Complexes of Rhodium and Iridium with the β-Ketophosphines PBu$^t_2$(CH$_2$COR) (R = Ph or Bu^t) †

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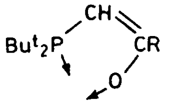
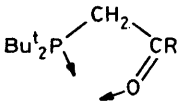
The bulky β-ketophosphines PBu$^t_2$(CH$_2$COPh) (Q) and PBu$^t_2$(CH$_2$COBu^t) (Q′) are shown to behave towards rhodium or iridium either as unidentate ligands (through phosphorus), as bidentate ligands through phosphorus and the keto-group, or as bidentate enolate ions. Treatment of [Rh$_2$Cl$_2$(CO)$_4$] with Q or Q′ gives *trans*-[RhCl(CO)Q$_2$] or *trans*-[RhCl(CO)Q′$_2$] These react with sodium methoxide to give complexes of type [Rh(CO){Bu$^t_2$PCH=C(O)R}{PBu$^t_2$(CH$_2$COR)}] (R = Ph or Bu^t) which with hydrogen chloride give back *trans*-[RhCl(CO){PBu$^t_2$(CH$_2$COR)}$_2$]. The salt RhCl$_3$·3H$_2$O with PBu$^t_2$(CH$_2$COPh) gives [RhCl$_2${Bu$^t_2$PCH=C(O)Ph}-{PBu$^t_2$(CH$_2$COPh)}] (4a) in which both phosphines are bidentate and which the keto-group is strongly co-ordinated, not being displaced by vigorous treatment with carbon monoxide. This six-co-ordinate rhodium(III) complex with sodium methoxide rapidly gives what appears to be an intensely blue rhodium(II) complex [Rh{Bu$^t_2$PCH=C(O)Ph}$_2$]. Iridium trichloride with PBu$^t_2$(CH$_2$COR) similarly gives the six-co-ordinate [IrCl$_2${Bu$^t_2$PCH=C(O)R}{PBu$^t_2$(CH$_2$COR)}] [R = Ph (4b) or Bu^t (4c)]. These with sodium ethoxide give purple five-co-ordinate square-pyramidal hydrides [IrH{Bu$^t_2$PCH=C(O)R}$_2$] (7a) and (7b) which are quite stable to prolonged exposure to air and show ^{1}H(hydride) shifts to exceptionally high field. They both take up carbon monoxide to give colourless hydridocarbonyls [IrH(CO){Bu$^t_2$PCH=C(O)R}$_2$] (9a) and (9b) which lose carbon monoxide on heating to give back the five-co-ordinate hydrides. Carbonylation of Na$_2$[IrCl$_6$] followed by addition of PBu$^t_2$(CH$_2$COPh) gives [IrH(Cl)(CO){Bu$^t_2$PCH=C(O)Ph}{PBu$^t_2$(CH$_2$COPh)}] (11a) with an unco-ordinated keto-group. With base (NaOEt) this gives a mixture of (9a) and *trans*-[IrCl(CO){PBu$^t_2$(CH$_2$COPh)}$_2$] (unidentate phosphines). Similar addition of PBu$^t_2$(CH$_2$COBu^t) to a carbonylated solution of Na$_2$[IrCl$_6$] gives a [IrHCl$_2$(CO){PBu$^t_2$CH$_2$COBu^t}$_2$] (10a) contaminated with about 10% of [IrH(Cl)(CO){Bu$^t_2$PCH=C(O)Bu^t}-{PBu$^t_2$(CH$_2$COBu^t)}] (11b). When this mixture is heated in chloroform it gives almost pure (11b) contaminated by *ca.* 2—3% of (10a). Proton and ^{31}P n.m.r. and i.r. data are given and discussed.

In the preceding paper [1] we have described the bulky β-ketophosphines PBu$^t_2$(CH$_2$COPh) (Q) and PBu$^t_2$(CH$_2$COBu^t) (Q′) and some of their complexes with nickel(II), palladium(II), or platinum(II). These phosphines were shown to act as unidentate ligands (through phosphorus) or, by loss of a proton, as the bidentate enolate ions (1). It had also been anticipated that these β-ketophosphines might act as neutral bidentate ligands (2) using the keto-oxygen as a donor atom. Another possibility was that interaction with the keto-oxygen (a hard donor) might not occur in the ground state but could stabilize a polar transition state; we have observed such an interaction (neighbouring-group participation or anchimeric assistance) in oxidative-addition reactions of *trans*-[IrCl(CO)(Me$_2$PC$_6$H$_4$OMe-2)$_2$].[2] We have now investigated the action of these two β-ketophosphines on rhodium and iridium chlorides. Several examples of each type of interaction, *viz.* unidentate, bidentate enolate (1), or bidentate keto (2), have been found and some unusual types of complex isolated and characterized.



