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COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) CONTAINING A *trans*-CHELATING BIDENTATE DITERTIARY PHOSPHINE OR ARSINE: INTERNAL OXIDATIVE ADDITION OF A BENZYLIC C—H BOND TO IRIDIUM(I)

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Summary

2,2′-Bis(diphenylphosphino)bibenzyl, $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o$ (bdpbz), and its arsenic analogue, $o\text{-}Ph_2AsC_6H_4CH_2CH_2C_6H_4AsPh_2\text{-}o$ (bdabz), form monomeric complexes of rhodium(I) and iridium(I) of general formula MCl(CO)(ligand) (M = Rh, Ir; ligand = bdpbz, bdabz) in which the Group V ligands span *trans*-coordination sites. The rhodium(I) complexes RhCl(CO)(bdpbz) and $[Rh(CO)_2(bdpbz)]^+$ exhibit temperature-dependent ^1H NMR spectra, probably owing to inversion of the nine-membered chelate ring; the estimated free energies of activation are 17.3 ± 0.3 kcal mol^{-1} at 93°C for the neutral complex and 13.2 ± 0.5 kcal mol^{-1} at about —15°C for the cationic complex.

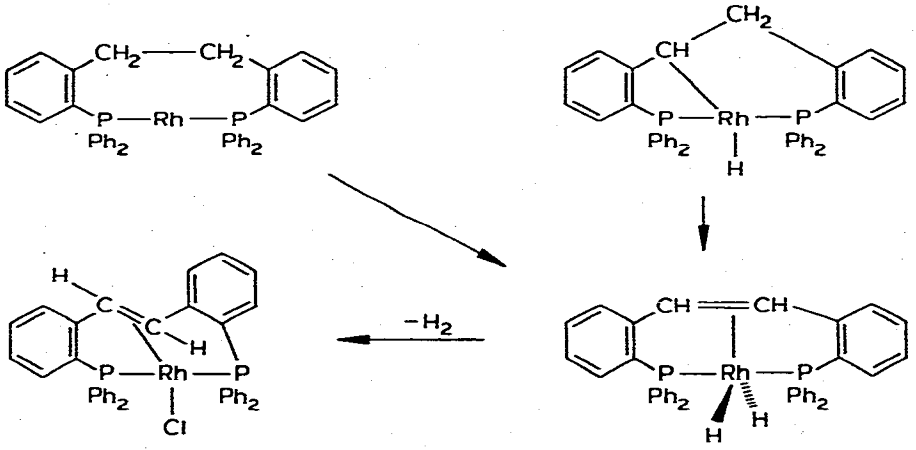
In contrast, bdpbz behaves as a *cis*-bidentate ligand in the complex $Pt(CH_3)_2$(bdpbz); the nine-membered chelate ring undergoes inversion with an estimated free energy of activation of 16.1 ± 0.1 kcal mol^{-1} at 69°C. The iridium(I) complex IrCl(CO)(bdpbz) isomerizes in solution at room temperature by transferring a benzylic hydrogen atom to the metal and forming a chelate metal—carbon σ-bonded complex $\overline{Ir(H)Cl(CO)(o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o)$; IrCl(CO)(bdabz) behaves similarly under more forcing conditions. Cationic metallated complexes $[\overline{Ir(H)(CO)_2\{o\text{-}Ph_2EC_6H_4C}HCH_2C_6H_4EPh_2\text{-}o\}]^+$ (E = P, As) have been identified in solution.

Introduction

We have shown [1,2] that 2,2′-bis(diphenylphosphino)bibenzyl, $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o$ (bdpbz) is dehydrogenated in the presence of rhodium complexes such as $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) to give a planar rhodium(I)—olefin complex $RhCl(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o)$ containing the tridentate chelate ligand 2,2′-bis(diphenylphosphino)-*trans*-stilbene (bdpps), and we suggested [2] that the first step involves *trans*-chelate coordination of bdpbz via its phosphorus atoms so as to bring the methylene groups close to rhodium(I). This could promote successive or concerted oxidative additions of C—H bonds to the metal giving a dihydride which eliminates hydrogen and forms the stilbene complex (Scheme 1). We now report on complexes derived from bdpbz

SCHEME 1

HYDROGEN ABSTRACTION FROM *trans*-COORDINATED 2,2'-BIS(DIPHENYLPHOSPHINO)BIBENZYL (AUXILIARY LIGANDS OMITTED).

