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TRIDENTATE CHELATE π-BONDED COMPLEXES OF RHODIUM(I), IRIDIUM(I), AND IRIDIUM(III) AND CHELATE σ-BONDED COMPLEXES OF NICKEL(II), PALLADIUM(II), AND PLATINUM(II) FORMED BY INTRAMOLECULAR HYDROGEN ABSTRACTION REACTIONS

M.A. BENNETT * and P.W. CLARK **

Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600 (Australia)

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Summary

2,2′-Bis(o-diphenylphosphino)bibenzyl, $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o$ (bdpbz), is dehydrogenated by various rhodium complexes to give the planar rhodium(I) complex $RhCl(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o)$, from which the ligand 2,2′-bis(o-diphenylphosphino)-*trans*-stilbene (bdpps) can be displaced by treatment with sodium cyanide. The stilbene forms stable chelate olefin complexes with planar rhodium(I) and iridium(I) and with octahedral iridium(III). On reaction with halide complexes of nickel(II), palladium(II) or platinum(II), the stilbene ligands $o\text{-}R_2PC_6H_4CH\overset{t}{=}CHC_6H_4PR_2\text{-}o$ (R = Ph or $o\text{-}CH_3C_6H_4$) lose a vinyl proton in the form of hydrogen chloride to give chelate, planar σ-vinyls of general formula $\overline{MX(o\text{-}R_2PC_6H_4C}{=}CHC_6H_4PR_2\text{-}o)$ (M = Ni, Pd, Pt; X = Cl, Br, I) of high thermal stability; analogous methyl derivatives $\overline{Pt(CH_3)(o\text{-}R_2PC_6H_4C}{=}CHC_6H_4PR_2\text{-}o)$ are obtained from $Pt(CH_3)_2(COD)$ (COD = 1,5-cyclooctadiene) and the stilbene ligands. The bibenzyl also forms chelate σ-benzyls $\overline{MX(o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o)$ (M = Pd, Pt; X = Cl, Br, I). The ^1H NMR spectra of the o-tolyl methyl groups in the compounds $\overline{MX(o\text{-}R_2PC_6H_4C}{=}CHC_6H_4PR_2\text{-}o)$ (M = Ni, Pd, Pt; R = $o\text{-}CH_3C_6H_4$) vary with temperature, probably as a consequence of interconversion of enantiomers arising from restricted rotation about the M—P and M—C bonds. Possible mechanisms for the dehydrogenation reactions are briefly discussed.

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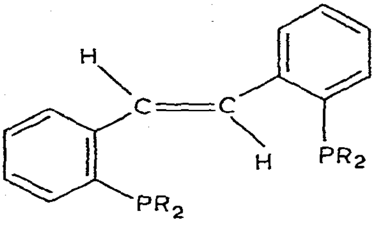
* Author to whom correspondence should be addressed.

** Present address: Department of Chemistry, University of Queensland, St. Lucia, Queensland 4067 (Australia).

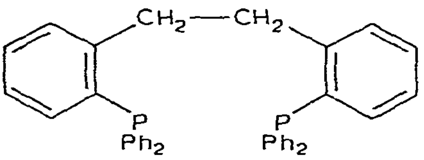
Introduction

Some years ago we found [1] that tri-*o*-tolylphosphine, (o-$CH_3C_6H_4)_3P$ [abbreviated to (o-tol)$_3$P], undergoes dehydrogenation and coupling in the presence of rhodium(III) chloride in refluxing 2-methoxyethanol to give a planar, chelate rhodium(I) complex $RhCl\{o(o\text{-tol})_2PC_6H_4CH\overset{t}{=}CHC_6H_4P(o\text{-tol})_2\text{-}o\}$. This complex contains a tridentate ligand 2,2′-bis(di-*o*-tolylphosphino)-*trans*-stilbene (bdtps) (I), which coordinates via the two phosphorus atoms and the olefinic double bond. We have also reported briefly [2] on the preparation and single crystal X-ray structure of the similar rhodium(I) complex $RhCl(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o)$, which contains 2,2′-bis(diphenylphosphino)-*trans*-stilbene (bdpps) (II). This complex was obtained by dehydrogenation of 2,2′-bis(diphenylphosphino)bibenzyl, (bdpbz) $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4\text{-}PPh_2\text{-}o$ (III), promoted by rhodium complexes. As a result of the tendency of the phosphorus atoms of these ligands to adopt a mutually *trans*-configuration, it seemed possible that I and II would stabilise olefin coordination for a variety of transition elements, and that III might show evidence of benzylic C—H interactions with transition metal atoms. We report here on the reactions of ligands I—III with a number of precursors containing rhodium, iridium, nickel, palladium or platinum. Preliminary communications of some of this work have appeared [2,3].



(I) R = o-$CH_3C_6H_4$ (bdtps)

(II) R = Ph (bdpps)



(III) (bdpbz)

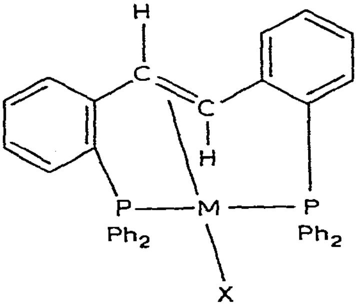
Results

Reactions with rhodium and iridium precursors

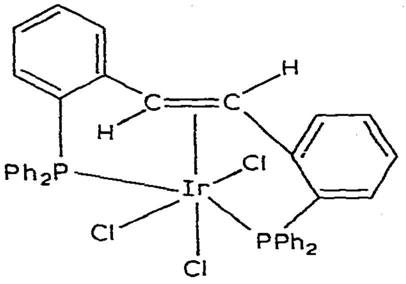
2,2′-Bis(diphenylphosphino)bibenzyl (III, bdpbz), which is prepared from the di-Grignard reagent of 2,2′-dibromobibenzyl and chlorodiphenylphosphine, reacts with the 1,5-cyclooctadiene complex $[RhCl(1,5\text{-}COD)]_2$ in refluxing toluene to give the yellow-orange rhodium(I) chelate complex of the stilbene ligands bdpps, II, almost quantitatively. The same product, $RhCl(o\text{-}Ph_2PC_6H_4\text{-}CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o)$, is obtained from $RhCl(PPh_3)_3$ in toluene or from rhodium trichloride in refluxing 2-methoxyethanol, but the yields are much lower. The fate of the hydrogen has not been determined. Treatment of the rhodium complex with sodium cyanide in refluxing 2-methoxyethanol displaces ligand II almost quantitatively. A similar reaction has been observed with the rhodium(I) complex of I (bdtps) [1]. The iridium(I) complex $IrCl(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4\text{-}PPh_2\text{-}o)$ cannot be obtained by dehydrogenation of III with iridium salts, but is formed by treatment of [IrCl(1,5-COD)]$_2$ with II. Analogous bromo and iodo compounds can also be isolated, and all members of the series are monomeric in chloroform and non-conducting in nitromethane. The ^{1}H NMR spectra provide good evidence for the presence of a coordinated double bond. The resonance due to the olefinic protons in ligands I and II, which appears as a broad singlet at δ 7.6 ppm, is shifted by about 4 ppm upfield in the rhodium and iridium complexes and appears as a 1 : 2 : 1 triplet owing to coupling with two mutually *trans*, equivalent phosphorus atoms. In the rhodium complexes, the triplet is doubled by coupling with ^{103}Rh (100% abundance, $I = ½$) (Table 1). Although the band due to C=C stretching in I and II does not appear in the infrared, a strong out-of-plane C—H deformation band is observed at ca. 960 cm^{-1}, this being characteristic of a *trans*-disubstituted olefin [4]. In the rhodium(I) complexes this band shifts to ca. 920 cm^{-1}, but in the iridium(I) complexes the band is usually split but not greatly shifted.