(1)

(a) R = Ph
(b) R = Bu^t



(2)

RESULTS AND DISCUSSION

Treatment of an ethanolic solution of [Rh$_2$Cl$_2$(CO)$_4$] with Q or Q′ gave *trans*-[RhCl(CO)Q$_2$] or *trans*-[RhCl(CO)Q′$_2$]. The microanalytical data are in Table 1 and i.r. and n.m.r. data in Table 2. The 1 : 2 : 1 triplet patterns of the Bu^t or CH$_2$ groups in the ^{1}H n.m.r. spectra indicate the *trans* arrangement. The keto-group gives a strong sharp, i.r. absorption peak at 1 689 cm^{-1} (Q) or 1 711 cm^{-1} (Q′), values which are very similar to those found for the complexes of type *trans*-[MCl$_2$L$_2$] (M = Pd or Pt, L = Q or Q′) and suggesting no interaction of the keto-group with the rhodium. These complexes *trans*-[RhCl(CO){PBu$^t_2$(CH$_2$COR)}$_2$] (R = Ph or Bu^t) were recovered unchanged after being heated under reflux in 2-methoxyethanol for 1 h, but when treated with sodium methoxide the complexes (3a) and (3b), containing both unidentate (Q and Q′) and enolate (1a and 1b) ligands, were formed in good yield. With these complexes a band due to ν(C=O) (unco-ordinated) is still present in the i.r. spectrum, but additional strong bands occur in the range 1 475—1 525 cm^{-1} attributed to mixed ν(C=C) + ν(C–O) of the enolate system (1). Similar bands were found in the i.r. spectra of nickel, palladium, and platinum complexes containing these enolate ligands and by Carty *et al.*[3] for [PdCl{Ph$_2$PCH=

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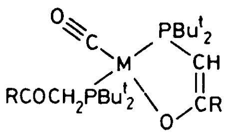
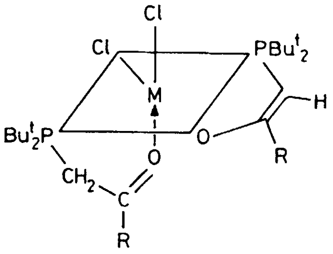
† No reprints available.

C(O)CF$_3$}{PPh$_2$(OEt)}]. The ^{31}P n.m.r. spectra of (3a) and (3b) show the *AB* portions of *ABX* patterns (*X* is ^{103}Rh): the large value of ^2J(PP) (*ca.* 300 Hz) indicates a *trans* arrangement of phosphorus nuclei. In the ^{1}H n.m.r. spectra the PBu$^t_2$ groups resonate as doublets of doublets and with (3b) the =C(O)Bu^t and (C=O)Bu^t groups as singlets at δ = 1.03 and 1.19 p.p.m. With (3a) the vinylic proton gives a doublet of doublets with couplings of 2.9 and 1.9 Hz, although we cannot say which of these is ^2J(PH) and which is ^4J(PH). With (3b) the vinylic proton resonates as a triplet since ^2J(PH) ≃ ^4J(PH) ≃ 2 Hz. The methylene protons show coupling to both phosphorus donor atoms. Treatment of either (3a) or (3b) with 1 mol equivalent of hydrogen chloride in diethyl ether caused ring opening (*i.e.* protonation with addition of chloride ion) to give back the complexes of type *trans*-[RhCl(CO){PBu$^t_2$(CH$_2$COR)}$_2$].



(3a) M = Rh, R = Ph
(3b) M = Rh, R = Bu^t
(3c) M = Ir, R = Ph



(4a) M = Rh, R = Ph
(4b) M = Ir, R = Ph
(4c) M = Ir, R = Bu^t

TABLE 1

Melting point, microanalytical, and molecular-weight data for rhodium and iridium complexes formed from PBu$^t_2$(CH$_2$COPh) (Q) and PBu$^t_2$(CH$_2$COBu^t) (Q′)

Compound	M.p. (θ$_c$/°C)	Analysis (%) C	H	Cl	*M* [a,b]
(*a*) Rhodium					
trans-[RhCl(CO)Q$_2$]	175—190	57.15 (57.0)	7.35 (7.25)	5.35 (5.1)	
(3a)	165—166	59.85 (60.2)	7.45 (7.5)		665 (658)
(4a)	190—193	54.95 (54.7)	7.3 (7.2)	10.3 (10.1)	695 (702)
trans-[RhCl(CO)Q′$_2$]	162—180	53.55 (53.2)	8.95 (8.9)	5.45 (5.4)	
(3b)	136—140	56.1 (56.3)	9.15 (9.3)		615 (618)
(*b*) Iridium					
(4b)	226—227	48.35 (48.5)	6.3 (6.5)	8.8 (8.9)	794 (793)
(7a)	220—223	53.1 (53.4)	6.75 (6.85)		703 (720)
(9a)	decomp. [d]	53.4 (53.0)	6.5 (6.6)		775 (748)
(11a)	165—175	50.7 (50.5)	6.5 (6.4)	4.75 (4.5)	784 (784)
(4c)	238—240 [c]	44.75 (44.7)	7.85 (7.9)	9.2 (9.4)	741 (753)
(7b)	222—225	49.55 (49.5)	8.55 (8.45)		673 (680)
(9b)	decomp.[e]	49.05 (49.2)	8.05 (8.1)		731 (708)
(11b)	165—180 [c]	46.0 (46.8)	7.5 (7.8)	5.0 (4.8)	