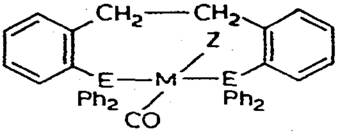


and its arsenic analogue, o-$Ph_2AsC_6H_4CH_2CH_2C_6H_4AsPh_2$-$o$ (bdabz), which provide support for the proposed mechanism. When our work started, the only reported *trans*-chelate ditertiary phosphine complexes were $NiCl_2\{(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_2\}$ (C_6H_{11} = cyclohexyl) [3] and planar dihalogeno-complexes of nickel(II), palladium(II) and platinum(II) formed by 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene [4]. Subsequently it has been shown that the α,ω-polymethylene ditertiary Group V ligands $t\text{-}Bu_2P(CH_2)_nP\text{-}t\text{-}Bu_2$ (n = 8, 9, 10 or 12) and $Me_2As(CH_2)_{12}AsMe_2$ form *trans*-chelate complexes with platinum(II) or palladium(II) [5—7], and that the phosphino ethers $Ph_2P(CH_2CH_2O)_n$-$CH_2CH_2PPh_2$ (n = 1, 2, 3) behave similarly with rhodium(I) [8]. The dehydrogenation of 1,6-bis(diphenylphosphino)hexane, $Ph_2P(CH_2)_6PPh_2$, by $[MCl(COD)]_2$ (M = Rh, Ir) to give chelate olefin complexes of 1,6-bis(diphenylphosphino)-*trans*-3-hexene, $MCl(Ph_2PCH_2CH_2CH\overset{t}{=}CHCH_2CH_2PPh_2)$, has also recently been reported [9].

Results and discussion

trans-Bidentate complexes of rhodium(I) with bdpbz and bdabz

Reaction of bdpbz with $[RhCl(COD)]_2$ in dichloromethane under carbon monoxide (25°C, 1 atm) gives a yellow solution from which the yellow crystalline carbonyl complex RhCl(CO)(bdpbz) can be isolated. The complex is monomeric in chloroform and shows a parent ion in its mass spectrum. The IR spectrum shows a single $\nu(CO)$ band at 1970 cm^{-1}, both in solution and in a Nujol mull, and in the far IR spectrum there is a band at 311 cm^{-1} due to $\nu(RhCl)$; both of these values agree well with the corresponding values for $RhCl(CO)(PPh_3)_2$ [10,11]. The $^{31}P\{^1H\}$ spectrum consists of a very closely spaced pair of doublets, the magnitude of $J(Rh—P)$, 127 Hz, being very close to that found for complexes of the type $RhCl(CO)(PR_3)_2$ [12—14]. Owing to the small chemical shift difference between the two phosphorus atoms, the outer lines of the expected *AB* quartet could not be observed, hence the magnitude of $^2J(P—P)$ could not be determined. The available evidence strongly supports the formulation of RhCl(CO)(bdpbz) as a planar rhodium(I) complex in which bdpbz functions as a *trans*-bidentate chelate ligand (I).



(I) M = Rh, E = P, Z = Cl
(II) M = Rh, E = As, Z = Cl
(III) M = Rh^+, E = P, Z = CO
(VI) M = Ir, E = P, Z = Cl
(VII) M = Ir, E = As, Z = Cl

The corresponding arsine complex, RhCl(CO)(bdabz) (II), precipitates from dichloromethane on reaction of the ligand with $[RhCl(COD)]_2$ under carbon monoxide. Its IR spectrum shows characteristic $\nu(CO)$ and $\nu(RhCl)$ bands (Table 1) and it is undoubtedly structurally similar to RhCl(CO)(bdpbz); its poor solubility has prevented NMR measurements.

The ^1H NMR spectrum of RhCl(CO)(bdpbz) in CD_2Cl_2 at 32°C shows two complex multiplets centred at δ 2.9 and 4.4 ppm due to the methylene protons, which are not strongly coupled to ^{31}P (Table 2). The resonances are not symmetrical about the mid-point, so that the spectrum is of the type *ABCD*, not *AA'BB'* i.e. all four methylene protons are inequivalent, in agreement with the proposed structure. On warming a solution of the complex in C_6D_5Br from 32°C the methylene resonances broaden and coalesce at 93°C to give a broad signal; this sharpens as the temperature is raised to 140°C, and finally appears as a singlet at δ 3.7 ppm, the width at half-height being about 8 Hz. In the same temperature range, a pair of aromatic multiplets at δ 7.7 and 8.1 ppm also broaden and coalesce; they appear as a singlet at δ 7.6 ppm at 140°C. On cooling to room temperature, the original spectrum is regained but, in addition, there is a characteristic 1 : 2 : 1 triplet of doublets at δ 3.74 ppm due to the coordinated olefinic protons of RhCl(bdpps) [2], so that dehydrogenation of the coordinated bibenzyl ligand is clearly occurring at about 140°C. The rate of the intramolecular exchange process at the coalescence temperature can be calculated from the equation $k = \pi\delta_{AB}/\sqrt{2}$ for exchange between two equally populated sites A and B, and this gives an estimate of the free energy of activation $\Delta G^{\neq}$ (93°C) as 17.3 ± 0.3 kcal mol^{-1}.