The X-ray study of RhCl(o-$Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2$-$o$) [2] confirms that this molecule, and by implication all members of the series, can reasonably be regarded as planar d^8 complexes (IV) analogous to MX(CO)(PPh$_3$)$_2$ (M = Rh or Ir; X = Cl, Br or I). In the solid state, the double bond of RhCl(o-$Ph_2PC_6H_4$-$CH\overset{t}{=}CHC_6H_4PPh_2$-$o$) is oriented at about 79° to the plane containing the rhodium and the two phosphorus atoms, so that the geometry approaches that observed in Zeise's Salt, K[PtCl$_3$(C$_2$H$_4$)] · H$_2$O [5] and many other olefin complexes of platinum(II) and palladium(II) [6]. However, the C=C bond length of 1.436(6) Å is significantly longer than that observed in Zeise's Salt (1.37(3) Å), indicating that there is more back-bonding to the double bond from rhodium(I) than from platinum(II). The marked upfield shift of the olefinic protons in the rhodium(I) and iridium(I) complexes may also be a consequence of extensive back-bonding.

The far IR spectra of MCl(o-$Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2$-$o$) (M = Rh or Ir) show bands at 299 (Rh) and 318 cm^{-1} (Ir) due to ν(MCl), which are close to the corresponding bands in the analogous carbonyl complexes RhCl(CO)(PPh$_3$)$_2$ (309 cm^{-1}) and IrCl(CO)(PPh$_3$)$_2$ (317 cm^{-1}) [7]. The stilbene complexes also resemble the carbonyl complexes in their ability to add other ligands forming five-coordinate adducts, and in undergoing oxidative additions with a variety of addends e.g. H$_2$, HCl and halogens; these reactions will be described separately [8].



(IV)



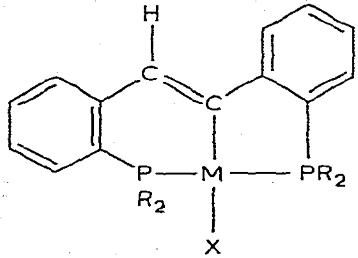
(V)

M = Rh or Ir; X = Cl, Br or I

In view of the stability of iridium(III)—carbon σ-bonded complexes and the ease with which ligand II is deprotonated on reaction with nickel(II), palladium(II) and platinum(II) to form chelate σ-bonded complexes (see below), it is surprising that II reacts with iridium trichloride in 2-methoxyethanol to give a yellow, chelate mono-olefin complex of iridium(III), $IrCl_3(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CH\text{-}C_6H_4PPh_2\text{-}o)$ which is monomeric in chloroform; no hydrogen chloride is eliminated in this reaction. The olefinic proton resonance is shifted upfield by ca. 1 ppm on coordination, and appears as a singlet, presumably because coupling to the two ^{31}P nuclei is very small. The characteristic C—H out-of-plane deformation band is shifted from ca. 960 to 935 cm^{-1}, and there is also a band at 330 cm^{-1} assignable to ν(IrCl) which is in the position expected for Cl *trans* to Cl in octahedral iridium(III) complexes such as $IrCl_3(CO)(PPh_3)_2$ [7,9]. The second ν(IrCl) band arising from Cl *trans* to the double bond could not be located with certainty. These data are in accord with the octahedral structure V for the complex, which appears to be the first example of a mono-olefin complex of iridium(III). Octahedral iridium(III) complexes containing 1,5-cyclooctadiene are known, however [10,11].

Reactions with nickel, palladium and platinum precursors

The stilbene ligands I and II eliminate hydrogen halide on reaction with a variety of complexes of divalent nickel, palladium or platinum e.g. $NiX_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, K_2PdBr_4, $PdI_2(PPh_3)_2$ and PtX_2(1,5-COD) (X = Cl or I) in refluxing toluene, xylene, mesitylene or 2-methoxyethanol. The products are air-stable complexes of apparent formula "MX(ligand)" which we formulate as chelate σ-vinyls $\overline{MX(o\text{-}R_2PC_6H_4C}{=}CHC_6H_4PR_2\text{-}o)$ (M = Ni, Pd or Pt; X = Cl, Br or I; R = Ph or $o\text{-}CH_3C_6H_4$). Qualitatively, reaction occurs more rapidly with ligand II than with I, e.g. hydrogen chloride is lost even at room temperature when solutions of $PdCl_2(PhCN)_2$ and II are mixed; this only occurs on heating in the case of I. Methane is eliminated when $Pt(CH_3)_2$(1,5-COD) is heated with I or II to give complexes containing two platinum—carbon σ-bonds, $\overline{Pt(CH_3)(o\text{-}R_2PC_6H_4C}{=}CHC_6H_4PR_2\text{-}o)$. The nickel complexes are red, the palladium and platinum com-



(VI)

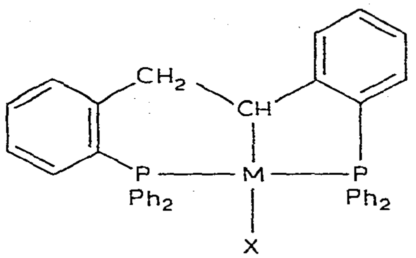
M = Ni ; X = Cl ; R = Ph, $o\text{-}CH_3C_6H_4$

M = Ni ; X = Br, I ; R = $o\text{-}CH_3C_6H_4$

M = Pd ; X = Cl, Br ; R = Ph, $o\text{-}CH_3C_6H_4$

M = Pd ; X = I ; R = $o\text{-}CH_3C_6H_4$

M = Pt ; X = Cl, Br, I, CH_3 ; R = Ph, $o\text{-}CH_3C_6H_4$



(VII)

(M = Pd or Pt; X = Cl, Br or I)

plexes are cream in the case of chlorides and bromides, orange in the case of iodides. All are remarkably stable to heat; they neither melt nor show apparent decomposition below 250°C. The complexes are monomeric in chloroform, and the mass spectra of $\overline{\mathrm{MX}(o\text{-}\mathrm{Ph_2PC_6H_4C}}{=}\mathrm{CHC_6H_4PPh_2}\text{-}o)$ (M = Pd, X = Cl; M = Pt, X = Cl or CH_3) show parent ions. The planar σ-bonded structure VI has been confirmed by single crystal X-ray structural analysis of the complex $\overline{\mathrm{PtCl}(o\text{-}\mathrm{Ph_2PC_6H_4C}}{=}\mathrm{CHC_6H_4PPh_2}\text{-}o)$ [3,12]. The palladium and platinum complexes show no resonance assignable to olefinic protons in their ^{1}H NMR spectra, presumably because it is buried beneath the aromatic resonances; however in the nickel complexes it appears as a singlet broadened by small ^{31}P couplings at ca. δ 6.1 ppm (Table 2), showing that metallation takes place at an olefinic carbon atom, not at an aromatic carbon atom, in agreement with the X-ray result. The proton-decoupled ^{31}P NMR spectra of representative complexes (Table 3) show an AB quartet [^2J(P—P) 400—450 Hz for the palladium and platinum complexes and ca. 300 Hz for the nickel complexes], the chemical shifts of the inequivalent phosphorus atoms being well downfield of those of the free ligands. These data confirm that both phosphorus atoms are coordinated and are mutually *trans*; similar values of ^2J(P—P) have been observed in *trans*-di-t-butylphosphine complexes of nickel(II), palladium(II) and platinum(II) [13]. In the infrared spectra of the complexes the characteristic ligand band at ca. 960 cm^{-1} is completely absent. Bands due to ν(MCl) have been tentatively assigned (Table 1); the values are in reasonable agreement with those reported previously for σ-vinyls or σ-aryls of divalent nickel [14], palladium [15] and platinum [16].