[a] Theoretical values in parentheses. [b] Osmometrically in chloroform at 30 °C. [c] With decomposition. [d] Above 200 °C loses carbon monoxide to give (7a). [e] Above 200 °C loses carbon monoxide to give (7b). [f] Contaminated with (10a), see text.

Treatment of hydrated rhodium trichloride with 4 mol equivalents of PBu$^t_2$(CH$_2$COPh) in ethanol at room temperature gave the complex [RhCl$_2${Bu$^t_2$PCH=C(O)-Ph}{PBu$^t_2$(CH$_2$COPh)}] (orange) which we formulate as (4a), containing a co-ordinated keto-group as in (2a). The far-i.r. spectrum shows two strong bands due to ν(Rh–Cl) at 310 and 337 cm^{-1} suggesting a *cis* arrangement of chlorines each *trans* to oxygen. The i.r. spectrum also shows the absence of an unco-ordinated keto-group, but the presence of a very strong band at 1 581 cm^{-1} which we attribute to ν(C=O) (co-ordinated). Additionally, a strong band at 1 519 cm^{-1} is attributed to ν(C=C) + ν(C=O) of the enolate system and a band at 1 554 cm^{-1} also to this enolate system or possibly to the keto-group. (Two bands appear because of solid-state effects.) No similar complexes have been reported before although acetone complexes of the platinum metals are known,[4,5] *e.g.* [RuCl$_3$(PPh$_3$)$_2$(CH$_3$COCH$_3$)] shows a band due to ν(C=O) at 1 656 compared with 1 712 cm^{-1} for unco-ordinated acetone.[5] These co-ordinated acetone ligands are easily replaced by other ligands and appear to be only weakly bonded. In contrast, (4a) was recovered unchanged after being treated with carbon monoxide in refluxing 2-methoxyethanol for 24 h. A five-co-ordinate rhodium(III) complex would be expected to take up carbon monoxide readily. The ^{31}P n.m.r. spectrum of (4a) shows the *AB* portion of an *ABX* pattern with a large (324 Hz) value for ^2J(PP), indicating mutually *trans*-phosphorus donor atoms. The ^{1}H n.m.r. spectrum shows a very complex signal for the four Bu^t groups, a doublet of doublets for the vinylic proton, and a poorly resolved pattern for the two non-equivalent methylene hydrogens.

The iridium analogues [IrCl$_2${Bu$^t_2$PCH=C(O)R}{PBu$^t_2$-(CH$_2$COR)}] (4b; R = Ph) and (4c; R = Bu^t) were obtained by heating hydrated iridium trichloride with the ketophosphine in propan-2-ol for 20 h. Values of ν(Ir–Cl), ν(C=O), and ν(C=C) + ν(C–O) (Table 2) are similar to those found for the rhodium complex (4a) and are consistent with the assigned structures. The ^{31}P n.m.r. pattern of (4c) shows an *AB* pattern with only 3 p.p.m. difference between the two chemical shifts, ^2J(P$_A$P$_B$) = 420 Hz. With (4b) the two phosphorus chemical shifts must be even closer and only a broad singlet is observed. The ^{1}H n.m.r. spectrum of (4b) is complex. Broad resonances due to PCH$_2$ and CH=C(O) are observed and the t-butyl resonances are overlapping and complex. The proton spectrum of (4c) was deter-

TABLE 2

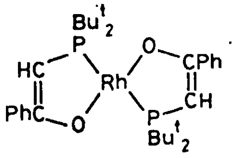
Phosphorus-31 and ^1H n.m.r. and i.r. data for some rhodium and iridium complexes of $PBu^t_2(CH_2COPh)$ (Q) and $PBu^t_2(CH_2COBu^t)$ (Q′)