The deep orange, cationic complex $[Rh(CO)_2(bdpbz)]^+$ (III), which is generated in situ by treatment of RhCl(CO)(bdpbz) with silver tetrafluoroborate in

TABLE 1

ANALYTICAL, MOLECULAR WEIGHT AND SELECTED IR DATA [a,b]

	Analysis found (calcd.)					IR bands (cm^{-1})	
	C (%)	H (%)	Cl (%)	P (%)	Mol.wt.	ν(CO)	Other
RhCl(CO)(bdpbz) (I) [c]	67.2 (65.3)	4.9 (4.5)	5.2 (5.0)	7.8 (8.6)	692 [d] (717)	1970s	311m [ν(RhCl)]
RhCl(CO)(bdabz) · 1.3CH_2Cl_2 (II) [e]	53.1 (52.7)	4.4 (3.8)	14.1 (13.9)			1960s	306m [ν(RhCl)]
IrCl(CO)(bdpbz) (VI)	57.2 (58.1)	4.8 (4.0)	4.2 (4.4)	6.8 (7.7)		1958s	310s
IrCl(CO)(bdabz) · 1.2CH_2Cl_2 (VII) [e]	48.5 (48.5)	3.4 (3.5)	11.9 (12.1)			1945s	
Ir(H)Cl(CO)(bdpbz-H) · 0.5CH_2Cl_2 (V) [e]	55.6 (55.9)	4.3 (3.9)	8.2 (8.4)	7.1 (7.3)	847 [f] (806)	2020s [g]	2178m [ν(IrH)] [h] 285m [ν(IrCl)] [i]
Ir(H)Cl(CO)(bdabz-H) · 0.3CH_2Cl_2 (VIII) [e]	52.0 (51.3)	4.0 (3.6)	6.7 (6.2)		916 [j] (894)	2026s [k]	2180m [ν(IrH)] [k]
Pt(CH_3)$_2$(bdpbz) (IV)	62.1 (61.9)	5.0 (4.9)			770 [l] (776)		

[a] Abbreviations: bdpbz-H = o-$Ph_2PC_6H_4\dot{C}HCH_2C_6H_4PPh_2$-o; bdabz-H ≡ o-$Ph_2AsC_6H_4\dot{C}HCH_2C_6H_4AsPh_2$-o; s, strong; m, medium. [b] Molecular weights determined by osmometry in CH_2Cl_2 at 25°C except where stated; calcd. values are those of unsolvated complexes. IR data taken from Nujol mull spectra, except where stated. [c] ^1H NMR spectrum showed presence of ca. 0.1 mol n-hexane per mol of complex. [d] 717 ($CHCl_3$, 37°C). [e] Presence of CH_2Cl_2 confirmed by peak at δ 5.3 ppm in ^1H NMR spectrum in $CDCl_3$. [f] 836 ($CHCl_3$, 37°C). [g] 2030 cm^{-1} (CH_2Cl_2). [h] 2200 cm^{-1} (CH_2Cl_2). [i] CsI disc. [j] 926 ($CHCl_3$, 37°C). [k] CH_2Cl_2 solution. [l] In $CHCl_3$ at 37°C.

TABLE 2

^{1}H AND ^{31}P NMR DATA FOR RHODIUM(I), IRIDIUM(I) AND PLATINUM(II) COMPLEXES OF bdpbz AND bdabz [a]

	Solvent (T (°C))	$\delta(CH_2)$	δ(P)	J(M—P)
bdpbz [b]	$CDCl_3$ (32)	3.09s	—15.8	
bdabz	CD_2Cl_2 (32)	3.06s		
RhCl(CO)(bdpbz) (I)	CD_2Cl_2 (32)	4.14m, 3.03m	27.7, 25.7 [c]	127
IrCl(CO)(bdpbz) (VI)	$CDCl_3$ (0)	3.31(br)m, 2.96(br)m	[d]	
$[Rh(CO)_2(bdpbz)]BF_4$ (III)	CD_2Cl_2 (32)	3.44s	27.1d	107
	(—35)	3.1—3.7m ($AA'BB'$)		
$Pt(CH_3)_2$(bdpbz) (IV) [e]	$CDCl_3$ (32)	4.0—4.3m, 2.3—2.6m ($AA'BB'$)	17.8 (1 : 4 : 1t)	1844

