strained approximately sp^3-hybridized divalent Te assumes a 95° C–Te–C angle in $[(CH_3)_3Te]I$.[39]

An operational mechanism for the formation of the adducts has been formulated which involves only modest rearrangement of the starting structure and which is consistent with the stereochemistry of both the adduct and the substitution product. Attack at an open face of 1 would place the addend on a basal iron meridional with respect to the tellurium atoms and would induce the tautomerization of the Fe–Fe and the Fe–Te bonding arrangement. This tautomerization involves loss of one Fe–Fe bond and a formal shift in the orientation of the tellurium lone pairs (Figure 6). Reversal of this process with explusion of a CO (which is also meridional with respect to the Te atoms) completes the cycle and affords the basally substituted derivative of 1 (e.g., **3a**). An alternative mechanism would involve attack by the ligand at the apical, seven-coordinated iron; however, this mechanism requires considerably more rearrangement of the cluster.

It is important to note that the reactivity associated with each ~60° M–Te–M angle is not independent since 1 binds *only one* donor which in turn opens only one of the two pairs of acute Fe–Te–Fe angles. Were there any tendency to bind an additional ligand to afford the open cluster, e.g., $Fe_3(\mu_3\text{-}Te)_2(CO)_9L_2$, one would expect this to occur in the derivatives which contain monodentate di(tertiary phosphine) ligands.

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Supplementary Material Available: A full crystallographic report including tables of positional and thermal parameters (34 pages). Ordering information is given on any masthead page.

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Chelate-Assisted Oxidative Addition of Functionalized Phosphines to Iridium(I)

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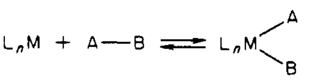
This paper is concerned with an evaluation of the factors which influence the facility of the oxidative addition of chelating substrates. Spectrophotometrically we determined the [Ir(III)]/[Ir(I)] ratios resulting from the oxidative addition of C_6H_5XH and $o\text{-}Ph_2PC_6H_4XH$ (X = O, CO_2) to *trans*-$IrCl(CO)(EPh_3)_2$ (E = P, 1; E = As, 2). The measured [Ir(III)]/[Ir(I)] ratios for the chelating substrates were 10^3–10^4 greater than those for the nonchelating substrates. While benzaldehyde does not detectably add to 1, $o\text{-}Ph_2PC_6H_4CHO$ (PCHO) does so quantitatively ($K \simeq 5 \times 10^4$) affording a stable acyl hydride, $\overline{IrH(PCO)}Cl(CO)(PPh_3)$. Related stable acyl hydrides prepared in this way are $\overline{IrH(PCO)}Cl(CO)(PCHO)$, $\overline{IrH(PCO)}Cl(CO)(AsPh_3)$, $\overline{IrH(AsCO)}Cl(CO)(AsPh_3)$, and $\overline{IrH(PCO}(CHO))Cl(CO)(PPh_3)$, the last compound being derived from (phenylphosphino)dibenzaldehyde ($P(CHO)_2$). Equilibrium measurements using 1, 2, PCHO, and the analogous arsine, AsCHO, established a strong dependence of the facility of the oxidative addition on the nature of the ancillary donor ligands. An attempted synthesis of a nonchelated acyl hydride from the reaction of "$IrH(CO)(PPh_3)_2$" and PhCOCl gave only 1 and PhCHO. This result establishes that the differing facilities for oxidative addition of PhCHO and PCHO to 1 is a thermodynamic and not a kinetic effect. The single-crystal X-ray diffraction study of PCHO itself revealed an unexceptional structure which closely resembles that of PPh_3. $o\text{-}Ph_2PC_6H_4CHO$ crystallizes in the triclinic space group $C_i^1\text{-}P\bar{1}$ with cell dimensions of $a = 10.663$ (3) Å, $b = 11.065$ (3) Å, $c = 8.585$ (2) Å, $\alpha = 103.20$ (2)°, $\beta = 105.95$ (2)°, $\gamma = 118.67$ (2)°, $V = 772.8$ (3) Å^3, and $Z = 2$.

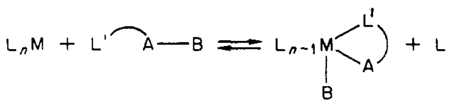
Introduction

The oxidative addition reaction is of great importance in inorganic and organometallic chemistry.[1a] Traditionally, this process involves the formal addition of two one-electron fragments to a single metal center[1b,2] (eq 1)



$$L_nM + A{-}B \rightleftharpoons L_nM\begin{matrix}\diagup A\\ \diagdown B\end{matrix} \qquad (1)$$

although several variations on this theme exist including addition to bimetallic complexes,[3-5] one-electron oxidative addition,[2] and oxidative elimination.[6] An alternative mode of addition is that involving chelating substrates where the addend fragments occupy three (or more) coordination sites in the product (eq 2). This last process can be considered a special case of the cyclometalation reaction.[7-9]



$$L_nM + L'\frown A{-}B \rightleftharpoons L_{n-1}M(L'\frown A)(B) + L \qquad (2)$$

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Table I. IR and ^{1}H NMR Data for New Iridium Complexes

	IR data (mineral oil mull, cm^{-1})			^{1}H NMR (CDCl$_3$)		
	$\nu_{\mathrm{Ir-H}}$	ν_{CO}	$\nu_{\mathrm{acyl-CO}}$	τ_{IrH}	$^2J_{\mathrm{PH}}$	$\tau_{\mathrm{OH(CHO)}}$
$\mathrm{IrH(PCO_2)Cl(CO)(PPh_3)}$[a]	2180	2105	1640	22.8	10.5, 11	
$\mathrm{IrH(PO)Cl(CO)(PPh_3)}$	2230	2010		24.7	9.8	
$\mathrm{IrH(PO)Cl(CO)(POH)}$[b]	2190	2025		25.2[c]	9.6	−0.9
$\mathrm{IrH(PCO)Cl(CO)(PPh_3)}$	2010	2105	1640	17.4	12, 10.5	
$\mathrm{IrH(PCO)Cl(CO)(PCHO)}$	2020	2110	1630, 1698	17.5	15.0	−0.2
$\mathrm{IrH[P(CO)(CHO)]Cl(CO)(PPh_3)}$	2010	2105	1630	17.5	15.0	+0.1, −0.5
$\mathrm{IrH(PCO)Cl(CO)(AsPh_3)}$	2010	2100	1630	17.4[b]	13.5	
$\mathrm{IrH(AsCO)Cl(CO)(AsPh_3)}$	2005	2095	1625	17.6[b]		

[a] $\mathrm{IrD(PCO_2)Cl(CO)}$, $\mathrm{(PPh_3)}$, $\nu_{\mathrm{Ir-D}} = 1715$, $\nu_{\mathrm{CO}} = 2050$, and $\nu_{\mathrm{acyl-CO}} = 1640$ cm^{-1}. [b] ν_{OH} was observed at 3060–2560 cm^{-1} (hexachlorobutadiene mull). [c] C_6D_6 solvent.