The ^{1}H NMR spectrum of $\overline{\mathrm{Pt(CH_3)}(o\text{-}\mathrm{Ph_2PC_6H_4C}}{=}\mathrm{CHC_6H_4PPh_2}\text{-}o)$ shows just one methyl resonance consisting of a 1 : 2 : 1 triplet, arising from equal coupling to the inequivalent phosphorus atoms (J 6.0 Hz), together with ^{195}Pt satellites (J 53.0 Hz). The magnitude of $^2J(^{195}\mathrm{Pt}—^1\mathrm{H})$ is considerably lower than that observed for CH_3 *trans* to the usual anionic ligands (ca. 80 Hz) [17], and lies between the values for σ-bonded aryls and carbenes (49—50 Hz) on the one hand and tertiary phosphines (55—57 Hz) on the other [18].

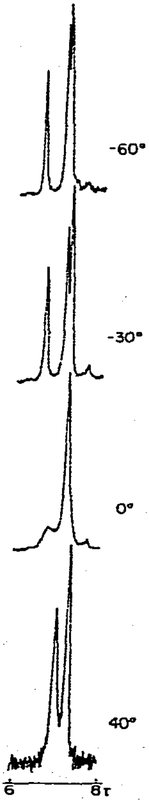
The signals due to the *o*-tolyl methyl groups in the complexes derived from ligand I vary with temperature. It is clear either from molecular models or from the single crystal X-ray structure of $\overline{\mathrm{PtCl}(o\text{-}\mathrm{Ph_2PC_6H_4C}}{=}\mathrm{CHC_6H_4PPh_2}\text{-}o)$ [1] (see Fig. 1 for a simplified representation) that molecules of this type possess no

TABLE 1

SELECTED ^{1}H NMR AND IR DATA FOR RHODIUM AND IRIDIUM COMPLEXES OF 2,2'-BIS(DIPHENYLPHOSPHINO)-*trans*-STILBENE (BDPPS) AND 2,2'-BIS(DI-*o*-TOLYLPHOSPHINO)-*trans*-STILBENE (BDTPS), $o\text{-}R_2PC_6H_4CH\overset{t}{=}CHC_6H_4PR_2\text{-}o$ (R = Ph OR $o\text{-}CH_3C_6H_4$)[a,b,c]

Compound	δ(=CH)	J(P—H)	=CH o.o.p. def. (cm^{-1})	ν(MCl) (cm^{-1})
bdpps	7.62(br)s	<1.0	955m	
RhCl(bdpps) · CH_2Cl_2	3.68(1 : 2 : 1)td	1.8 [d]	917s	299w
RhBr(bdpps)	3.76(1 : 2 : 1)td	2.5 [e]	915m	
RhI(bdpps)	3.83(1 : 2 : 1)td	2.0 [f]	n.m.	
IrCl(bdpps) · CH_2Cl_2	2.78(1 : 2 : 1)t	3.0	958m, 943m	318m
IrBr(bdpps)	2.83(1 : 2 : 1)t	3.0	n.m.	
IrI(bdpps)	2.84(1 : 2 : 1)t	2.8	n.m.	
$IrCl_3$(bdpps)	6.55(s)	<1.0	935m	330ms
bdtps	7.64(br,s)	<1.0	964s	
IrCl(bdtps)	[g]	[g]	958m, 944m	316m

[a] Chemical shifts (δ) in ppm downfield of internal TMS, measured in $CDCl_3$, coupling constants (J) in Hz (±0.5); IR spectra measured as Nujol mulls on CsI plates. Aromatic resonances are complex multiplets in the range δ 6.5—7.5 ppm. [b] Abbreviations (NMR): s, singlet; t, triplet; td, triplet of doublets; br, broad. [c] Abbreviations (IR): s, strong; m, medium; w, weak; nm, not measured; o.o.p. def., out-of-plane deformation. [d] J(Rh—H) 1.0. [e] J(Rh—H) 2.0. [f] J(Rh—H) 1.0. [g] Complex too insoluble for NMR measurement.



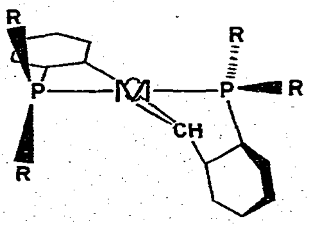


Fig. 1. View of $\overline{MX(o\text{-}R_2PC_6H_4C}{=}CHC_6H_4PR_2\text{-}o)$ down the C—M—X axis (M = Ni, Pd, Pt; X = Cl, Br, I; R = Ph or $o\text{-}CH_3C_6H_4$). The σ-bonded carbon atom (C) is behind M; the halogen atom (X) in front of M is not shown for the sake of clarity.

Fig. 2. Variable temperature behaviour of the *o*-tolyl methyl resonances of $\overline{NiCl\{(o\text{-}CH_3C_6H_4)_2PC_6H_4C}{=}CH\text{-}C_6H_4(o\text{-}CH_3C_6H_4)_2\}$ in CD_2Cl_2.

TABLE 2

^{1}H NMR DATA AT +34°C FOR NICKEL(II), PALLADIUM(II) AND PLATINUM(II) COMPLEXES DERIVED FROM 2,2′-BIS(DIPHENYLPHOSPHINO)-*trans*-STILBENE (BDPPS) AND 2,2′-BIS(DI-*o*-TOLYLPHOSPHINO)-*trans*-STILBENE (BDTPS) $o\text{-R}_2\text{PC}_6\text{H}_4\text{CH}\overset{t}{=}\text{CHC}_6\text{H}_4\text{PR}_2\text{-}o$ (R = Ph OR $o\text{-CH}_3\text{C}_6\text{H}_4$) [a,b]