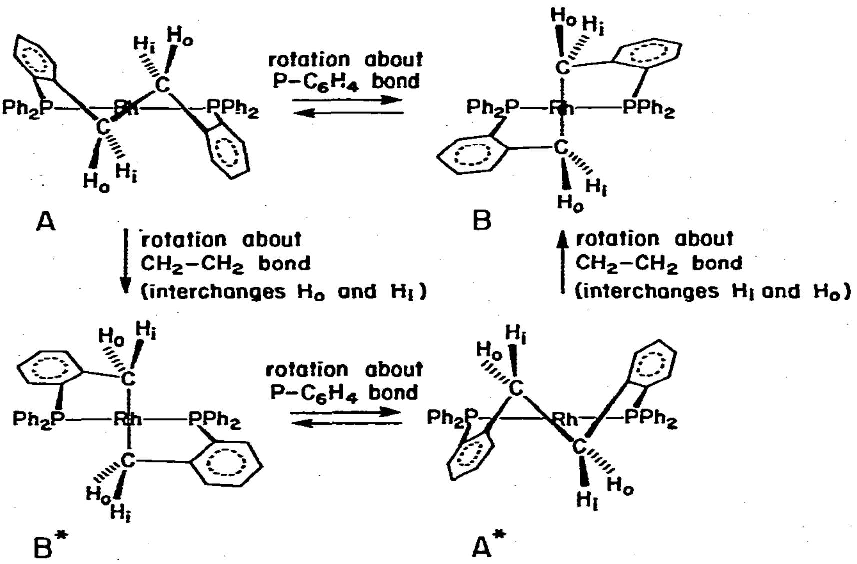
[a] ^{1}H NMR spectra measured at 100 MHz in solvent indicated with internal TMS as reference, $^{31}P\{^1H\}$ spectra measured at 24.3 MHz in CH_2Cl_2 with external 85% H_3PO_4 as reference. Chemical shifts (δ) are in ppm, downfield from reference being taken as positive, ±0.01 ppm for δ(H), ±0.3 ppm for δ(P). Coupling constants are in Hz, ±5 for J(Rh—P) or J(Pt—P). Abbreviations: s, singlet; d, doublet; m, multiplet; t, triplet; br, broad. Aromatic resonances were complex multiplets in range δ 6.8—8.1 ppm. [b] Data from ref. 2. [c] Calculated assuming ^2J(P—P) = 400 Hz, since δ/J is small and weak outer lines of AB quartet were not detected. [d] Could not be measured owing to rapid metallation. [e] $\delta(CH_3)$ 0.39 ppm, J(Pt—H) 70 Hz; splittings due to ^{31}P-coupling 7, 2, and 7 Hz; Aromatic resonances were sharp multiplets in range δ 6.3—7.2 ppm which remained invariant with temperature and broader resonances in range δ 7.2—7.6 ppm which broadened further on heating to 135°C.

an atmosphere of carbon monoxide, is also believed to contain *trans*-chelating bdpbz, since the IR spectrum in dichloromethane shows just one strong ν(CO) band at 2045 cm^{-1}, typical of a *trans*-dicarbonyl. Also, the value of J(Rh—P) obtained from the doublet resonance in the $^{31}P\{^1H\}$ spectrum, 107 Hz, is in reasonable agreement with the values quoted for other cationic carbonyls of rhodium(I) containing *trans*-tertiary phosphines, e.g. $[Rh(CO)(CH_3CN)(PPh_3)_2]ClO_4$, 119 Hz [15], and $[Rh(CO)(bdpps)]BF_4$, 107 Hz [16]. At 32°C in CD_2Cl_2 the methylene protons of $[Rh(CO)_2(bdpbz)]^+$ appear as a singlet which on cooling broadens, sharpens and reaches a limiting spectrum at —51°C. This consists of a complex multiplet spread over 66 Hz (at 100 MHz) (Table 2) which, in contrast with the corresponding multiplet of RhCl(CO)(bdpbz), is symmetrical about the midpoint, and is clearly an $AA'BB'$ spectrum. Owing to the small chemical shift difference between the two sets of protons and the resolution of only ten peaks in the spectrum, individual coupling constants could not be determined. The free energy of activation for the averaging process at the coalescence temperature, between —5°C and —20°C, is estimated to be 13.2 ± 0.5 kcal mol^{-1}.

Examination of a molecular model of $[Rh(CO)_2(bdpbz)]^+$ shows that the nine-membered chelate ring formed by bridging bdpbz can take up two possible conformations in which the carbon—carbon bond of the aliphatic chain is oriented at about 45° (A) or at about 90° (B) respectively to the P—Rh—P axis (Scheme 2). The conformers, which are both chiral, are readily interconverted by rotation about the phosphorus—aromatic carbon bonds of the P—C_6H_4 units. In both conformers each methylene group has an *endo*- and an *exo*-proton with respect to the P—Rh—P axis, so that there are two *endo*- and two *exo*-protons. The molecular model suggests that A is the more stable of the two conformations, because *trans*-annular hydrogen to metal or ligand interaction appears less severe in A than in B. Rotation about the C—C bond of A interchanges the *exo*-

SCHEME 2

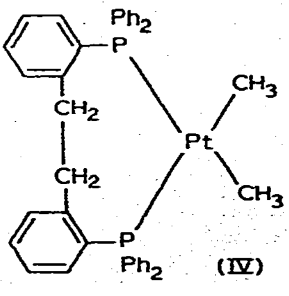
INVERSION OF *trans*-BIDENTATE BDPBZ. A*, B* ARE MIRROR IMAGES OF A AND B, THE OUTER (*exo*) AND INNER (*endo*) PROTONS H_o AND H_i RESPECTIVELY HAVING BEEN INTERCHANGED BY RING INVERSION. A SIMILAR PROCESS CAN BE INVOKED FOR *cis*-BIDENTATE BDPBZ.