The chelate-assisted oxidative addition ("chelate trapping"[9,10]) is a reaction of potential utility for the selective activation of organic functional groups.[1,10–14] Application of this methodology, however, must be predicated upon an understanding of its scope and limitations. To this end we have measured the chelate enhancement (eq 1 vs. eq 2) as a function of the oxidatively added functional group, A–B, comparing the aptitude of simple protic organic compounds and their chelating derivatives for oxidative addition to iridium(I). The chelating agents employed in this project were the ortho functionalized aryl phosphines[14] (Figure 1). These phosphines bear substituents which exhibit a range of aqueous acidities and whose conjugate bases vary widely in their "hardness".

One of the major accomplishments of the present work was the oxidative addition of an aldehyde to afford unusual examples of a transition-metal acyl hydrides. Interest in this process is heightened since it is generally accepted that acyl hydride intermediates are involved in certain metal-catalyzed carbonylation[15] and decarbonylation processes.[16] Simple aldehydes are perplexing substrates in that they generally to not oxidatively add to give stable acyl hydrides[17] although the reaction of formaldehyde with highly nucleophilic iridium(I) compounds represents a recent exception.[18] The reason for the reticence of aldehydes to react with metals which otherwise add such apolar substrates as H_2 is not known but could be either kinetic or thermodynamic in origin.[19]

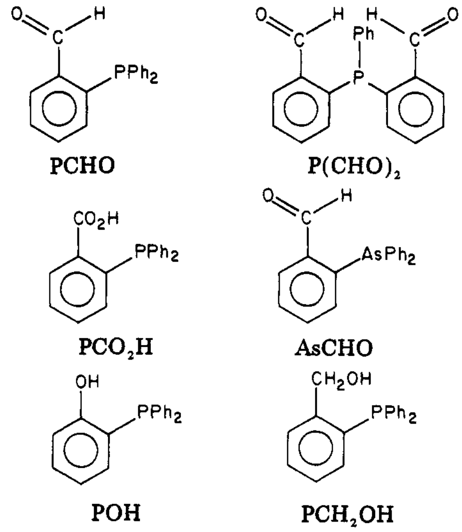

Figure 1. Ortho-substituted triarylphosphines and -arsines employed in this study.

Experimental Section

Materials and Methods. ^{1}H NMR spectra were obtained at 90 MHz on a Varian EM-390 spectrometer; proton chemical shifts are reported in parts per million with tetramethylsilane (Me_4Si) as an internal standard (τ scale). ^{31}P NMR spectra were obtained at 40.503 MHz on a modified Varian XL-100 spectrometer; chemical shifts are reported in parts per million from 85% H_3PO_4 as an external standard. Infrared spectra (mineral oil or hexachlorobutadiene mulls) were measured on a Perkin-Elmer 599B spectrophotometer. Mass spectral data were obtained on a Varian CH-5 mass spectrometer by the Mass Spectrometry Laboratory of the University of Illinois. Gas chromatographic (GC) analyses were performed on a Tracor 560 gas chromatograph equipped with a flame ionization detector. Elemental analyses were performed by the microanalytical laboratory of this department. Analytical data for the compounds reported in this paper are included in the supplementary material. NMR and IR data are summarized in Tables I and II.

Toluene was distilled from sodium under nitrogen. Benzaldehyde was trap-to-trap distilled on a vacuum line prior to use. Benzoic acid and phenol were reagent grade and were used without further purification. *p*-Toluidine was sublimed prior to use. Triphenylarsine was prepared via the Grignard method from bromobenzene and arsenic trichloride. *o*-(Diphenylphosphino)benzaldehyde, *o*-(diphenylphosphino)phenol, and *o*-(diphenylphosphino)benzoic acid are known compounds and were prepared

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Table II. ^{31}P NMR Data

compd	δ ^{a}(CDCl$_3$ soln)	$J_{\mathrm{PP'}}$, Hz	Δ ^{b}
PCO$_2$H	−5.01		
POH	−29.54		
PCH$_2$OH	−16.67		
PCHO	−12.23		
P(CHO)$_2$	−17.44		
IrH(PO)Cl(CO)(PPh$_3$)	23.11, −5.47	402	52.65
IrH(PO)Cl(CO)(POH)	28.81, 7.97	339	59.35 37.51
IrH(PCO)Cl(CO)(PPh$_3$)	25.25, 11.09	310	34.47
IrH(PCO)Cl(CO)(PCHO)	25.53, 9.72 ^{c}	313	37.76 21.95
IrH(PCO(CHO))Cl(CO)(PPh$_3$)	38.29, 0.77	340	55.73
	23.88, 11.08	311	41.32
IrH(PCO)Cl(CO)(AsPh$_3$)	26.13		38.36

^{a} In ppm vs. 85% H$_3$PO$_4$; upfield shifts are negative. ^{b} Δ = coordination chemical shift, ^{31}P chemical shift difference between free and coordinated phosphines. ^{c} C$_6$D$_6$ solvent.

according to literature preparations.[20-22] *o*-(Diphenylarsino)benzaldehyde was readily prepared by using the method applicable to the phosphine aldehyde and exists as pale yellow air-stable crystals. *o*-(Phenylphosphino)dibenzaldehyde was prepared from its ethylene glycol acetal by using the hydrolysis method of Hellwinkle and Krapp.[23] The yield was substantially improved by neutralization of the acidic layer with sodium carbonate. *trans*-Chlorocarbonylbis(triphenylphosphine)iridium was prepared by the method of Collman[24] and chlorodicarbonyl(*p*-toluidine)iridium was prepared by the method of Klabunde.[25] Trihydridocarbonylbis(triphenylphosphine)iridium and hydridocarbonyltris(triphenylphosphine)rhodium were made according to literature preparations.[26,27]