Complex	Solvent	δ(=CH)	δ(CH$_3$)
NiCl(bdpps — H)	$CDCl_3$	6.52(s) [c]	
Pt(CH$_3$)(bdpps — H)	CD_2Cl_2	[d]	0.25(1 : 4 : 1)td [e]
NiCl(bdtps — H)	CD_2Cl_2	6.10(s) [c]	2.83s, 2.98s
NiBr(bdtps — H)	$CDCl_3$	6.07(s) [c]	2.84s, 2.95s
NiI(bdtps — H)	$CDCl_3$	6.06(s) [c]	2.82s, 2.91s
PdCl(bdtps — H)	$CDCl_3$	[d]	2.68(br)s
PdBr(bdtps — H)	$CDCl_3$	[d]	2.70(br)s
PdI(bdtps — H)	CD_2Cl_2	[d]	2.68(br)s
PtCl(bdtps — H)	CD_2Cl_2	[d]	2.68s, 2.75s
PtBr(bdtps — H)	$CDCl_3$	[d]	2.68s, 2.74s
PtI(bdtps — H)	CD_2Cl_2	[d]	2.62s, 2.67s
Pt(CH$_3$)(bdtps — H)	$CDCl_3$	[d]	2.48s, 2.56s, —0.20(1 : 4 : 1)td [f]

[a] Abbreviations: (bdpps — H) ≡ $o\text{-Ph}_2\text{PC}_6\text{H}_4\dot{\text{C}}\text{=CHC}_6\text{H}_4\text{PPh}_2\text{-}o$; (bdtps — H) ≡ $o\text{-}(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PC}_6\text{H}_4\text{-}\dot{\text{C}}\text{=CHC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_4\text{CH}_3\text{-}o)_2$; s, singlet; td, triplet of doublets; br, broad. [b] Aromatic resonances were complex multiplets in approximate range δ 6.5—8.0 ppm. Vinyl resonances of complexes MX(bdpps — H) (M = Pd or Pt; X = Cl, Br, I) could not be located and were presumably buried beneath aromatic mutiplets. [c] $J(\text{P—H}) < 1.0$ Hz. [d] Not observed, presumably beneath aromatic multiplets. [e] Pt—C$\underline{\text{H}}_3$ resonance; J(Pt—H) 53 Hz, J(P—H) 6.0 Hz. [f] Pt—C$\underline{\text{H}}_3$ resonance; J(Pt—H) 54 Hz, J(P—H) 6.0 Hz.

symmetry elements, hence the four *o*-tolyl methyl groups in $\overline{\text{MX}\{(o\text{-tol})_2\text{PC}_6\text{H}_4\text{C}}\text{=CHC}_6\text{H}_4\text{P}(o\text{-tol})_2\}$ (M = Ni, Pd or Pt; X = Cl, Br or I) should be inequivalent. At +34°C the nickel(II) and platinum(II) halo complexes show a broad doublet, which sharpens on warming to +60°C, whereas the palladium(II) complexes at +34°C show a broad singlet (Table 2). On cooling a solution of $\overline{\text{NiCl}\{(o\text{-tol})_2\text{PC}_6\text{H}_4\text{C}}\text{=CHC}_6\text{H}_4\text{P}(o\text{-tol})_2\}$, the lower field methyl resonance initially broadens and finally separates into three distinct sharp methyl resonances at —60°C (Fig. 2). The behaviour of the corresponding platinum(II) complex is similar, except that three resonances can be distinguished at 0°C and four at —30°C. The palladium(II) complex shows only a broad singlet even at 0°C, but from —20 to —60°C the resonance separates into a broad doublet. Clearly in the latter case the methyl groups on the different phosphorus atoms must have almost identical chemical shifts. Owing to the similarity of *o*-tolyl methyl chemical shifts in all the complexes, reliable estimates of rates and activation energies cannot be given. A projected study of analogous complexes derived from $o\text{-}(\text{CH}_3)_2\text{PC}_6\text{H}_4\text{CH}\overset{t}{=}\text{CHC}_6\text{H}_4\text{P}(\text{CH}_3)_2\text{-}o$, for which larger chemical shift differences may be expected, may give this information. The process clearly involves the exchange of *o*-tolyl methyl sites on each phosphorus atom, and molecular models show that this is readily achieved by rotation about the Pt—P bonds and about the Pt—C bond, i.e. the molecule passes through a transition state in which the coordination plane containing the metal atom and the ligand atoms is a mirror plane. The process is one of racemisation, and it undoubtedly accounts for the observation [12] that solutions of individual crystals of $\overline{\text{PtCl}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{C}}\text{=CHC}_6\text{H}_4\text{PPh}_2\text{-}o)$ are optically inactive at room temperature, even though the crystals chosen for the X-ray study contained dissymmetric molecules of only one configuration (Δ).

The bibenzyl ligand III also undergoes deprotonation on heating with the palladium(II) and platinum(II) halide precursors, though not as readily as the stilbene ligand II. Reaction occurs more rapidly in the more basic solvent 2-methoxyethanol than in aromatic solvents. Pink colorations develop when III is heated with nickel(II) complexes, suggesting that organonickel(II) species are formed, but only unchanged ligand could be recovered on work-up. The palladium and platinum complexes $\overline{\mathrm{MX}(o\text{-}\mathrm{Ph_2PC_6H_4C}}\mathrm{HCH_2C_6H_4PPh_2}\text{-}o)$ (M = Pd, X = Cl or Br; M = Pt, X = Cl, Br or I) are very similar to the corresponding products derived from I or II, and are assigned a similar, planar chelate σ-alkyl structure VII. The ^{31}P NMR spectra consist of an AB pattern, J_{AB} being in the usual range for strongly coupled *trans*-phosphines (Table 3), and the ^{1}H NMR spectra (Table 4) show a complex multiplet corresponding to three protons assignable to the CH and CH_2 protons of the deprotonated aliphatic chain. In the case of the palladium complexes, this multiplet is simplified by ^{31}P decoupling to an eight-line ABC spectrum from which ^{1}H—^{1}H coupling constants J_{BC} ca. 17 Hz, J_{AC} ca. 10 Hz and J_{AB} ca. 1 Hz could be extracted. These are reasonable values for the geminal benzylic coupling constant and for the two vicinal coupling constants in an aliphatic chain [19]. The proton chemical shifts in the platinum complexes are closer together than in the palladium complexes and the spectra are further complicated by couplir[illegible]h ^{195}Pt, so that accurate chemical shifts and coupling constants could not be obtained. The ν(MCl) values for $\overline{\mathrm{MCl}(o\text{-}\mathrm{Ph_2PC_6H_4C}}\mathrm{HCH_2C_6H_4PPh_2}\text{-}o)$ (M = Pd or Pt) are slightly lower than those found for the analogous complexes derived from stilbene ligands I and II.

TABLE 3

^{31}P NMR DATA AT 32°C FOR THE LIGANDS 2,2′-BIS(DIPHENYLPHOSPHINO)-*trans*-STILBENE (BDPPS), 2,2′-BIS(DI-*o*-TOLYLPHOSPHINO)-*trans*-STILBENE (BDTPS) AND 2,2′-BIS(DIPHENYLPHOSPHINO)BIBENZYL (BDPBZ) AND SOME COMPLEXES DERIVED FROM THEM BY DEPROTONATION [a]

Compound	Solvent	δ(P)	^2J(P—P)
bdpps	CD_2Cl_2	—13.7 [b]	
NiCl(bdpps — H)	CH_2Cl_2	41.4, 26.3	326
PdCl(bdpps — H)	CH_2Cl_2	44.9, 26.1	435
PtCl(bdpps — H)	CH_2Cl_2	43.7, 23.4	425
Pt(CH_3)(bdpps — H)	C_6H_6	47.2, 28.9	433
bdtps	CD_2Cl_2	—29.9 [c]	
NiCl(bdtps — H)	$CHCl_3$	33.5, 21.6	324
PdCl(bdtps — H)	CH_2Cl_2	33.3, 19.3	440
PtCl(bdtps — H)	CH_2Cl_2	36.6, 17.3	438
bdpbz	CH_2Cl_2	—15.8	
PdCl(bdpbz — H)	CH_2Cl_2	43.5, 14.5	410
PtCl(bdpbz — H)	CH_2Cl_2	37.3, 13.9	421
PtBr(bdpbz — H)	CH_2Cl_2	43.4, 19.0	425

[a] Chemical shifts in ppm relative to external 85% H_3PO_4, downfield being taken as positive. Coupling constants accurate to within ±5 Hz. Ligand abbreviations as in Table 2. [b] Obtained by INDOR on olefinic resonance at δ 7.62 ppm. [c] Obtained by INDOR on olefinic resonance at δ 7.64 ppm.