and *endo*-protons and gives the mirror image of B which, by rotation about the P—C_6H_4 bonds, gives the mirror image of A. We suggest that this inversion may be responsible for the variable temperature NMR behaviour of $[Rh(CO)_2(bdpbz)]^+$, and tentatively assign the more highly shielded multiplet to the *endo*-protons which are closer to the metal. In the case of RhCl(CO)(bdpbz), inversion separately exchanges the *endo*- and *exo*-protons on each carbon atom, so that the high temperature limiting spectrum should be an $AA'BB'$ pattern. The fact that a rather broad singlet is observed at the fast exchange limit is probably due to the small difference in time-averaged chemical shifts of the protons on the two carbon atoms. At present, there is no obvious explanation for the unexpectedly large difference in free energy of activation for inversion in RhCl(CO)(bdpbz) and $[Rh(CO)_2(bdpbz)]^+$.

cis-Bidentate coordination of bdpbz in a platinum(II) complex

Reaction of bdpbz with $Pt(CH_3)_2(COD)$ gives a colourless, monomeric complex $Pt(CH_3)_2(bdpbz)$ (IV) in which bdpbz functions as a *cis*-bidentate ligand.



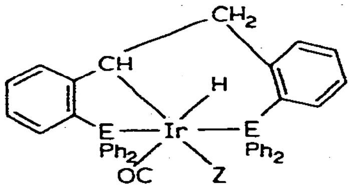
(IV)

The methyl ^{1}H NMR signal consists of a doublet of doublets with ^{195}Pt satellites, the two central lines of the doublet being much more intense than the outer lines (Table 2); this pattern is observed in many other *cis*-dimethylplatinum(II) complexes [17—19], and, as recently noted [18], it cannot be analysed on the basis of $[AX_3]_2$ or $A_3XX'A'_3$. The ^{31}P{^{1}H} NMR spectrum consists of a 1 : 4 : 1 triplet, the magnitude of J(Pt—P), 1844 Hz, being as expected for phosphorus *trans* to methyl [20]. The methylene resonances of bdpbz appear at room temperature as a somewhat broadened pair of resonances at δ 4.0—4.3 and 2.3—2.6 ppm respectively, which, on cooling to 0°C and ^{31}P-decoupling, appear as a well-resolved mirror-image $AA'BB'$ pattern. On warming above room temperature, the signals broaden, coalesce at 69 ± 2°C, and sharpen further, finally appearing as a singlet with a half-height width of about 5 Hz at 135°C. The changes are completely reversible and, over the same temperature range, the methyl resonance pattern remains unchanged, thus ruling out the possibility of ligand exchange. The free energy of activation $\Delta G^{\neq}$ at the coalescence temperature is estimated as 16.1 ± 0.1 kcal mol^{-1}, and the process is presumably inversion of the nine-membered chelate ring. Clearly this can take place irrespective of the mode of attachment (*cis* or *trans*) of the bidentate ligand.

There is no indication of thermal elimination of methane from $Pt(CH_3)_2$(bdpbz) in refluxing benzene or toluene to give a chelate σ-bonded complex $\overline{Pt(CH_3)(o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o)$, whereas on heating bdpbz with various dichloroplatinum(II) complexes, hydrogen chloride is evolved and the chelate σ-bonded complex $\overline{PtCl(o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o)$ is formed [2]. The presumed intermediate in this reaction is $PtCl_2$(bdpbz), containing *trans*-bidentate bdpbz; this geometry forces the CH_2 groups into the axial positions of the metals' coordination sphere and promotes the elimination of HCl.

Metallation of bdpbz and bdabz by iridium(I)

Reaction of bdpbz with $[IrCl(COD)]_2$ in dichloromethane under carbon monoxide at room temperature gives a colourless, crystalline hydrido complex which is formulated as an octahedrally coordinated, metallated species $\overline{Ir(H)Cl(CO)(o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o)$ (V). This is derived by transfer of a benzylic hydrogen atom to the metal and formation of a σ-bond between the metal and the benzylic carbon atom. The IR spectrum in dichloromethane shows a ν(CO) band at 2030 cm^{-1} and a ν(IrH) band at 2200 cm^{-1}, the latter value