UV–Visible Measurements. Stock 10^{-3} M toluene solutions of *o*-Ph$_2$EC$_6$H$_4$X (E = P, As; X = OH, CHO, CO$_2$H) and *trans*-IrCl(CO)(EPh$_3$)$_2$ (E = As, P) were prepared in an inert atmosphere box. Equal volumes of iridium and substrate solutions were mixed and the measurements were made 30 min after addition. In some cases, measured portions of the neat reactants PhX (X = OH, CO$_2$H, CHO, CH$_2$OH) and *o*-Ph$_2$PC$_6$H$_4$CH$_2$OH were dissolved in the stock iridium solutions. Using the latter method we were able to detect 2×10^{-6} M iridium(I), $\lambda_{\max}$ = 440 nm (ϵ = 766). For the equilibrium measurements of the additions of *o*-Ph$_2$PC$_6$H$_4$CHO to *trans*-IrCl(CO)(EPh$_3$)$_2$ (E = P, As) and the addition of *o*-Ph$_2$AsC$_6$H$_4$CHO to *trans*-IrCl(CO)(AsPh$_3$)$_2$, the following solutions were prepared in an inert atmosphere box and monitored spectrophotometrically for 48 h: (1) 5×10^{-4} M IrCl(CO)(PPh$_3$)$_2$, 5×10^{-4} M *o*-Ph$_2$PC$_6$H$_4$CHO, and 0.35 M PPh$_3$; (2) 5×10^{-4} M IrH(*o*-Ph$_2$PC$_6$H$_4$CO)Cl(CO)(PPh$_3$) and 0.35 M PPh$_3$; (3) 5×10^{-4} M IrCl(CO)(AsPh$_3$)$_2$ and 5×10^{-4} M *o*-Ph$_2$AsC$_6$H$_4$CHO; (4) 5×10^{-4} M IrH(*o*-Ph$_2$AsC$_6$H$_4$CO)Cl(CO)(AsPh$_3$) and 5×10^{-4} M AsPh$_3$; (5) 5×10^{-4} M IrCl(CO)(AsPh$_3$)$_2$ and 5×10^{-4} M *o*-Ph$_2$PC$_6$H$_4$CHO; (6) 5×10^{-4} M IrH(*o*-Ph$_2$PC$_6$H$_4$CO)Cl(CO)(AsPh$_3$) and 5×10^{-4} M AsPh$_3$.

***trans*-Chlorocarbonylbis(triphenylarsine)iridium, 2.** A refluxing solution of IrCl$_3$·3H$_2$O (1.18 g, 3.4 mmol) and LiCl (0.14 g, 3.4 mmol) in 10 mL of CH$_3$OCH$_2$CH$_2$OH was purged with Ar for 15 min and treated with CO for 3 h at which time a pale yellow solution was obtained. The solution was cooled, and triethylamine (0.8 mL, 6.0 mmol) and AsPh$_3$ (2.13 g, 6.9 mmol) dissolved in a small quantity of degassed CH$_2$Cl$_2$ were added. The dark brown solution was refluxed 10 min, then cooled, and filtered, giving 1.10 g (37%) of yellow crystals which showed one IR peak in the CO region (ν_{CO} = 1960 cm^{-1}).

***o*-(Diphenylphosphino)benzyl Alcohol, *o*-Ph$_2$PC$_6$H$_4$CH$_2$OH.** *o*-Ph$_2$PC$_6$H$_4$CHO (1.03 g, 3.5 mmol) and NaBH$_4$ (0.12 g, 3.1 mmol) were stirred in 50 mL of CH$_3$OH for 10 min. The resulting pale orange solution was added to 50 mL of H$_2$O, and the product was extracted with CH$_2$Cl$_2$. The dried (Na$_2$SO$_4$) organic phase was evaporated to an oil and Kugelrohr distilled (205 °C, 0.05 mm), giving 0.98 g (95%) of the product as a pale yellow oil: ^{1}H NMR (CDCl$_3$) τ 2.0–2.9 (14 H, m), 5 (2 H, s), 7.5 (1 H, br s.).

***o*-(Diphenylphosphino)benzoic acid-*d*, *o*-Ph$_2$PC$_6$H$_4$CO$_2$D.** Methanolic NaOH (ca. 0.3 M) was added to *o*-Ph$_2$PC$_6$H$_4$CO$_2$H dissolved in CH$_2$Cl$_2$. The resulting salt was filtered and suspended in CH$_2$Cl$_2$. Deuterium chloride in D$_2$O was added until the solution was acidic and homogeneous. The CH$_2$Cl$_2$ layer was dried (Na$_2$SO$_4$) and evaporated to obtain the product.

Addition of *o*-Ph$_2$PC$_6$H$_4$CO$_2$H to IrCl(CO)(PPh$_3$)$_2$. IrCl(CO)(PPh$_3$)$_2$ (0.15 g, 0.19 mmol) and Ph$_2$PC$_6$H$_4$CO$_2$H (0.12 g, 0.38 mmol) were dissolved in 15 mL of degassed benzene. After 90 min the product mixture was precipitated with ethyl ether to give 0.099 g of pale yellow powder.

Addition of *o*-Ph$_2$PC$_6$H$_4$OH to IrCl(CO)(PPh$_3$)$_2$. A 20-mL sample of degassed CH$_2$Cl$_2$ was added to 0.20 g of IrCl(CO)(PPh$_3$)$_2$ (0.26 mmol) and 0.07 g of *o*-Ph$_2$PC$_6$H$_4$OH (0.21 mmol) in an Ar-flushed 50-mL flask. The mixture was stirred 135 min and then filtered. The filtrate was concentrated, and the reaction product was precipitated with hexane to give 0.11 g of light yellow powder.

***trans*-IrH(*o*-Ph$_2$PC$_6$H$_4$O)Cl(CO)(*o*-Ph$_2$PC$_6$H$_4$OH), 3.** IrCl(CO)$_2$(p-NH$_2$C$_6$H$_4$CH$_3$) (0.7 g, 0.18 mmol) was added to *o*-Ph$_2$PC$_6$H$_4$OH (0.10 g, 0.38 mmol) dissolved in 20 mL of degassed ethyl ether. After 45 min the product was collected by filtration and rinsed with acetone to give 0.079 g (53%) of a light yellow powder. The crude product can be recrystallized from degassed CH$_2$Cl$_2$–ether to give the off-white microcrystals.

***trans*-IrH[*o*-Ph$_2$PC$_6$H$_4$C(O)]Cl(CO)(PPh$_3$), 4.** IrCl(CO)(PPh$_3$)$_2$ and *o*-Ph$_2$PC$_6$H$_4$CHO were added in a 1:1 molar ratio to degassed benzene. After 1 h, the solution was concentrated and the product was precipitated with hexane. The crude pale yellow product was recrystallized from CH$_2$Cl$_2$–ether.

***trans*-IrH[*o*-Ph$_2$PC$_6$H$_4$C(O)]Cl(CO)(*o*-Ph$_2$PC$_6$H$_4$CHO), 5.** IrCl(CO)$_2$(*p*-NH$_2$C$_6$H$_4$CH$_3$) (0.07 g, 0.18 mmol) was added to *o*-Ph$_2$PC$_6$H$_4$CHO (0.12 g, 0.04 mmol) dissolved in 20 mL of degassed ethyl ether. After being stirred 1 h, the solution was concentrated and the crude product was precipitated with hexane as a beige powder, 0.10 g (71%). This crude product was extracted well with ethyl ether. The extract was concentrated and the cream product precipitated with hexane.