TABLE 4

^{1}H NMR DATA AT +34°C FOR PALLADIUM(II) AND PLATINUM(II) COMPLEXES DERIVED FROM 2,2′-BIS(DIPHENYLPHOSPHINO)BIBENZYL, o-$Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2$-o (bdpbz) [a]

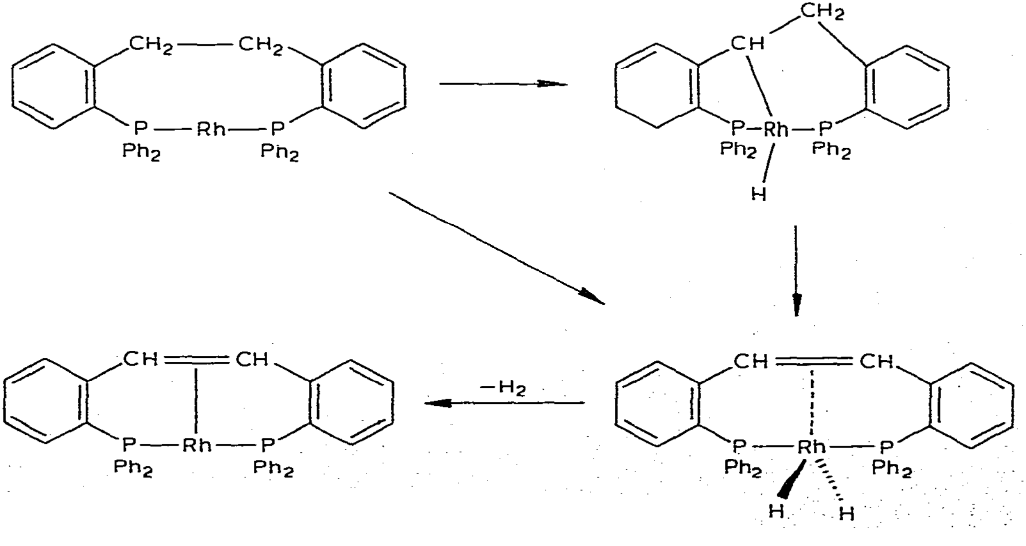
Compound	Solvent	$\delta(H_A)$	$\delta(H_B)$	$\delta(H_C)$	J_{AB}	J_{AC}	J_{BC}
bdpbz	$CDCl_3$	← 3.09 →					
PdCl(bdpbz — H)	$CDCl_3$	3.84	3.15	3.53	1.0	9.5	17.0
PdBr(bdpbz — H)	CD_2Cl_2	3.94	3.15	3.57	1.0	10.0	18.0
PdI(bdpbz — H)	CD_2Cl_2	4.00	3.13	3.55	1.0	11.0	18.0
PtCl(bdpbz — H)	$CDCl_3$	← 3.2—4.0 →			[b]	[b]	[b]
PtBr(bdpbz — H)	CD_2Cl_2	← 3.3—4.1 →			[b]	[b]	[b]
PtI(bdpbz — H)	CD_2Cl_2	← 3.2—4.0 →			[b]	[b]	[b]

[a] Abbreviation: bdpbz — H ≡ o-$Ph_2PC_6H_4\dot{C}H_ACH_BH_CC_6H_4PPh_2$-o. [b] Could not be derived from observed spectrum.

Discussion

Dehydrogenation of the bibenzyl ligand III by rhodium complexes probably proceeds by initial *trans*-bridging, bidentate coordination of the phosphorus atoms and subsequent stepwise or simultaneous loss of hydrogen via mono- or di-hydride intermediates (Scheme 1). III and its *o*-tolyl substituted analogue may well be intermediates in the coupling-dehydrogenation reactions of diphenyl-*o*-tolylphosphine and tri-*o*-tolylphosphine [1]. Of the transition elements so far investigated only rhodium has shown the ability to promote these dehydrogenations. However, the first step in the suggested sequence, in which one hydrogen atom is abstracted from the carbon chains of ligands I—III, is promoted by other d^8 complexes. The abstraction of olefinic protons from *N*-donor ligands to give chelate σ-vinyls is known [20—22], but so far as we know ours are the first examples involving a coordinated tertiary phosphine.

SCHEME 1. Hydrogen abstraction from *trans*-coordinated 2,2′-bis(diphenylphosphino)bibenzyl (Auxiliary ligands omitted).



The first step is probably *trans*-bidentate coordination of the ditertiary phosphines. Preliminary studies suggest that ligands I and III form isolable intermediates of general formula $PtCl_2$(ligand) which subsequently eliminate hydrogen chloride to form the metallated complexes. In the case of the stilbene ligands I and II the intermediate complex may be ionic and the double bond may be coordinated, i.e. $[PtCl(o\text{-}R_2PC_6H_4CH{=}CHC_6H_4PR_2\text{-}o]^+Cl^-$ (R = Ph or *o*-tolyl). This feature could account for the faster elimination of hydrogen chloride observed with the stilbene ligand II compared with its bibenzyl analogue III. The elimination of methane from $Pt(CH_3)_2(COD)$ and ligands I and II probably proceeds by an initial oxidative addition of the vinylic C—H bond to the metal atom giving a transient platinum(IV) hydrido—methyl complex cf. the formation of $Rh(o\text{-}C_6H_4PPh_2)(PPh_3)_2$ from $Rh(CH_3)(PPh_3)_3$ [23]. Although a similar mechanism may operate in the case of the halide complexes, a more likely alternative involves electrophilic attack by the metal atom on the C—H bond, as suggested also for the metallation of triarylphosphites [24], azobenzenes [25] and tertiary benzylamines [26] by palladium(II) and platinum(II).

Ligands I—III seem to undergo metallation with d^8 metal complexes more readily than do the bulky t-butyl or *o*-tolyl monophosphines studied by Shaw et al. [27—30], which have not so far been reported to form chelate nickel(II)—carbon σ-bonded species. Although the driving force for metallation may well be similar in the two cases viz. forcing the C—H bonds into proximity with the metal atom by steric or geometric control, there is one interesting difference. As noted above, I undergoes metallation more slowly than II, presumably as a consequence of steric hindrance by the bulky *o*-tolyl groups, whereas the ligands studied by Shaw et al. undergo metallation more rapidly as they become more sterically hindered. Interpretation of these observations will be deferred until intermediates have been identified and comparative rate studies have been carried out.