	^{31}P N.m.r.[a]			^1H N.m.r.[b]				I.r. (cm^{-1}, in Nujol)				
Complex	δ	^2J(PP)	^1J(RhP)	δ(Bu^t)[c]	δ(CH_2CO)	δ(*CH*=C)	δ(IrH)	ν(C≡O)	ν(Ir–H)	ν(C=O)	ν(C=C) + ν(C–O)	ν(M–Cl)
(*a*) Rhodium												
trans-[RhCl(CO)Q_2]	73.0 [d]		126	1.51 (t) (14.2)	4.21 (br)			1 951s, 1 931s, 1 939s (in benzene)		1 689		286s
(3a)	65.8 [d] 82.8	283	127 132	1.46 (dd) (12.2) [e] (1.1) 1.38 (dd) (12.7) [e] (1.2)	4.03 ^2J(HH) = 1.0 4.04	4.73 (dd) J(PH) = {2.9, 1.9		1 927s, 1 974s, 1 933s (in benzene)			1 512s 1 480s	
(4a) [f]	66.8 [d] 57.8	325	88 88	1.6 (m)	3.93 ^2J(HH) nr 4.03	4.75 (dd) J(PH) = {5.5, 2.4				1 581 1 554s	1 519	310s 337s
trans-[RhCl(CO)Q'_2]	62.5 [d]		122	1.45 (t) (14.0), 1.25 [g]	3.66 (t) [e]			1 930s, 1 936s (in benzene)		1 711s		289s
(3b) [f]	56.5 [d] 83.8	279	127 132	1.40 (d) (13.2) 1.32 (d) (13.2), 1.19 (s) [g] 1.03 (s) [g]	1.03 ^2J(HH) nr 1.19	3.89 (t)		1 939s		1 711s 1 709 (in benzene)	1 509s	
(*b*) Iridium												
(4b)	24.9			1.61 (t) (11.7), 1.49 (t) (12.7)	3.74 (m)	4.66(m)				1 538s	1 525s	328s, 299s
(7a)	65.8			1.36 (t) (14.6)		4.99 (t) (6.7) [e]	−47.3 (t) (11.5) [e]				1 514s	
(9a)	59.8			1.64 (t) (14.0), 1.55 (t) (14.0)		4.85 (t) (7.3) [e]	−6.3 (t) (14.5) [e]	1 992s, 1 995 (in benzene)	2 218m		1 520s	
(11a)	65.9	290		1.60 (d) (14.7),[e] 1.50 (d) (14.0),[e] 1.40 (d) (14.0),[e] 1.26 (d) (13.9)[e]	5.33 (7.9),[e] 4.97 (9.6) [e] ^2J(HH) = 17	4.78 (t) (9.8)	−15.6 (dd) (13.0, 9.6)	2 009s 2 005 (in benzene)	2 342m	1 674s	1 533s	257s
(4c) [h]	24.4 21.3	420		1.81 (dd) (8.0, 5.0),[e] 1.57 (dd) (7.7, 5.6),[e] 1.37 (dd) (7.8, 4.9),[e] 1.45,[g] 0.96 (s) [g]	3.2 (7.0),[e] 3.0 (7.0),[e] ^2J(HH) = 17	4.23 (t) (9.0)[e]				1 586s	1 523s	327s 297s
(7b)	65.8			1.43 (t) (13.6), 1.45 (s) [g]		4.3 (t) (6.8) [e]	−48.1 (t) (11.5)				1 510s	
(9b)	59.4			1.56 (t) (13.8), 1.49 (t) (14.0)		4.11 (t) (8.6)	−6.8 (t) (15.5)	1 992s 1 991 (in benzene)	2 220m 2 218 (in benzene)		1 512s	
(11b)	66.4 54.7	288		1.73 (d) (14.2),[e] 1.69 (d) (13.7),[e] 1.61 (d) (13.7),[e] 1.39 (d) (13.2),[e] 1.43 (s),[g] 1.39 (s) [g]	5.29 (4.6),[e] 4.39 (10.6) [e] ^2J(HH) = 18.3							
(10a)	32.6			1.64 (t) (14.0), 1.69 (t) (14.2), 1.28 (s) [g]	4.86 (7.6), 4.10 (5.2), ^2J(HH) = 18.0		−15.4 (t) (23.0)	2 105s 2 010 (in benzene)	2 310m	1 705s		299s 240s

[a] Recorded at 36.43 MHz and ambient temperature in C_6D_6 unless stated otherwise. δ±0.1 p.p.m., J ±3 Hz. [b] Recorded at 60 MHz and 34 °C in $CDCl_3$ solution unless stated otherwise. s = Singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad, nr = not resolved. J ±0.5 Hz shown in parentheses, δ ±0.2 p.p.m. [c] Values of ^{3+5}J(PH) shown in parentheses unless marked *e*. [d] In $CDCl_3$. [e] J(PH) values, other than ^{3+5}J(PH), are given in parentheses and/or in text. [f] Proton spectrum at 90 MHz. [g] δ(CBu^t). [h] Proton spectrum at 220 MHz.

mined at 220 MHz and confirms the assigned structure. The methylene protons resonate as the *AB* part of an *ABX* spectrum (*X* is the phosphorus to which they are attached), the =C(O)Bu^t and Bu^tC=O groups give singlet resonances, and the four PBu^t groups give doublets of doublets [due to ^3J(PH) and ^5J(PH) coupling], two of which overlap.