***trans*-IrH[*o*-PhPC$_6$H$_4$C(O)(C$_6$H$_4$CHO)]Cl(CO)(PPh$_3$), 6.** IrCl(CO)(PPh$_3$)$_2$ (0.10 g, 0.12 mmol) and *o*-PhP(C$_6$H$_4$CHO)$_2$ (0.04 g, 0.13 mmol) were placed in an Ar-flushed flask to which was added 20 mL of degassed toluene. After 1 h, the solution was concentrated and the product was precipitated with hexane. The crude pale yellow product was washed well with ethyl ether. The filtrate was concentrated, and the product was precipitated with hexane to give 0.057 g (53%) of pale yellow powder.

***trans*-IrH[*o*-Ph$_2$PC$_6$H$_4$C(O)]Cl(CO)(AsPh$_3$).** This compound was prepared in a manner similar to that for 4 from IrCl(CO)(AsPh$_3$)$_2$ and *o*-Ph$_2$PC$_6$H$_4$CHO.

***trans*-IrH[*o*-Ph$_2$AsC$_6$H$_4$C(O)]Cl(CO)(AsPh$_3$).** This com-

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Table III. [Ir(III)]/[Ir(I)] Ratios for the Addition of HX to *trans*-$IrCl(CO)(EPh_3)_2$ (E = As, P)

$[IrCl(CO)(PPh_3)_2] = 5 \times 10^{-4}$ M				$[IrCl(CO)(AsPh_3)_2] = 5 \times 10^{-4}$ M			
nonchelating[a]		chelating[c]		nonchelating[a]		chelating[c]	
$PhCO_2H$	5.60×10^{-4}	PCO_2H	1.34	$PhCO_2H$	3.45×10^{-3}	PCO_2H	1.48
PhOH	8.82×10^{-5}	POH	1.76	PhOH	1.95×10^{-4}	POH	1.61
PhCHO	$<4 \times 10^{-5}$	PCHO	103	PhCHO	$<4 \times 10^{-5}$	PCHO	2.73
		AsCHO	9.97×10^{-3}			AsCHO	7.12
$PhCH_2OH$	2.73×10^{-4}	PCH_2OH[b]	0.19	$PhCH_2OH$	6.38×10^{-5}	PCH_2OH[b]	0.29

[a] $[HX] = 5 \times 10^{-4}$ M. Calculated from experimental equilibrium constants obtained at $[HX]_0 = 2 \times 10^{-2}$ M and $[Ir]_0 = 1 \times 10^{-3}$ M. [b] $[PCH_2OH] = [Ir] = 1 \times 10^{-3}$ M. [c] $[HX] = 5 \times 10^{-4}$ M.

pound was prepared in a manner similar to that for 4 from $IrCl(CO)(AsPh_3)_2$ and *o*-$Ph_2AsC_6H_4CHO$.

Addition of Benzoyl Chloride to Trihydridocarbonylbis(triphenylphosphine)iridium. $IrH_3(CO)(PPh_3)_2$ (0.103 g, 0.138 mmol) was dissolved in 2 mL of degassed toluene to which 4 μL of phenetole had been added as an internal standard. Benzoyl chloride (15.5 μL, 0.133 mmol) was added, and the reaction mixture was kept at 43 °C for 2 days during which time the progress of the reaction was monitored by GC. After completion, the yellow precipitate that had formed was collected and washed with ethyl ether to give 0.0681 g of product identified by IR and elemental analysis as $IrCl(CO)(PPh_3)_2$ (63% yield based on iridium).

The volatile reaction products were separated on a 6-ft stainless-steel column packed with 10% OV-101 on 80/100 Chromosorb-HP using a temperature program of 2 min at 70 °C followed by a gradient of 10°/min to a final temperature of 100 °C.

X-ray Structure Determination of *o*-(Diphenylphosphino)benzaldehyde. X-ray crystallography was performed by Dr. S. Wilson of the School of Chemical Sciences, University of Illinois. A suitable crystal (dimensions 0.18 × 0.28 × 0.93 mm) was obtained by slow evaporation of a benzene-methanol solution.

Crystal Data. $C_{19}H_{15}OP$: mol wt 209.30; triclinic; at 22 °C $a = 10.663$ (3) Å, $b = 11.065$ (3) Å, $c = 8.585$ (2) Å, $\alpha = 103.20$ (2)°, $\beta = 105.95$ (2)°, $\gamma = 118.67$ (2)°, $V = 772.8$ (3) Å^3, $Z = 2$, $\rho = 1.247$ g cm^{-3}, $F(000) = 304.00$ e, $\mu = 15.20$ cm^{-1}, space group $P\bar{1}$—C_i^1 (No. 2). Unit-cell parameters were determined by a least-squares fit to the settings for 15 accurately centered high-order reflections (Cu Kα, $\lambda = 1.54178$ Å graphite monochromater). Successive refinement of the structure confirmed the choice of the space group.

Intensity data were collected on a computer-controlled four-circle Syntex $P2_1$ diffractometer (Cu Kα). Reflections in the range $2\theta = 3$–$130°$ ($\pm h, \pm k, +l$) were measured by a $2\theta/\theta$ scan method. A total of 2297 nonzero reflections out of a possible 2564 unique reflections were obtained at the 3.0σ significance level. There was good agreement between equivalent reflections. There was no evidence for absorption or extinction in the observed intensities. An empirical adsorption correction did not significantly improve the residuals nor alter the proposed model, and since all crystal dimensions were less than $2/\mu$, this correction was deemed unnecessary.

The structure was solved by direct methods;[28] positions for 19 of the 21 nonhydrogen atoms were deduced from an E map. Subsequent difference Fourier syntheses revealed positions for all of the remaining atoms including the hydrogens. The final cycle of least squares, which employed anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms, converged to $R = 0.0444$ and $R_w = 0.0608$ with a maximum change/error of 0.005.[29]

Results and Discussion

Methodology. Following the procedure originally outlined by Deeming and Shaw,[30] we measured the abilities of various chelating and nonchelating substrates to oxidatively add to *trans*-$IrCl(CO)(PPh_3)_2$, **1** and *trans*-$IrCl(CO)(AsPh_3)_2$, **2**, by determining the diminuation of their MLCT bands[31] at 440 and 437 nm, respectively (Figure 2). Due to the fact that the units of the equilibrium constants for the simple and chelate-assisted oxidative addition reactions (eq 1 and 2) are different, these constants are not comparable. Furthermore, determination of the equilibrium constants for chelating substrates is complicated by the occurrence of substitution *without* oxidative addition. For these reasons, we express our data in terms of [Ir(III)]/[Ir(I)] ratios. This quotient is a measure of the *net* conversion of iridium(I) to iridium(III). Comparison of the [Ir(III)]/[Ir(I)] ratio for a given substrate with that for its chelating counterpart provides a measure of the influence of chelation upon the "facility" of the oxidative addition process. The magnitude of this effect varies widely. For all of the reactions discussed in this paper, the oxidative addition to the coordinatively unsaturated iridium(I) precursors are virtually complete within the time of mixing of the reactants; therefore we assume that our measurements reflect the relative thermodynamic stabilities of the oxidative addition products.[32] Slower ($t_{1/2} \gtrsim$ 12 h) redistribution reactions do occur however. When the spectrophotometric measurements are taken soon after mixing, the effects of such secondary processes are minimized.