(V) E = P, Z = Cl
(VIII) E = As, Z = Cl
(IX) E = As, Z = CO$^+$
(X) E = P, Z = CO$^+$

being typical of an iridium—hydrogen bond *trans* to chloride in octahedral iridium(III) complexes [21]. The structural assignment is supported by the appearance of a triplet resonance in the metal—hydride region of the ^{1}H NMR spectrum at δ —17.43 ppm (τ 27.43), the splittings by the two inequivalent phosphorus atoms being fortuitously equal; the magnitude of the splitting, 14 Hz, indicates that both phosphorus atoms are *cis* to the hydride. The inequivalence of the phosphorus atoms is demonstrated by the observation of an *AB* quartet in the ^{31}P{^{1}H} spectrum; the magnitude of ^{2}J(P—P), 322 Hz, shows that the phosphorus atoms are mutually *trans*. The three aliphatic protons appear as a complex multiplet in the ^{1}H NMR spectrum; after ^{31}P-decoupling the resulting *ABC* pattern can be analysed to yield the coupling constants in Table 3, the magnitudes of which are very similar to those found in the complexes $\overline{\mathrm{IrCl_2(CO)(}o\text{-}\mathrm{Ph_2PC_6H_4C}}\mathrm{HCH_2C_6H_4PPh_2\text{-}}o\mathrm{)}$ [16] and $\overline{\mathrm{PdCl(}o\text{-}\mathrm{Ph_2PC_6H_4C}}\mathrm{HCH_2C_6H_4PPh_2\text{-}}o\mathrm{)}$ [2]. As in these two compounds, the largest coupling constant of 15 Hz is reasonably assigned to that between the geminal CH_2 protons and the remaining two are of the magnitude expected for vicinal couplings in an aliphatic chain [22].

The precursor to V is the iridium(I) complex IrCl(CO)(bdpbz) (VI) which can be isolated in an impure state by carrying out the reaction between [IrCl(COD)]$_2$, bdpbz, and carbon monoxide in toluene at —10°C; it has been identified by IR and ^{1}H NMR spectroscopy (Tables 1 and 2).

Reaction of bdabz with [IrCl(COD)]$_2$ under carbon monoxide gives an immediate precipitate of the iridium(I) complex IrCl(CO)(bdabz) (VII) which re-

TABLE 3

^{1}H AND ^{31}P NMR DATA FOR HYDRIDO—IRIDIUM(III) COMPLEXES DERIVED FROM bdpbz AND bdabz [a]

	Solvent	δ(H)	J(H—H)	J(P—H)
IrCl(H)(CO)(bdpbz-H) (V) [b]	$CDCl_3$	3.17dd (H_A)	AB 15.0	A: sum ~0.5
		3.88m (H_B)	AC 12.5	B: 6, 0
		3.80m (H_C)	BC 2.5	C: 2.5, 0
		—17.43t (IrH)		14, 14
IrCl(H)(CO)(bdabz-H) (VIII)	CD_2Cl_2	3.24dd (H_A)	AB 15.5	
		3.77dd (H_B)	AB 11.0	
		3.83dd (H_C)	BC 2.5	
		—18.90s (IrH)		
[Ir(H)(CO)$_2$(bdpbz-H)]BF_4 (X)	CD_2Cl_2	3.45dd (H_A)	AB 16.5	A: 0
		3.86m (H_B)	AC 11.5	*c*
		3.90m (H_C)	BC 3.0	*c*
		—9.56dd (IrH)		12.5, 16.0
[Ir(H)(CO)$_2$(bdabz-H)]BF_4 (IX)	CD_2Cl_2	3.5—3.65 (H_A, H_B) [d]	AC 11.0	
		3.88dd (H_C)	BC 3.0	
		—10.23s (IrH)		

[a] Ligand abbreviations: bdpbz-H ≡ o-$Ph_2PC_6H_4\dot{C}H_CCH_BH_AC_6H_4PPh_2$-$o$; bdabz-H ≡ o-$Ph_2AsC_6H_4$-$\dot{C}H_CCH_BH_AC_6H_4AsPh_2$-$o$. Other abbreviations as in Table 2, plus: dd, doublet of doublets. ^{1}H—^{1}H coupling constants in Hz, ±0.5. All spectra recorded at 32°C, other conditions as in Table 2. [b] δ(P) (by INDOR on Ir—H resonance in CD_2Cl_2) 28.4, 0.6 ppm (from 85% H_3PO_4); ^{2}J(P—P) 322 Hz (±10). [c] Coupled to ^{31}P, but overlap prevented determination of J(P—H). [d] Overlapping impurity resonance prevented determination of δ(H_A), δ(H_B), and J(*AB*).

sembles the analogous rhodium(I) compound in being almost insoluble in chloroform or dichloromethane. On refluxing in chloroform, VII undergoes metallation at a benzylic carbon atom to give a colourless hydrido complex VIII, the spectroscopic parameters of which are very similar to those of the corresponding bdpbz complex V (Table 3). Owing to the low solubility of VII in organic solvents, quantitative comparisons of the rates of internal metallation of VI and VII cannot be made, but qualitatively the order is VI > VII. The same trend was also found in the *ortho*-metallation of $\mathrm{IrCl(EPh_3)_3}$ (E = P, As) [23]. No further dehydrogenation of the bibenzyl ligands to coordinated stilbenes is observed in the iridium complexes under the relatively mild conditions so far employed.