Since the keto-group in complexes of type (4) is co-ordinated to the metal one would anticipate that a base-promoted conversion into the co-ordinated enolate ligand (1) should occur readily. Treatment of an alcoholic solution of the rhodium(III) complex (4a) with sodium methoxide gave an immediate, intensely blue precipitate of what we suggest is a rhodium(II) complex *trans*-$[Rh\{Bu^t_2PCH{=}C(O)Ph\}_2]$ (5). Several rhodium(II) complexes with bulky tertiary phosphine ligands (L) have been described previously,[6-8] *e.g.* of types *trans*-$[RhCl_2L_2]$ [L = $P(C_6H_4Me\text{-}o)_3$, $PPh(C_6H_4Me\text{-}o)_2$,[6] $PMeBu^t_2$, $PEtBu^t_2$, or $PPr^nBu^t_2$ [7]] and *trans*-$[Rh(Bu^t_2PC_6H_4O\text{-}2)_2]$ (6).[8] These are highly coloured, *e.g.* *trans*-$[Rh(Bu^t_2PC_6H_4O\text{-}2)_2]$ is intensely blue.[8] They are also paramagnetic although $\mu_{eff.}$ in the solid state is often very much lower than the 'spin-only' value expected for one unpaired electron.[6,7] This was attributed to some interaction in the solid; in solution $\mu_{eff.}$ is much closer to the value expected for one unpaired electron.[7] These paramagnetic rhodium(II) complexes all show broad and ill defined ^{1}H n.m.r. spectra, whereas for example the corresponding rhodium(III) hydrides *trans*-[RhHCl$_2$L$_2$] show well defined ^{1}H n.m.r. spectra. Although not fully chracterized, we suggest that the blue material described in this paper is the rhodium(II) complex *trans*-[Rh{Bu$^t_2$PCH=C(O)Ph}$_2$] since: (*i*) its i.r. spectrum (250—4 000 cm^{-1}) is virtually identical to that of *trans*-[Pd{Bu$^t_2$PCH=C(O)Ph}$_2$]; (*ii*) its ^{1}H n.m.r. spectrum is very broad and ill defined as are the spectra of other rhodium(II)-tertiary phosphine complexes; and (*iii*) the microanalytical data (C, H) are close to that expected (Found: C, 60.3; H, 7.2. Calc. for C$_{32}$H$_{48}$P$_2$Rh: C, 61.0; H, 7.7%).



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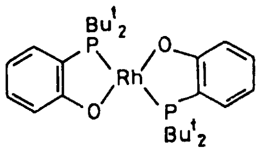
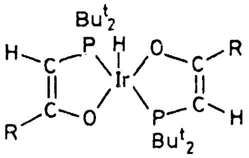


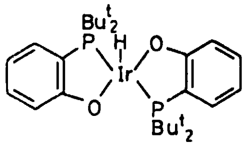
(6)

When carbon monoxide was bubbled through a dichloromethane solution of (5) a colour change from intense blue to golden brown occurred but we were unable to isolate any solid compounds from the solution. Treatment of a benzene–methanol solution of (5) with sodium tetrahydridoborate gave a red solution which immediately turned blue on exposure to air and (5) could be recovered. An orange-red solid was isolated from the red solution but we were unable to purify or identify it. Its ^{1}H n.m.r. spectrum (in C$_6$H$_6$) showed two well defined triplets for the Bu^t groups [δ = 1.50 p.p.m., ^{3+5}J(PH) = 14.0 Hz; δ 1.52 p.p.m., ^{3+5}J(PH) = 13.7 Hz] and a triplet for the vinylic protons [δ = 4.99 p.p.m., ^{2+4}J(PH) = 4.8 Hz]. No resonance due to a hydride or borohydride group was detected. We tentatively suggest that this very air-sensitive orange-red product is a borohydride complex [Rh(BH$_4$){Bu$^t_2$PCH=C(O)Ph}$_2$] for which the resonance of the BH$_4$ group is so broadened by quadrupole broadening that we could not observe it. We have previously found that compounds of type [MH$_2$(BH$_4$)(PBu$^t_2$R)$_2$] (M = Rh or Ir) have BH$_4$ resonances which are very difficult to detect because of quadrupole broadening.[9,10]