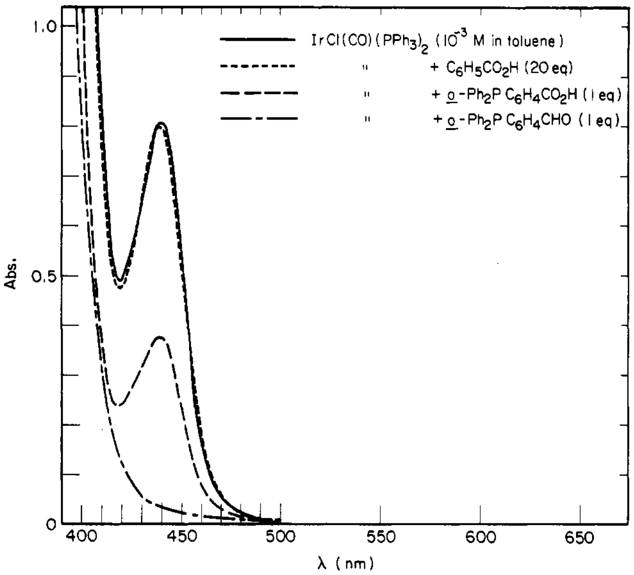

Figure 2. Spectral changes associated with the reaction of various substrates with Vaska's complex.

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(28) Sheldrick, G. M. SHELX 76, a program for crystal structure determination, University of Cambridge, England, 1976.

(29) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The function minimized was $\sum w||F_o| - |F_c||^2$. Scattering factor tables for neutral atoms were taken from: "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974: Vol. IV, pp 99–100. Anomalous dispersion corrections for non-hydrogen atoms were taken from pp 148–51.

(30) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 1802.

(31) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J., Jr.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485.

(32) van Doorn, J. A.; Masters, C. A.; van der Woude, C. *J. Chem. Soc., Dalton Trans.* **1978**, 1213.

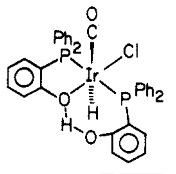


Figure 3. Proposed structure for IrH(PO)Cl(CO)(POH) showing the intramolecular hydrogen bonding.

Oxidative Addition of Protic Substrates to *trans*-$IrCl(CO)(EPh_3)_2$ (E = As, P). Weakly acidic substrates interact only slightly with 1. In order to detect the addition of PhOH and $PhCO_2H$ to 1, it was necessary to use a 20-fold excess of these compounds relative to the iridium(I) (under comparable conditions no interaction of 1 or 2 with PhCHO was detected). The observed equilibrium constants were used to calculate the [Ir(III)]/[Ir(I)] ratios which would exist if the initial concentrations were both 5×10^{-4} M. (Table III) These determinations were straightforward and the agreement between ours and Shaw's data for the addition of $PhCO_2H$ to 1 is good.

The chelating substrates oxidatively add to 1 considerably more effectively than do the simpler addends. Thus the [Ir(III)]/[Ir(I)] ratio observed for the reaction of 1 with *o*-(diphenylphosphino)benzoic acid, PCO_2H, was 2000 times greater than that determined for benzoic acid itself (Table III). Despite this enhancement, the overall effectiveness of PCO_2H in this oxidative addition is of no utility preparatively. For instance, treatment of 1 with PCO_2H on a larger scale followed by isolation of the iridium-containing products gave a mixture which by IR was composed of equal quantities of iridium(I) carbonyls ($\nu_{CO} \simeq 1960$ cm^{-1}) and the iridium(III) hydridocarboxylate, $IrH(PCO_2)Cl(CO)(PR_3)$ (see Table I for spectral details). The ability of *o*-(diphenylphosphino)phenol, POH, to protonate 1 proved to be comparable to that for PCO_2H; however, the chelate enhancement for the phenols was greater than that observed for the benzoic acids. Our spectrophotometric study of the reaction of POH with 1 was complicated by the fact that after the addition of POH, the low-energy absorption maximum which is attributable to residual iridium(I) was red-shifted by 5 nm. We suggest that the substituted iridium(I) compound $IrCl(CO)(POH)(PPh_3)$ is responsible for this small spectral shift. Despite this complication, the important result is that POH is comparable to PCO_2H in its overall effectiveness in oxidatively adding to 1.

Examination of solutions prepared from 1 and POH (1:1) by ^1H NMR indicated the presence of two bis(phosphine)iridium(III) hydrides. We assume that one is $IrH(PO)Cl(CO)(PPh_3)$ while the HP and PP′ coupling constants for the other correspond to that for IrH(PO)Cl(CO)(POH), **3**. The latter was prepared in good yield from $IrCl(CO)_2(H_2NC_6H_4CH_3)$ (eq 3). IR, ^1H and ^{31}P

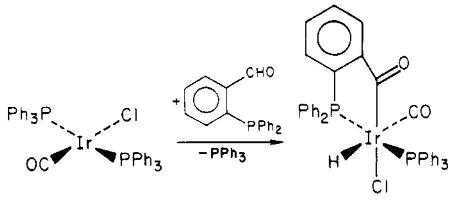
$$IrCl(CO)_2(H_2NC_6H_4CH_3) + 2POH \rightarrow IrH(PO)Cl(CO)(POH) + H_2NC_6H_4CH_3 + CO \quad (3)$$

NMR, and UV–visible spectroscopy indicate that **3** exists exclusively in the iridium(III) form. Consistent with the anticipated exchange inert character, **3** did not readily equilibrate with 1. The obvious conclusion which must be drawn from these experiments is that POH adds much more effectively to "IrCl(CO)(POH)" than to "$IrCl(CO)(PPh_3)$". This result is surprising since the donor characteristics (at P) for PPh_3 and POH are expected to be very similar; therefore the nucleophilicity of the two iridium(I) fragments would also be similar. IR measurements on **3** do, however, indicate that the nonchelating POH ligand is strongly hydrogen bonded, presumably to the chelated phenoxide ligand (Figure 3). This additional interaction stabilizes **3** relative to $IrH(PO)Cl(CO)(PPh_3)$. The stability attributed to **3** contributes significantly to the [Ir(III)]/[Ir(I)] ratio observed in the 1:1 reaction. In fact, addition of *two* equivalents of POH to solutions of 1 results in the complete bleaching of the iridium(I) charge-transfer band over a period of 2 days.