Experimental

Analytical, IR and NMR spectroscopic procedures are as previously described [31]. Aromatic and ether solvents were dried over sodium before use and THF was distilled from $LiAlH_4$; other solvents were dried over molecular sieves (BDH4A). The complexes $NiX_2(PPh_3)_2$, $[RhX(1,5\text{-COD})]_2$ (X = Cl, Br), $RhCl(PPh_3)_3$, $[IrCl(1,5\text{-COD})]_2$, $PtX_2(1,5\text{-COD})$ (X = Cl, I, CH_3), $MCl_2(PhCN)_2$ (M = Pd, Pt) and $PdI_2(PPh_3)_2$ were prepared by standard methods. 2,2'-Dibromobibenzyl and 2,2'-bis(di-*o*-tolylphosphino)-*trans*-stilbene (bdtps) were prepared following the respective literature procedures [1,32]. All reactions were carried out under a nitrogen atmosphere, though the complexes were air-stable once they had been isolated from solution. Analytical data are in Table 5.

Preparations

2,2'-Bis(diphenylphosphino)bibenzyl, $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o$ (bdpbz). A solution of 2,2'-dibromobibenzyl (20 g, 0.059 mol) in tetrahydrofuran (200 ml) was added dropwise under nitrogen to a stirred suspension of magnesium turnings (9.8 g, 0.4 mol) in refluxing tetrahydrofuran (60 ml). Formation of the Grignard reagent was initiated with a few drops of ethylene dibro-

TABLE 5

COLOURS AND ANALYTICAL AND MOLECULAR WEIGHT DATA [a]

	Colour	Analysis found (calcd.) (%)				
		C	H	P	Hal	Mol. wt.
bdpps [b]	White	83.2	5.4	11.6		557
		(83.2)	(5.5)	(11.3)		(549)
bdpbz [c]	White	83.3	5.7	11.4		530
		(82.9)	(5.9)	(11.25)		(551)
RhCl(bdpps) · CH_2Cl_2	Orange	61.35	4.6	7.6	14.6	773
		(60.7)	(4.2)	(8.0)	(13.3)	(686)
RhBr(bdpps)	Orange	62.9	4.3	8.1	12.1	751
		(62.4)	(4.1)	(8.5)	(10.9)	(731)
IrCl(bdpps) · CH_2Cl_2	Orange	54.3	3.8	6.7	12.0	842
		(54.4)	(3.75)	(7.2)	(12.35)	(776)
IrBr(bdpps)	Orange	53.8	3.7	7.5	9.35	851
		(55.6)	(3.7)	(7.55)	(9.7)	(821)
IrI(bdpps)	Red	53.5	3.7	6.8	14.3	796
		(52.6)	(3.5)	(7.1)	(14.6)	(868)
$IrCl_3$(bdpps)	Yellow	54.2	3.9	7.35	12.4	753
		(53.9)	(3.6)	(7.3)	(12.55)	(847)
IrCl(bdtps)	Orange	60.3	4.6	7.1	5.45	
		(60.6)	(4.6)	(7.4)	(4.3)	
NiCl(bdpps — H)	Orange-red	72.1	4.9	8.6	4.9	641
		(71.1)	(4.55)	(9.65)	(5.5)	(641)
PdCl(bdpps — H)	Cream	66.3	4.6	8.7	5.2	643
		(66.2)	(4.2)	(9.0)	(5.1)	(689)
PdBr(bdpps — H)	Cream	63.9	4.3	8.1	10.3	725
		(62.2)	(4.0)	(8.4)	(10.9)	(734)
PtCl(bdpps — H)	Cream	58.0	4.35	7.4	4.5	730
		(58.65)	(3.8)	(8.0)	(4.6)	(778)
PtBr(bdpps — H)	Cream	56.0	3.9	7.05	10.2	697
		(55.5)	(3.55)	(7.5)	(9.7)	(823)
PtI(bdpps — H)	Yellow	53.0	3.45	6.9	14.05	
		(52.5)	(3.4)	(7.1)	(14.6)	
Pt(CH_3)(bdpps — H)	Orange	63.4	4.5	7.7		745
		(61.8)	(4.3)	(8.2)		(758)
NiCl(bdtps — H)	Red	71.1	5.5	8.35	5.0	653
		(72.3)	(5.35)	(8.9)	(5.1)	(698)
NiBr(bdtps — H)	Red	67.7	5.1	7.9	9.8	722
		(68.0)	(5.0)	(8.3)	(10.8) [d]	(742)
NiI(bdtps — H)	Red	66.2	5.1	7.5	14.9	864
		(63.9)	(4.7)	(7.85)	(16.1) [e]	(787)
PdCl(bdtps — H)	Yellow	67.3	5.0	8.0	4.6	712
		(67.7)	(5.0)	(8.3)	(4.75) [f]	(746)
PdBr(bdtps — H)	Cream	62.9	5.0	7.6	10.25	734
		(63.85)	(4.7)	(7.8)	(10.1)	(790)
PdI(bdtps — H)	Yellow	61.2	4.9	7.1	15.0	833
		(60.3)	(4.5)	(7.4)	(15.2)	(837)
PtCl(bdtps — H)	Cream	60.3	4.6	7.0	4.3	833
		(60.5)	(4.5)	(7.4)	(4.25)	(834)
PtBr(bdtps — H)	Cream	57.7	4.2	6.8	8.7	862
		(57.4)	(4.25)	(7.05)	(9.1)	(879)
PtI(bdtps — H)	Yellow	54.8	4.3	6.5	12.9	815
		(54.5)	(4.0)	(6.7)	(13.7)	(926)
Pt(CH_3)(bdtps — H) [g]	Pale yellow	62.2	5.3	7.0		786
		(63.5)	(4.95)	(7.6)		(814)
PdCl(bdpbz — H) [h]	Cream	66.5	4.6	8.8	5.4	685
		(66.0)	(4.5)	(9.0)	(5.1)	(691)
PdBr(bdpbz — H)	Cream	61.95	4.5	8.3	10.8	723
		(62.0)	(4.25)	(8.4)	(10.9)	(736)

(Table continued)

TABLE 5 (continued)

	Colour	Analysis: found (calcd.) (%)				
		C	H	P	Hal	Mol. wt.
PdI(bdpbz — H)	Yellow	57.9 (58.3)	4.2 (4.0)	7.8 (7.9)	15.6 (16.2)	766 (783)
PtCl(bdpbz — H)	White	58.6 (58.5)	4.2 (4.0)	7.8 (7.9)	4.6 (4.5)	791 (780)
PtBr(bdpbz — H)	White	55.4 (55.35)	3.7 (3.8)	7.3 (7.5)	9.7 (9.7)	828 (825)
PtI(bdpbz — H)	Cream	52.7 (52.4)	3.7 (3.6)	6.9 (7.1)	14.3 (14.6)	842 (872)

[a] Except where noted, compounds decomposed >250°C in a capillary sealed under nitrogen. [b] M.p. 165°C. [c] M.p. 162°C. [d] Ni: Found, 8.1; calcd., 8.4%. [e] Ni: Found 8.1; calcd., 7.9%. [f] Ni: found, 7.2; calcd., 7.4%. [g] M.p. 235°C. [h] Dec. >230°C.

mide, and the addition took ca. 1 h. After heating under reflux for 30 min, the solution was filtered, cooled to 0°C and treated dropwise under nitrogen with chlorodiphenylphosphine (23.2 g, 0.101 mol) in tetrahydrofuran (100 ml). The solution was heated under reflux for 30 min, then cooled to 0°C and hydrolysed by dropwise addition of a solution of ammonium chloride (17 g) in water (100 ml). The THF layer was separated, the aqueous layer was washed with ether (2 X 50 ml), and the organic extracts were combined. After drying (Na_2SO_4), solvent was removed under reduced pressure until the product crystallised. After washing with n-hexane and drying in vacuo the yield was 18.3 g (33%).