Preliminary experiments show that VII, suspended in dichloromethane, undergoes metallation on treatment with silver tetrafluoroborate in the presence of carbon monoxide. Monitoring of the course of the reaction by IR spectroscopy shows the presence of a transient intermediate species, presumably $[\mathrm{Ir(CO)_2(bdabz)}]^+$, which has a $\nu(\mathrm{CO})$ at 2020 $\mathrm{cm^{-1}}$. This absorption is rapidly replaced by the $\nu(\mathrm{CO})$ and $\nu(\mathrm{IrH})$ bands of the stable, colourless, cationic complex $[\overline{\mathrm{Ir(H)(CO)_2\{\textit{o}\text{-}Ph_2AsC_6H_4C}}\mathrm{HCH_2C_6H_4AsPh_2\text{-}\textit{o}\}}]^+$ (IX) which has been further characterised by its ^{1}H NMR parameters (Table 3). The corresponding metallated cationic bdpbz complex X can be similarly generated in solution by treating either V or VI with silver tetrafluoroborate under carbon monoxide. Both IX and X show two strong $\nu(\mathrm{CO})$ bands in solution, as expected for a *cis*-dicarbonyl, and the chemical shifts of the hydride ligands are in the region δ —10 ppm (τ 20) characteristic of H *trans* to CO in octahedral iridium(III) complexes [24,25], in agreement with the proposed structures.

The isolation of stable hydridoiridium(III) complexes formed by hydrogen abstraction from the bibenzyl chain of bdpbz supports the mechanism given in Scheme 1 for the rhodium-promoted dehydrogenation of bdpbz to RhCl(bdpps). It is well known that a benzylic hydrogen atom of tri-*o*-tolylphosphine or phenyldi-*o*-tolylphosphine can be eliminated on reaction with various metal complexes in the form of a simple molecule such as HCl or $\mathrm{CH_4}$, a stable five membered chelate ring being formed (eq. 1—4). The present work provides the first instance in which the type of hydrido complex which may be intermediate in some of these cyclometallations has been isolated.

$$\mathrm{RhCl_3 + (\textit{o}\text{-}tol)_3P \xrightarrow[heat]{CH_3OCH_2CH_2OH} [\overline{RhCl_2\{P(\textit{o}\text{-}C_6H_4C}H_2)(\textit{o}\text{-}tol)_2\}]_3} \qquad [26]\ (1)$$

$$\mathit{trans}\text{-}\mathrm{PtCl_2\{P(\textit{o}\text{-}tol)_2Ph\}_2 \xrightarrow[heat]{CH_3OCH_2CH_2OH}}$$

$$\mathrm{\overline{PtCl\{P(\textit{o}\text{-}C_6H_4C}H_2)(\textit{o}\text{-}tol)Ph\}\{P(\textit{o}\text{-}tol)_2Ph\}} \qquad [27,28]\ (2)$$

$$\mathrm{Pt(CH_3)_2\{(\textit{o}\text{-}tol)_2P(CH_2)_\textit{n}P(\textit{o}\text{-}tol)_2\} \xrightarrow{heat}}$$

$$\mathrm{\underline{\overline{Pt(\textit{o}\text{-}tol)(\textit{o}\text{-}C_6H_4C}H_2)P(CH_2)_\textit{n}P(\textit{o}\text{-}C_6H_4C}H_2)(\textit{o}\text{-}tol)}$$

$$(n = 2, 3) \qquad [29]\ (3)$$

$$\mathrm{CH_3Mn(CO)_5 + (\textit{o}\text{-}tol)_3P \xrightarrow[heat]{THF} \overline{Mn(CO)_4\{P(\textit{o}\text{-}C_6H_4C}H_2)(\textit{o}\text{-}tol)_2\}} \qquad [30]\ (4)$$

Experimental

Analytical, solvent drying, IR and NMR spectroscopic procedures have been described elsewhere [31]. The ^1H NMR spectrum of RhCl(CO)(bdpbz) (I) in the temperature range 32—143°C was measured in C_6D_5Br using hexamethyldisiloxane as internal reference. The ^1H NMR spectrum of $Pt(CH_3)_2$(bdpbz) (IV) in the same temperature range was measured in C_6D_5Br containing 10% C_6H_6 as internal reference; in the range 0—34°C CD_2Cl_2 was used as solvent with internal TMS as reference. The chemical shifts of the methylene resonances were insensitive to these changes of solvent. Temperatures were obtained from the variation of chemical shift of ethylene glycol hydroxyl protons, and are probably accurate to ±3°C.

2,2′-Bis(diphenylphosphino)bibenzyl, bdpbz, [2] and the 1,5-cyclooctadiene complexes $[MCl(COD)]_2$ (M = Rh, Ir) [32,33] and $Pt(CH_3)_2$(COD) [34] were prepared as described. 2,2′-Bis(diphenylarsino)bibenzyl, bdabz, was prepared as colourless crystals, m.p. 152°C, in 43% yield from chlorodiphenylarsine and the di-Grignard reagent of 2,2′-dibromobibenzyl, following the procedure described for bdpbz [2].