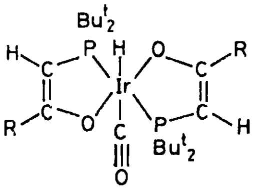
Similar treatment of the iridium(III) complexes (4b) or (4c) with sodium ethoxide in ethanol produces colourless solutions which rapidly turn purple. Purple five-co-ordinate hydrides [IrH{Bu$^t_2$PCH=C(O)R}$_2$] (7a) and (7b) were readily isolated and found to be quite stable in solution when exposed to air (dioxygen). This contrasts with the behaviour of the related purple five-co-ordinate hydride (8) which decomposes rapidly in air to the red iridium(II) complex [Ir(Bu$^t_2$PC$_6$H$_4$O-2)$_2$] and then the cyclometallated [Ir{Bu$^t_2$PCMe$_2$CH$_2$(C$_6$H$_4$O)}(Bu$^t_2$PC$_6$H$_4$O)] complex.[11,12] We cannot explain the difference in behaviour between complexes of types (7) and (8). The ^{1}H n.m.r. spectra of (7a) and (7b) show the expected t-butyl and vinyl hydrogen triplets (Table 2) and the hydride resonances at very high field [(7a), δ = −47.25 p.p.m., ^2J(PH) = 11.5 Hz; (7b), δ = −48.1 p.p.m., ^2J(PH) = 11.5 Hz]. The i.r. spectra showed no bands due to ν(Ir–H) but this is not uncommon for square-pyramidal iridium(III) hydrides with bulky phosphine ligands.[11,12] Strong bands due to ν(C=C) + ν(C–O) were present in the i.r. spectra (Table 2). A characteristic of five-co-ordinate iridium(III) hydrides such as (8) is a rapid reaction with small rod-like molecules such as carbon monoxide to give six-co-ordinate species. We find that (7a) or (7b) react rapidly with carbon monoxide in benzene solution to give colourless carbonyl hydrides (9a) or (9b) respectively. The microanalytical, n.m.r., and i.r. data are in agreement with the formulation. The hydride resonance shifts to high frequency by over 40 p.p.m. on carbonylation, which is typical for such a reaction. When heated strongly (to *ca.* 200 °C) the six-co-ordinated carbonyl hydrides (9a) or (9b) lose carbon monoxide and give back the five-co-ordinated hydrides (7a) or (7b) in good yield. The pyrolyses were conducted in air which illustrates the great thermal stability and stability to oxygen of these five-co-ordinate hydrides (7a) or (7b).



(7a) R = Ph
(7b) R = Bu^t



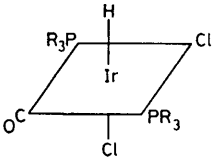
(8)



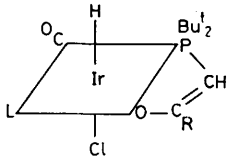
(9a) R = Ph
(9b) R = Bu^t

It has been shown previously that prolonged carbonylation of ethanolic solutions of Na$_2$[IrCl$_6$] or H$_2$IrCl$_6$, followed by addition of tertiary phosphines, gives hydridocarbonyliridium(III) complexes [IrHCl$_2$(CO)(PR$_3$)$_2$] (10).[13] We have now investigated the products formed by adding the ketophosphines PBu$^t_2$(CH$_2$COR) to the carbonylated solutions. The results for R = Ph will be described first and were different from those with R = Bu^t. After adding PBu$^t_2$(CH$_2$COPh) to the carbonylated ethanolic solution of Na$_2$[IrCl$_6$] white crystals of [IrH(Cl)(CO){Bu$^t_2$PCH=C(O)Ph}{PBu$^t_2$(CH$_2$COPh)}] (11a) were deposited. The i.r. spectrum of this compound showed a band at the very high value of 2 342 cm^{-1} due to ν(Ir–H), *i.e.* *trans* hydride to chlorine. This appears to be the highest value for a transition-metal hydride stretching frequency which has been reported, see for example ref. 14. There is also a strong band (at 2 009 cm^{-1}) due to ν(C≡O) and a strong band at 257 cm^{-1} characteristic of chlorine *trans* to hydride. A strong band at 1 533 cm^{-1} is attributed to ν(C=C) + ν(C–O) and a band at 1 674s cm^{-1} to the unco-ordinated keto-carbonyl group. This value contrasts with that (1 538 cm^{-1}) for (4b) containing a co-ordinated keto-carbonyl group.

The ^{1}H n.m.r. spectrum of (11a) at 60 or 90 MHz is complex due to overlapping resonances but is simplified by measurement at 220 Hz in C_6D_6. The four non-equivalent t-butyl groups each give a doublet (Table 2), the CH_2 protons are non-equivalent and give the *AB* part of an *ABX* pattern, and the vinyl proton gives a triplet pattern. The hydride resonance consists of a doublet of doublets at δ = –15.6 p.p.m., ^2J(PH) = 13.0 and 9.6 Hz. The ^{31}P n.m.r. spectrum of (11a) shows the expected *AB* pattern with a large value of ^2J(PP) = 290 Hz.