The ability of the chelating benzyl alcohol, PCH_2OH, to oxidatively add to 1 was measured spectrophotometrically. As can be seen from the low value of the associated [Ir(III)]/[Ir(I)] ratio, this process is considerably less favorable than the addition of POH or PCO_2H to 1. Conceivably, this addition process could occur via scission of either the O–H bond or the benzylic C–H bond.

As indicated by the data presented in Table III, the observed affinity of *trans*-$IrCl(CO)(AsPh_3)_2$, **2**, for simple and phosphinated protic substrates is distinctly higher than that observed for 1. It is interesting that PCO_2H adds to 2 more effectively than does POH while the reverse was true for 1. This observation is consistent with the suggestion that 2 is the better base for hard acids.[30]

Oxidative Addition of Chelating Aldehydes to *trans*-$IrCl(CO)(EPh_3)_2$ (E = As, P). The reaction of 1 with *o*-(diphenylphosphino)benzaldehyde, PCHO, is an extremely efficient process (Figure 2). Unlike the reactions of 1 or 2 with PCO_2H, POH, or PCH_2OH, spectrophotometric measurements on solutions prepared from 1 and 1 equiv of PCHO showed only traces, if any, of residual iridium(I). The product of this reaction $IrH(PCO)Cl(CO)(PPh_3)$ was isolated in crystalline form and subjected to the usual spectroscopic examination. The stereochemistry indicated in eq 4 is supported by the preliminary results of a single-crystal X-ray study.[33]



(4)

The preparation of other acyl hydrides from iridium(I) was undertaken to provide more insight into the stability and nature of this unusual species. Treatment of $IrCl(CO)_2(H_2NC_6H_4CH_3)$ with 2 equiv of PCHO afforded IrH(PCO)Cl(CO)(PCHO), **5**. ^1H NMR and IR demonstrated the presence of both metalated bidentate and monodentate PCHO ligands in **5**. ^1H NMR spectroscopy indicated that the pendant formyl group does not exchange readily with the metalated one. An indication that effects other than those involving chelation are not influencing the reactivity of PCHO toward 1 is provided by the ^{31}P NMR chemical shift differences between monodentate PCHO and its deprotonated chelate in IrH(PCO)Cl(PCHO)(CO). The measured value of 15.81 ppm is similar to that of 21.84 ppm measured for the analogous POH system, IrH(PO)Cl(POH)(CO). These "Δ_R" values are reasonable for tertiary phosphines in 5-member chelate rings.[34]

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[33] *o*-(Diphenylphosphino)benzoyl chelates were first prepared by the insertion of carbon monoxide into the Rh–C bond of ortho metalated triphenylphosphine: Keim, W. *J. Organomet. Chem.* **1969**, *19*, 161.

[34] Garrou, P. E. *Chem. Rev.*, in press.

Table IV. Positional Parameters

atom	x/a	y/b	z/c
P	0.71323 (6)	0.35856 (5)	−0.12520 (7)
O	0.6632 (3)	0.0921 (2)	−0.0920 (4)
Cl	0.7410 (2)	0.3945 (3)	0.1057 (3)
C2	0.7328 (3)	0.2873 (3)	0.1731 (4)
C3	0.7635 (4)	0.3201 (6)	0.3508 (5)
C4	0.8023 (4)	0.4544 (7)	0.4646 (5)
C5	0.8105 (4)	0.5587 (5)	0.4020 (4)
C6	0.7807 (3)	0.5313 (3)	0.2243 (3)
C7	0.6940 (4)	0.1396 (4)	0.0616 (6)
CA1	0.7373 (2)	0.5305 (2)	−0.1399 (3)
CA2	0.6120 (3)	0.5366 (3)	−0.2301 (3)
CA3	0.6432 (4)	0.6663 (3)	−0.2536 (4)
CA4	0.7972 (4)	0.7913 (3)	−0.1858 (4)
CA5	0.9234 (3)	0.7872 (3)	−0.0947 (4)
CA6	0.8938 (3)	0.6586 (3)	−0.0724 (3)
CB1	0.4956 (2)	0.2161 (2)	−0.2554 (3)
CB2	0.3880 (3)	0.2000 (3)	−0.1865 (3)
CB3	0.2254 (3)	0.0865 (3)	−0.2910 (4)
CB4	0.1709 (3)	−0.0101 (3)	−0.4633 (5)
CB5	0.2760 (4)	0.0059 (3)	−0.5350 (4)
CB6	0.4375 (3)	0.1187 (3)	−0.4318 (3)
H3	0.746 (4)	0.235 (4)	0.390 (5)
H4	0.822 (4)	0.466 (4)	0.568 (5)
H5	0.845 (4)	0.662 (4)	0.466 (5)
H6	0.781 (3)	0.597 (3)	0.177 (3)
H7	0.681 (4)	0.059 (4)	0.134 (5)
HA2	0.502 (3)	0.453 (3)	−0.282 (3)
HA3	0.557 (4)	0.669 (4)	−0.314 (4)
HA4	0.830 (3)	0.886 (3)	−0.209 (4)
HA5	1.040 (3)	0.876 (3)	−0.047 (4)
HA6	0.986 (3)	0.658 (3)	−0.013 (3)
HB2	0.432 (3)	0.274 (3)	−0.059 (3)
HB3	0.156 (3)	0.085 (3)	−0.226 (3)
HB4	0.069 (4)	−0.001 (3)	−0.539 (4)
HB5	0.252 (4)	−0.051 (3)	−0.644 (4)
HB6	0.504 (3)	0.129 (3)	−0.491 (3)

Compound 1 and (phenylphosphino)dibenzaldehyde, $P(CHO)_2$, react smoothly to give an acyl hydride. Interestingly, ^1H and ^{31}P NMR established that the product, $IrH(PCO(CHO))Cl(CO)(PPh_3)$, exists as a ~1:1 mixture of noninterconverting diastereoisomers arising from the presence of chiral centers at both phosphorus and iridium (Figure 4). Thus, the synthesis of this complex represents an unusual example of asymmetric induction involving a prochiral tertiary phosphine.

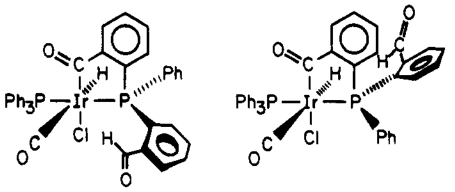

Figure 4. Two diastereoisomeric acyl hydrides derived from the addition of (phenylphosphino)dibenzaldehyde to *trans*-IrCl(CO)$(PPh_3)_2$.