Preparations

{2,2′-Bis(diphenylphosphino)bibenzyl}carbonylchlororhodium(I), RhCl(CO)(bdpbz) (I). A solution of bdpbz (0.222 g, 0.4 mmol) in dichloromethane (20 ml) was saturated with carbon monoxide and treated with 0.1 g (0.2 mmol) of $[RhCl(COD)]_2$. After being stirred under carbon monoxide for 1 min, the orange solution was chromatographed on 60—100 mesh Florisil, and the complex was eluted as a yellow band with dichloromethane. The eluate was evaporated to ca. 10 ml under reduced pressure, and the product was crystallised as a pale yellow, microcrystalline n-hexane solvate by slow addition of n-hexane (20 ml). Drying at 25°C/10^{-3} mmHg did not remove all the occluded solvent. The yield was about 85%.

{2,2′-Bis(diphenylarsino)bibenzyl}carbonylchlororhodium(I), RhCl(CO)(bdabz) (II). This was prepared as above, starting from bdabz (0.26 g, 0.4 mmol) and $[RhCl(COD)]_2$ (0.1 g, 0.2 mmol) in dichloromethane (20 ml). The yellow, crystalline product, solvated with dichloromethane, precipitated almost quantitatively from the reaction mixture over a 30 min period.

The corresponding iridium(I) complex, IrCl(CO)(bdabz) (VII) was prepared similarly.

{2,2′-Bis(diphenylphosphino)bibenzyl}carbonylchloroiridium(I), IrCl(CO)(bdpbz) (VI). A solution of bdpbz (0.164 g, 0.3 mmol) in chloroform (20 ml) or toluene (20 ml) was cooled to 0°C, saturated with carbon monoxide, and treated with $[IrCl(COD)]_2$ (0.20 g, 0.3 mmol). The cold solution was filtered rapidly into n-hexane to precipitate pale yellow microcrystals of the product.

{2,2′-Bis(diphenylphosphino)bibenzyl}dimethylplatinum(II), $Pt(CH_3)_2$(bdpbz) (IV). A solution of $Pt(CH_3)_2$(COD) (0.066 g, 0.2 mmol) and bdbpz (0.11 g, 0.2 mmol) in benzene (20 ml) was heated under reflux in a nitrogen atmosphere for 2 h. The mixture was evaporated to dryness under reduced pressure and the residue was recrystallized from dichloromethane/methanol to give colourless crystals of the product, m.p. 224—225°C (dec.) (0.45 g, 61%).

{1,2-Bis[(o-diphenylphosphino)phenyl]ethyl}carbonylchlorohydridoiridium(III), $\overline{Ir(H)Cl(CO)\{o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o\}$ *(V).* A solution of bdpbz (0.164 g, 0.3 mmol) in dichloromethane (50 ml) was saturated with carbon monoxide at room temperature, and treated with $[IrCl(COD)]_2$ (0.20 g, 0.3 mmol). The solution was allowed to stand under carbon monoxide, and the isomerisation from VI to V was followed by monitoring the band at 1960 cm^{-1} due to VI. After ca. 1 h, the almost colourless solution was filtered, evaporated under reduced pressure to ca. 10 ml volume, and treated dropwise with n-hexane (20 ml). After 24 h, the supernatant liquid was decanted, and the resulting colourless crystalline product was washed with isopentane. After drying in vacuo, the yield was 90%.

{1,2-Bis[(o-diphenylarsino)phenyl]ethyl}carbonylchlorohydridoiridium(III), $\overline{Ir(H)Cl(CO)\{o\text{-}Ph_2AsC_6H_4C}HCH_2C_6H_4AsPh_2\text{-}o\}$ *(VIII).* The complex IrCl(CO)(bdabz), VII, (0.2 g) was heated under reflux in chloroform (50 ml) for 4 h. The solution was filtered, and worked-up as described for V to give the colourless, crystalline product in 88% yield.

trans-{2,2'-Bis(diphenylphosphino)bibenzyl}dicarbonylrhodium(I)tetrafluoroborate, $[Rh(CO)_2(bdpbz)]BF_4$ *(III).* This was generated in situ, but not isolated. A solution of complex I (~50 mg) in dry dichloromethane or chloroform was saturated with carbon monoxide and treated with an excess of silver tetrafluoroborate which had previously been dried in vacuo. The mixture was stirred for 1 min under carbon monoxide and filtered to give a deep orange-yellow solution, IR (CH_2Cl_2): 2045s cm^{-1} [ν(CO)]. Solutions for NMR work were prepared similarly using CD_2Cl_2 or $CDCl_3$.

The hydridoiridium(III) cations IX and X were similarly generated in solution from V, VI or VIII and silver tetrafluoroborate. IR (CH_2Cl_2) (IX): 2155m [ν(IrH)], 2100s, 2056s cm^{-1} [ν(CO)]; (X) 2166m [ν(IrH)], 2104s, 2065s cm^{-1} [ν(CO)].

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