(10a) $PR_3 = PBu^t{}_2(CH_2COBu^t)$



(11a) R = Ph, L = $PBu^t{}_2(CH_2COPh)$
(11b) R = Bu^t, L = $PBu^t{}_2(CH_2COBu^t)$

Although complexes of type (10) when treated with 1 mol of base (*e.g.* sodium methoxide) are very smoothly converted into complexes *trans*-[IrCl(CO)$(PR_3)_2$] [13] we find that on treating (11a) with 1 mol of sodium ethoxide in ethanol a mixture was produced which could not be separated. The i.r. spectrum was consistent with a mixture consisting of the hydridocarbonyliridium(III) complex (9a) and an iridium(I) complex (3c). Bands at the following wavenumbers (with the suggested assignments shown in square brackets) were observed: 2 215 [ν(Ir–H)]; 1 995 [ν(C≡O), iridium(III)]; 1 920 [ν(C≡O), iridium(I)]; 1 668 [ν(C=O)]; and 1 534 and 1 510 cm^{-1} [ν(C=C) + ν(C–O)]. Thus, on the addition of base, proton removal from the activated methylene group and from the iridium compete and a mixture of products (isomers) (9b) and (3c) results.

When $PBu^t{}_2(CH_2COBu^t)$ was added to a solution by treating $Na_2[IrCl_6]$ with carbon monoxide a mixture was obtained. The main component was very probably $[IrHCl_2(CO)\{PBu^t{}_2(CH_2COBu^t)\}_2]$ (10a) based on the i.r. and n.m.r. data (Table 2) but this was contaminated by *ca.* 10% of another component, probably the complex $[\overline{IrHCl_2(CO)\{Bu^t{}_2PCH=C(O})Bu^t\}\{PBu^t{}_2(CH_2COBu^t)\}]$ of configuration (11b). The ^{31}P n.m.r. spectrum showed a singlet at 32.6 p.p.m. which we attribute to the component of configuration (10a) and a very weak *AB* pattern [δ_A = 66.4, δ_B = 43.0 p.p.m., ^2J(AB) = 288 Hz] due to (11b). The i.r. spectrum showed peaks predominantly due to the complex $[IrHCl_2(CO)\{PBu^t{}_2(CH_2COBu^t)\}_2]$ (10a) with bands at 2 310 cm^{-1} [ν(Ir–H)], 2 015 cm^{-1} [ν(C≡O)], and at 1 705 cm^{-1} due to the unco-ordinated keto-carbonyl groups. A weak band at 1 522 cm^{-1} was attributed to ν(C=C) + ν(C–O) of the minor component. The far-i.r. spectra showed bands at 240 and 299 cm^{-1} due to ν(Ir–Cl). In the hydride region of the ^{1}H n.m.r. spectrum resonances due to both components were observed. The major component showed a triplet at δ = –15.4 p.p.m. [^2J(PH) = 23 Hz] due to (10a) and a doublet of doublets at δ = –16.0 p.p.m. [^2J(PH) = 12.8 and 9.0 Hz] due to (11b). The ^{1}H n.m.r. spectrum showed t-butyl triplets at 1.64 and 1.69 p.p.m. with ^{3+5}J(PH) = 14.0 and 14.2 Hz respectively due to (10a). The PCH_2 region of the spectrum showed the *AB* part of an ABX_2 pattern due to the non-equivalent, 'virtually coupled,' methylene protons of (10a) (Table 2). The resonances of the vinylic and methylene hydrogens of the minor component (11b) were too weak to be assigned and were probably masked (in part) by the stronger signals of the major component.

We could not separate the mixture of (10a) and (11b) in spite of several attempts using different solvents. However, we found that on heating the mixture in chloroform solution for 1 h the ratio of (10a) to (11b) changed from *ca.* 10 : 1 to *ca.* 1 : 40 (based on relative intensities in the ^{31}P and ^{1}H n.m.r. patterns). The i.r. and ^{1}H n.m.r. data for this new mixture are the same as those given above except that now (11b) is by far the major component. Thus in the ^{1}H n.m.r. pattern although the hydride resonance of (10a) was still detectable the t-butyl region showed only the resonances due to (11b), *viz.* four doublets due to the four inequivalent PBu^t groups and the two singlet CBu^t resonances. Both the vinylic and PCH_2 resonances of (11b) were readily observed (see Table 2). The i.r. data for (11b) in the mixture were similar to those for (11a) (Table 2). Although the pure complexes (10a) and (11b) were not obtained, (11b) of sufficient purity to give a reasonably good elemental analysis for carbon, hydrogen, and chlorine was obtained (see Table 1). The i.r. and n.m.r. data for (10a) and (11b) given in Table 2 are based on their 10 : 1 and 1 : 40 mixtures.