Scheme I

$$1 + \mathrm{PCHO} \overset{K_1}{\rightleftarrows} \mathrm{IrH(PCO)Cl(CO)(PPh_3)} + \mathrm{PPh_3}$$

$$5.7 \times 10^4 < K_1 < 8.9 \times 10^4$$

$$2 + \mathrm{AsCHO} \overset{K_2}{\rightleftarrows} \mathrm{IrH(AsCO)Cl(CO)(AsPh_3)} + \mathrm{AsPh_3}$$

$$290 < K_2 < 690$$

$$2 + \mathrm{PCHO} \overset{K_3}{\rightleftarrows} \mathrm{IrH(PCO)Cl(CO)(AsPh_3)} + \mathrm{AsPh_3}$$

$$23 < K_3 < 250$$

o-(Diphenylarsino)benzaldehyde, AsCHO, was prepared in a manner analogous to the PCHO synthesis.[20] Comparative studies involving PCHO, AsCHO, 1, and 2 yielded further insight into the factors influencing the formation of the acyl hydrides. The mixed-ligand complexes $IrH(AsCO)Cl(CO)(AsPh_3)$ and $IrH(PCO)Cl(CO)(AsPh_3)$ were easily isolable in pure form and were characterized in the usual way. The equilibrium constants indicated in Scheme I were determined spectrophotometrically starting from both the iridium(I) and iridium(III) directions. In this way we were able to obtain an accurate, although not very precise, measure of the dependence of the stabilities of the acyl hydrides on the nature of the coligands. Since AsCHO reacts very slowly with 1, equilibrium data for this acyl hydride were not obtained. As can be seen in Scheme I, the neutral donor ligands have a large impact on the thermodynamics of this cyclometalation reaction.

The Solid-State Structure of *o*-(Diphenylphosphino)benzaldehyde. The spectrophotometric data reveal an affinity of PCHO for iridium(I) which is un-

Table V. Atoms with Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	4.42 (2)	4.35 (2)	4.89 (3)	2.80 (2)	2.12 (2)	2.03 (2)
O	8.6 (1)	6.7 (1)	10.7 (1)	5.0 (1)	3.9 (1)	4.5 (1)
Cl	3.80 (8)	6.0 (1)	4.83 (9)	2.64 (7)	1.68 (7)	2.42 (8)
C2	4.39 (9)	7.8 (1)	7.2 (1)	3.3 (1)	2.64 (9)	4.8 (1)
C3	6.1 (1)	13.2 (3)	8.3 (2)	5.1 (2)	3.7 (1)	7.4 (2)
C4	6.0 (1)	15.5 (4)	5.5 (2)	4.3 (2)	2.9 (1)	5.0 (2)
C5	6.1 (1)	10.4 (2)	5.2 (1)	3.1 (1)	2.5 (1)	1.1 (1)
C6	5.5 (1)	6.7 (1)	5.0 (1)	2.9 (1)	2.22 (9)	1.6 (1)
C7	7.1 (2)	8.2 (2)	11.4 (2)	5.0 (1)	4.3 (2)	6.8 (2)
CA1	4.56 (8)	4.29 (8)	4.36 (8)	2.59 (7)	1.00 (7)	1.61 (7)
CA2	5.1 (1)	4.98 (9)	6.1 (1)	3.18 (8)	2.12 (9)	2.32 (8)
CA3	7.2 (1)	5.6 (1)	6.6 (1)	4.2 (1)	1.9 (1)	2.8 (1)
CA4	8.4 (2)	4.6 (1)	7.4 (1)	3.6 (1)	2.6 (1)	2.7 (1)
CA5	6.4 (1)	4.2 (1)	8.1 (2)	2.21 (9)	2.2 (1)	2.2 (1)
CA6	4.86 (9)	4.68 (9)	6.1 (1)	2.42 (8)	1.62 (9)	1.88 (8)
CB1	4.76 (8)	3.86 (7)	5.20 (9)	2.70 (7)	1.92 (7)	2.03 (7)
CB2	4.67 (9)	5.13 (9)	6.1 (1)	2.90 (8)	2.12 (8)	2.44 (9)
CB3	4.6 (1)	6.3 (1)	8.6 (2)	3.0 (1)	2.2 (1)	3.6 (1)
CB4	4.9 (1)	4.9 (1)	8.7 (2)	2.32 (9)	0.2 (1)	2.4 (1)
CB5	7.4 (2)	5.2 (1)	5.8 (1)	3.8 (1)	0.4 (1)	1.0 (1)
CB6	6.3 (1)	4.78 (9)	5.3 (1)	3.48 (9)	1.92 (9)	1.81 (8)

[a] Anisotropic thermal parameters are expressed as $\exp[-\frac{1}{4}(a^{*2}B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$.

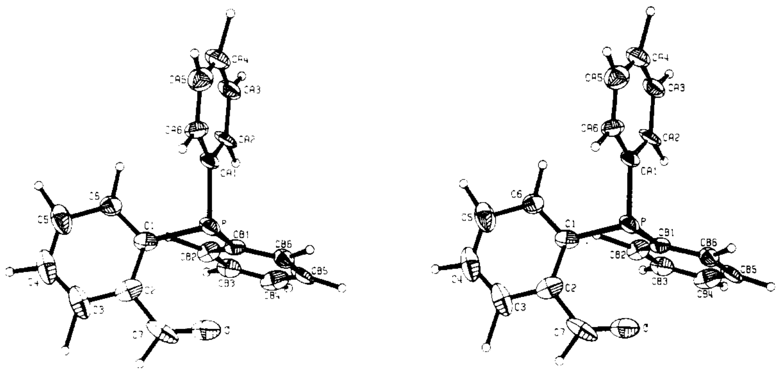

Figure 5. ORTEP drawing of the PCHO molecule with thermal ellipsoids set at the 50% probability level.

Table VI. Bond Distances (Å)

P	C1	1.839 (2)	CA2	HA2	0.95 (3)
P	CA1	1.833 (2)	CA3	CA4	1.370 (5)
P	CB1	1.838 (3)	CA3	HA3	0.94 (4)
O	C7	1.185 (5)	CA4	CA5	1.387 (5)
C1	C2	1.411 (4)	CA4	HA4	1.02 (3)
C1	C6	1.396 (4)	CA5	CA6	1.373 (4)
C2	C3	1.387 (5)	CA5	HA5	1.02 (4)
C2	C7	1.476 (5)	CA6	HA6	0.98 (4)
C3	C4	1.363 (7)	CB1	CB2	1.388 (4)
C3	H3	1.02 (4)	CB1	CB6	1.392 (3)
C4	C5	1.357 (8)	CB2	CB3	1.389 (4)
C4	H4	0.81 (4)	CB2	HB2	1.01 (2)
C5	C6	1.396 (4)	CB3	CB4	1.370 (5)
C5	H5	0.97 (4)	CB3	HB3	1.04 (4)
C6	H6	0.91 (3)	CB4	CB5	1.379 (6)
C7	H7	1.17 (4)	CB4	HB4	0.88 (4)
CA1	CA2	1.390 (4)	CB5	CB6	1.379 (5)
CA1	CA6	1.398 (4)	CB5	HB5	0.88 (3)
CA2	CA3	1.386 (4)	CB6	HB6	0.96 (3)

