. Amer. Chem. Soc., 94 (1972) 7364.
9 J.C. Douek and G. Wilkinson, J. Chem. Soc. A, (1969) 2604.
10 E.M. Miller and B.L. Shaw, J. Chem. Soc. Dalton, (1974) 480.
11 A.J. Pryde, B.L. Shaw and B. Weeks, Chem. Commun., (1973) 947.
12 R. Mason, K.M. Thomas, H.D. Empsall, S.R. Fletcher, P.N. Heys, E.M. Hyde, C.E. Jones and B.L. Shaw, Chem. Commun., (1974) 612.
13 A. Schoenberg, I. Bartoletti and R.F. Heck, J. Org. Chem., 23 (1974) 3318.
14 A. Schoenberg and R.F. Heck, J. Org. Chem., 23 (1974) 3327.