EXPERIMENTAL

The general technique and apparatus used were the same as in other recent papers from this laboratory.[15]

trans-$[RhCl(CO)\{PBu^t{}_2(CH_2COPh)\}_2]$.—A solution of di-μ-chloro-tetracarbonyldirhodium (0.26 g, 0.67 mmol) in methanol (10 cm^3) was treated with the ketophosphine (0.75 g, 2.82 mmol). The solution was evaporated to dryness and the residue recrystallized from dichloromethane–light petroleum (b.p. 80—100 °C) giving the *product* (0.69 g, 70%) as yellow prisms. The complex *trans*-$[RhCl(CO)\{PBu^t{}_2(CH_2COBu^t)\}_2]$ was made similarly in 87% yield.

(3a).—A solution of *trans*-$[RhCl(CO)\{PBu^t{}_2(CH_2COPh)\}_2]$ (0.39 g, 0.43 mmol) in benzene (10 cm^3) was treated with sodium ethoxide in ethanol (10 cm^3, 0.8 mol dm^{-3}). The mixture was heated under reflux for 30 min, evaporated to dryness under reduced pressure, and the residue recrystallized from dichloromethane–ethanol to give the product

(0.24 g, 85%) as yellow prisms. Complex (3b) was made similarly in 65% yield as yellow prisms.

(4a).—The phosphine $PBu^t_2(CH_2COPh)$ (1.16 g, 4.2 mmol) was added to a warm solution of hydrated rhodium trichloride (0.25 g, 1.0 mmol) in ethanol (20 cm^3). The resulting orange-yellow suspension was shaken at 20 °C for 1 h and then cooled to −15 °C to give the required product as orange prisms (0.53 g, 76%).

trans-$[\overline{Rh\{Bu^t_2PCH=C(O}\,)Ph\}_2]$ (5).—Sodium methoxide in methanol (5 cm^3, 0.9 mol dm^{-3}) was added to a solution of the dichloro-complex (0.15 g, 0.21 mmol) in benzene–ethanol (1 : 1, 15 cm^3). The resulting blue suspension was evaporated to dryness and the residue recrystallized from dichloromethane–ethanol to give the product as royal blue prisms (0.84 g, 64%).

Conversion of (3a) *into trans*-$[RhCl(CO)\{PBu^t_2(CH_2COPh)\}_2]$.—A solution of hydrogen chloride in diethyl ether (0.02 cm^3, 3.8 mol dm^{-3}, 0.08 mmol) was added to a solution of (3a) (0.05 g, 0.08 mmol) in dichloromethane (5 cm^3). After 5 min the mixture was evaporated to dryness to give the product (0.050 g, 93%) identified by its i.r. spectrum.

(4b).—The ketophosphine $PBu^t_2(CH_2COPh)$ (1.13 g, 4.25 mmol) was added to a warm solution of hydrated iridium trichloride (0.38 g, 1.06 mmol) in propan-2-ol (20 cm^3). The resulting orange slurry was heated under reflux for 21 h. The blood-red solution was cooled to *ca.* −15 °C giving the required product (0.41 g, 49%) as blood-red prisms. Complex (4c) was prepared similarly as orange prisms (57%).

(7a).—A solution of sodium hydroxide (3 cm^3, 2 mol dm^{-3}, 6 mmol) was added to a solution of the dichloro-complex (4b) (95 mg) in ethanol (10 cm^3). The product precipitated out almost immediately as purple prisms. Yield 83 mg, 96%. Complex (7b) was prepared by an analogous method as purple prisms. Yield 90%.

(9a).—Carbon monoxide was bubbled through a solution of the five-co-ordinate hydrido-complex (7a) (50 mg, 0.07 mmol) in benzene (15 cm^3) for 10 min. The resulting colourless solution was evaporated to dryness and the residue recrystallized from benzene–light petroleum (b.p. 80—100 °C) to give the product (44 mg, 85%) as white prisms. Complex (9b) was prepared similarly as white prisms. Yield 72%.

(11a).—Carbon monoxide was bubbled through a boiling solution of sodium hexachloroiridate(IV) (1.14 g, 2.0 mmol) in ethanol (25 cm^3) for 22 h. The resulting yellow solution was cooled to room temperature and $PBu^t_2(CH_2COPh)$ (1.11 g, 4.2 mmol) added. The mixture was stirred at room temperature for 1 h during which the required product separated as white prisms. Yield 0.64 g, 43%.

Mixture of (11b) *and* (10a).—This mixture was prepared by an analogous method to (11a) above. The ratio (11b) : (10a) was established as *ca.* 1 : 10 by ^{31}P and ^1H n.m.r. spectroscopy. When a solution of this mixture was heated in chloroform for 1 h and propan-2-ol added, almost pure (11b) contaminated by *ca.* 2—3% of (10a) was deposited as white prisms, the overall yield being 41%.

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