2,2'-Bis(o-diphenylphosphino)-trans-stilbenechlororhodium(I) $RhCl(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o)$ *(RhCl(bdpps)).*

(1). A mixture of di-1,5-cyclooctadienedi-μ-chlorodirhodium(I), $[RhCl(1,5\text{-}COD)]_2$, (3.16 g, 6.4 mmol), 2,2'-bis(diphenylphosphino)bibenzyl (bdpbz) (7.1 g, 13.0 mmol) and toluene (350 ml) was heated under reflux for 24 h. Toluene was removed under reduced pressure and the resulting orange solid was recrystallised from dichloromethane—methanol to give 7.8 g (88%) of the complex.

(2). A mixture of chlorotris(triphenylphosphine)rhodium(I), $RhCl(PPh_3)_3$, (0.16 g, 0.17 mmol), bdpbz (0.1 g, 0.18 mmol) and toluene (10 ml) was heated under reflux for 16 h. Toluene was removed under reduced pressure, and the residue, dissolved in benzene, was transferred to an alumina column. Triphenylphosphine was eluted with benzene—hexane (1 : 11), and the complex was eluted with dichloromethane to give a yellow solution. Addition of methanol gave 8 mg (7%) of the complex.

(3). Hydrated rhodium trichloride (0.40 g, 1.5 mmol) and bdpbz (2.08 g, 3.8 mmol) were heated under reflux in 2-methoxyethanol (80 ml) for 16 h. Solvent was removed under reduced pressure and the residue was dissolved in benzene and chromatographed on alumina. After recrystallisation from dichloromethane—methanol, the yield of product was 0.15 g (14%).

2,2'-Bis(o-diphenylphosphino)trans-stilbene $(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o$ *(bdpps).* The complex RhCl(bdpps) (6.0 g, 8.8 mmol) was heated under reflux

TABLE 6

DEPROTONATION REACTIONS [a]

Product	Starting complex	Ligand	Solvent (volume)	Reflux time (h)	Yield
NiCl(bdpps — H)	$NiCl_2(PPh_3)_2$ (0.18 g, 0.26 mmol)	bdpps (0.15 g, 0.27 mmol)	2-Methoxyethanol (40 ml)	8	0.13 g (74%) [b]
PdCl(bdpps — H)	$PdCl_2(PhCN)_2$ (0.10 g, 0.26 mmol)	bdpps (0.15 g, 0.27 mmol)	Benzene (20 ml)	1	0.13 g (72%)
PdBr(bdpps — H)	K_2PdBr_4 (0.13 g, 0.26 mmol)	bdpps (0.15 g, 0.27 mmol)	2-Methoxyethanol (15 ml)	2	0.15 g (79%)
PtCl(bdpps — H)	$PtCl_2$(1,5-COD) (0.20 g, 0.54 mmol)	bdpps (0.30 g, 0.55 mmol)	Benzene (20 ml)	3	0.33 g (79%)
PtBr(bdpps — H)	K_2PtBr_4 (0.15 g, 0.25 mmol)	bdpps (0.14 g, 0.26 mmol)	2-Methoxyethanol (15 ml)	2	0.16 g (76%)
PtI(bdpps — H)	PtI_2(1,5-COD) (0.15 g, 0.27 mmol)	bdpps (0.15 g, 0.27 mmol)	2-Methoxyethanol (15 ml)	1	0.15 g (65%)
$Pt(CH_3)$(bdpps — H)	$Pt(CH_3)_2$(1,5-COD) (0.15 g, 0.45 mmol)	bdpps (0.25 g, 0.46 mmol)	Toluene (15 ml)	4	0.31 g (94%) [c]
NiCl(bdtps — H)	$NiCl_2(PPh_3)_2$ (0.20 g, 0.31 mmol)	bdtps (0.19 g, 0.32 mmol)	Mesitylene (20 ml)	22	0.12 g (57%)
NiBr(bdtps — H)	$NiBr_2(PPh_3)_2$ (0.18 g, 0.24 mmol)	bdtps (0.15 g, 0.25 mmol)	*m*-Xylene (20 ml)	22	0.10 g (56%)
NiI(bdtps — H)	NiCl(bdtps — H) (0.20 g, 0.29 mmol), NaI (0.40 g, excess)		Methanol (20 ml)	18	0.12 g (55%)
PdCl(bdtps — H)	$PdCl_2(PhCN)_2$ (0.20 g, 0.52 mmol)	bdtps (0.32 g, 0.53 mmol)	Benzene (70 ml)	16	0.24 g (62%)
PdBr(bdtps — H)	K_2PdBr_4 (0.15 g, 0.30 mmol)	bdtps (0.18 g, 0.30 mmol)	Mesitylene (10 ml)	24	0.16 g (67%)
PdI(bdtps — H)	$PdCl_2$ (0.09 g, 0.51 mmol), NaI (1.0 g, excess)	bdtps (0.33 g, 0.55 mmol)	2-Methoxyethanol (15 ml)	96	0.21 g (50%)
PtCl(bdtps — H)	$PtCl_2$(1,5-COD) (0.23 g, 0.53 mmol)	bdtps (0.33 g, 0.55 mmol)	*m*-Xylene (50 ml)	18	0.20 g (44%)
PtBr(bdtps — H)	K_2PtBr_4 (0.15 g, 0.25 mmol)	bdtps (0.15 g, 0.25 mmol)	Mesitylene (15 ml)	48	0.16 g (73%)
PtI(bdtps — H)	PtI_2(1,5-COD) (0.15 g, 0.27 mmol)	bdtps (0.17 g, 0.28 mmol)	Mesitylene (15 ml)	24	0.17 g (68%)
$Pt(CH_3)$(bdtps — H)	$Pt(CH_3)_2$(1,5-COD) (0.10 g, 0.30 mmol)	bdtps (0.19 g, 0.31 mmol)	Toluene (10 ml)	4	0.072 g (30%) [c]
PdCl(bdpbz — H)	$PdCl_2(PhCN)_2$ (0.11 g, 0.29 mmol)	bdpbz (0.15 g, 0.27 mmol)	2-Methoxyethanol (15 ml)	1.5	0.15 g (75%)
PdBr(bdpbz — H)	K_2PdBr_4 (0.13 g, 0.26 mmol)	bdpbz (0.15 g, 0.27 mmol)	2-Methoxyethanol (15 ml)	2	0.05 g (26%)
PdI(bdpbz — H)	$PdI_2(PPh_3)_2$ (0.24 g, 0.27 mmol)	bdpbz (0.15 g, 0.27 mmol)	2-Methoxyethanol (15 ml)	10	0.18 g (86%)
PtCl(bdpbz — H)	$PtCl_2(PhCN)_2$ (0.20 g, 0.42 mmol)	bdpbz (0.23 g, 0.42 mmol)	Mesitylene (15 ml)	16	0.21 g (64%)
PtBr(bdpbz — H)	K_2PtBr_4 (0.15 g, 0.25 mmol)	bdpbz (0.15 g, 0.27 mmol)	2-Methoxyethanol (15 ml)	24	0.16 g (76%)
PtI(bdpbz — H)	PtI_2(1,5-COD) (0.15 g, 0.27 mmol)	bdpbz (0.15 g, 0.27 mmol)	Mesitylene (15 ml)	16	0.16 g (70%)

[a] Ligand abbreviations as in Table 2. Products were recrystallised from benzene—ethanol, except where stated. [b] Recrystallised from benzene—n-hexane. [c] Recrystallised from dichloromethane—n-hexane.

with a solution of sodium cyanide (15 g) in water (45 ml) and 2-methoxyethanol (150 ml) until the solution lost its original yellow colour and a white precipitate had formed (ca. 1 h). The solution was filtered at room temperature, and the solid washed with water, ethanol and ether. After drying in vacuo, the yield of product was 4.8 g (86%).

2,2'-Bis(o-diphenylphosphino)-trans-stilbenechloroiridium(I), IrCl(o-$Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2$*-o) (IrCl(bdpps)).* Di-1,5-cyclooctadiene-di-μ-chlorodiiridium(I), $[IrCl(1,5\text{-}COD)]_2$ (0.20 g, 0.3 mmol) and bdpps (0.33 g, 0.6 mmol) were heated under reflux for 10 min in dichloromethane (10 ml). The orange product which crystallised on addition of methanol at 0°C was filtered, washed successively with methanol and ether and dried in vacuo. The yield of dichloromethane solvate was 0.43 g (93%).

The complex RhBr(bdpps) was obtained in 90% yield from $[RhBr(1,5\text{-}COD)]_2$ by a similar procedure to that described above for RhCl(bdpps). The complexes IrX(bdpps) (X = Br, I) were obtained by metathetical reaction of IrCl(bdpps) with the appropriate lithium halide in refluxing methanol. Yields were almost quantitative.

2,2'-Bis(o-diphenylphosphino)-trans-stilbenetrichloroiridium(III), $IrCl_3$*(o-*$Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2$*-o) (*$IrCl_3$*(bdpps)).* A solution of hydrated iridium trichloride (0.066 g, 0.19 mmol) in aqueous 2-methoxyethanol (12 ml, ca. 1 : 1) was treated with bdpps (0.20 g, 0.37 mmol). The solution rapidly turned yellow at room temperature, but was heated under reflux for 6 h to ensure completion of the reaction. Solvent was removed under reduced pressure, and the yellow residue was recrystallised from dichloromethane—methanol to give 0.056 g (35%) of product.

Deprotonation reactions

One such reaction is described in detail. The conditions and yields for the remainder are given in Table 6.

Chloro{trans-1,2[o-(di-o-tolylphosphino)phenyl]vinyl}platinum(II), $\overline{PtCl\{o\text{-}(o\text{-}CH_3C_6H_4)_2PC_6H_4C}=CHC_6H_4P(C_6H_4CH_3\text{-}o)_2\text{-}o\}$ *(PtCl(bdtps — H)).* A mixture of 1,5-cyclooctadienedichloroplatinum(II), $PtCl_2(1,5\text{-}COD)$ (0.20 g, 0.54 mmol), 2,2'-bis(di-*o*-tolylphosphino)-*trans*-stilbene (bdtps) (0.33 g, 0.55 mmol) and *m*-xylene was heated under reflux for 18 h, after which time evolution of hydrogen chloride had ceased. The solution was allowed to cool to room temperature and *m*-xylene was removed under reduced pressure. The cream-coloured residue was recrystallised from benzene—ethanol to give 0.22 g (50%) of product.

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References

1 M.A. Bennett and P.A. Longstaff, J. Amer. Chem. Soc., 91 (1969) 6266.
2 M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, Chem. Commun., (1972) 1011.

3 M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, J. Organometal. Chem., 63 (1973) C15.
4 L.J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd. Ed., Methuen, London, 1958, p. 45.
5 J.A.J. Jarvis, B.T. Kilbourn, and P.G. Owston, Acta Crystallogr., Sect. B, 27 (1971) 366.
6 F.R. Hartley, The Chemistry of Platinum and Palladium, Applied Science, London, 1973, pp. 472, 495.
7 M.A. Bennett, R.J.H. Clark and D.L. Milner, Inorg. Chem., 6 (1967) 1647.
8 M.A. Bennett, R.N. Johnson and I.B. Tomkins, unpublished work.
9 B.L. Shaw and A.C. Smithies, J. Chem. Soc. A, (1968) 2784.
10 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1965) 4997.
11 R.N. Haszeldine, R.J. Lunt and R.V. Parish, J. Chem. Soc. A, (1971) 3711.
12 G.B. Robertson and P.O. Whimp, Inorg. Chem., 13 (1974) 2082.
13 A. Bright, B.E. Mann, C. Masters, B.L. Shaw, R.M. Slade and R.E. Stainbank, J. Chem. Soc. A, (1971) 1826.
14 D.R. Fahey, Organometal. Chem. Rev. A., 7 (1972) 245.
15 P.E. Fitton and E.A. Rick, J. Organometal. Chem., 28 (1971) 287.
16 B.E. Mann, B.L. Shaw and N.I. Tucker, J. Chem. Soc. A, (1971) 2667.
17 F.H. Allen and A. Pidcock, J. Chem. Soc. A, (1968) 2700.
18 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335, and references cited therein.
19 A.A. Bothner-By, Advan. Magn. Resonance, 1 (1965) 195.
20 J.M. Kliegman and A.C. Cope, J. Organometal. Chem., 16 (1969) 309.
21 R.J. Foot and B.T. Heaton, J. Chem. Soc., Chem. Commun., (1973) 838.
22 J.F. van Baar, K. Vrieze and D.J. Stufkens, J. Organometal. Chem., 85 (1975) 249.
23 W. Keim, J. Organometal. Chem., 14 (1968) 179.
24 N. Ahmad, E.W. Ainscough, T.A. James and S.D. Robinson, J. Chem. Soc., Dalton Trans., (1973) 1148.
25 A.C. Cope and R.W. Siekman, J. Amer. Chem. Soc., 87 (1965) 3272.
26 A.C. Cope and E.C. Friedrich, J. Amer. Chem. Soc., 90 (1968) 909.
27 A.J. Cheney, B.E. Mann, B.L. Shaw and R.M. Slade, J. Chem. Soc., Dalton Trans., (1971) 3833.
28 A.J. Cheney and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1972) 255.
29 A.J. Cheney and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1973) 860.
30 D.F. Gill and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1973) 270.
31 M.A. Bennett, R.N. Johnson and I.B. Tomkins, J. Amer. Chem. Soc., 96 (1974) 61.
32 R.L. Letsinger and I.H. Skoog, J. Amer. Chem. Soc., 77 (1955) 5176.