Table VII. Bond Angles (Deg)

C1	P	CA1	102.3 (1)
C1	P	CB1	101.9 (1)
CA1	P	CB1	102.0 (1)
P	C1	C2	120.6 (2)
P	C1	C6	122.0 (2)
C2	C1	C6	117.4 (3)
C1	C2	C3	119.9 (3)
C1	C2	C7	122.4 (3)
C3	C2	C7	117.7 (3)
C2	C3	C4	121.9 (5)
C2	C3	H3	117 (3)
C4	C3	H3	121 (3)
C3	C4	C5	119.0 (5)
C3	C4	H4	116 (3)
C5	C4	H4	125 (3)
C4	C5	C6	121.3 (4)
C4	C5	H5	130 (3)
C6	C5	H5	109 (3)
C1	C6	C5	120.6 (3)
C1	C6	H6	116 (2)
C5	C6	H6	123 (2)
O	C7	C2	127.0 (4)
O	C7	H7	119 (2)
C2	C7	H7	114 (2)
P	CA1	CA2	124.4 (2)
P	CA1	CA6	116.9 (2)
CA2	CA1	CA6	118.2 (2)
CA1	CA2	CA3	120.2 (3)
CA1	CA2	HA2	123 (2)
CA3	CA2	HA2	117 (2)
CA2	CA3	CA4	120.9 (3)
CA2	CA3	HA3	119 (2)
CA4	CA3	HA3	120 (2)
CA3	CA4	CA5	119.5 (3)
CA3	CA4	HA4	125 (2)
CA5	CA4	HA4	115 (2)
CA4	CA5	CA6	120.1 (3)
CA4	CA5	HA5	122 (2)
CA6	CA5	HA5	110 (3)
CA1	CA6	CA5	121.0 (3)
CA1	CA6	HA6	121 (2)
CA5	CA6	HA6	118 (2)
P	CB1	CB2	123.5 (2)
P	CB1	CB6	117.6 (2)
CB2	CB1	CB6	118.8 (2)
CB1	CB2	CB3	120.4 (3)
CB1	CB2	HB2	118 (2)
CB3	CB2	HB2	122 (2)
CB2	CB3	CB4	119.8 (3)
CB2	CB3	HB3	114 (2)
CB4	CB3	HB3	126 (2)
CB3	CB4	CB5	120.6 (3)
CB3	CB4	HB4	125 (2)
CB5	CB4	HB4	114 (2)
CB4	CB5	CB6	119.8 (3)
CB4	CB5	HB5	127 (2)
CB6	CB5	HB5	113 (2)
CB1	CB6	CB5	120.5 (3)
CB1	CB6	HB6	123 (2)
CB5	CB6	HB6	116 (2)

usually high, particularly in view of the chelate enhancements measured for the phenols and benzoic acids. As a demonstration of the conventional nature of PCHO itself, its structure was characterized by single-crystal X-ray diffraction. The gross structure of this tertiary phosphine (Figure 5) closely resembles that for triphenylphosphine.[35] The only possible unusual feature is that the formyl oxygen is oriented directly toward the phosphorus atom, the C–O distance is normal, however, and the long P···O distance precludes a strong interaction. Some important structural data are collected in Tables IV–VII.

On the Stability of $IrH(PhCO)Cl(CO)(PPh_3)_2$. Critical to a more complete interpretation of the oxidative addition observed for chelating aldehydes is an explanation of nonreactivity of 1 and 2 toward PhCHO. Our failure to prepare $IrH(PhCO)Cl(CO)(EPh_3)_2$ may, of course, be due to a slow rate of oxidative addition and that, once formed, this acyl hydride would be as robust as the chelated ones. To test this proposal, we devised an experiment to generate the acyl hydride formally derived from 1 and PhCHO. Our plan simply called for the addition of benzoyl chloride to an appropriate iridium(I) hydride. It is known that $IrH_3(CO)(PPh_3)_2$ reversibly dissociates in solution to afford $IrH(CO)(PPh_3)_2$[26] which, unlike its precursor and the related $IrH(CO)(PPh_3)_3$, is quite reactive. By monitoring the progress of the reaction of $IrH_3(CO)(PPh_3)_2$ and PhCOCl by gas chromatography, we observed the steady conversion of the acid chloride to benzaldehyde. At the end of the reaction, the reaction solution was filtered, affording ca. 60% of pure 1. A mechanistic rationale for this process, Figure 6, is based on a classical reductive elimination, oxidative addition, reductive elimination cycle. We conclude from these results that the difference in the

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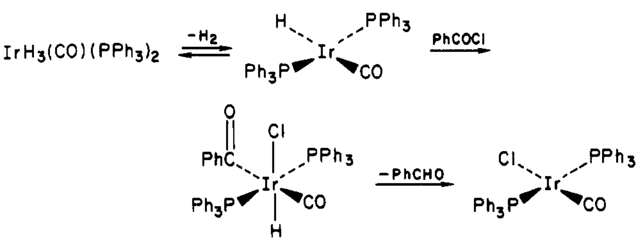

Figure 6. Mechanism proposed for the reaction of $IrH_3(CO)(PPh_3)_2$ with PhCOCl.

facilities of the oxidative additions of PhCHO and PCHO to **1** is not solely due to a kinetic enhancement but is related to the greater thermodynamic stability associated with the cyclometalated product.[36]

Summary

1. The overall effectiveness of simple substrates to add to *trans*-$IrCl(CO)(EPh_3)_2$ (E = P, As) follows the order of their aqueous acidities $PhCO_2H > PhOH \gg PhCHO$.

2. The effectiveness of the chelating substrates toward *trans*-$IrCl(CO)(PPh_3)_2$ follows the order: PCHO > POH $\gtrsim$ PCO_2H. It follows that the intermolecular versions of the oxidative addition reaction do *not* serve as reliable indicators for the corresponding intramolecular processes.

3. The kinetic and thermodynamic facility of the oxidative addition reaction depends heavily on the identity of the ancillary donor component of the bifunctional addend.

4. The differing abilities of PhCHO and PCHO to add to **1** is a consequence of the differing thermodynamic stabilities of the resultant acyl hydrides.

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Registry No. **1**, 15318-31-7; **2**, 23954-42-9; **3**, 80062-98-2; **4**, 69721-41-1; **5**, 80062-99-3; **6** isomer 1, 80063-14-5; **6** isomer 2, 80124-62-5; *o*-$Ph_2PC_6H_4CH_2OH$, 53772-42-2; *o*-$Ph_2PC_6H_4CHO$, 50777-76-9; *o*-$Ph_2PC_6H_4CO_2D$, 80049-09-8; *o*-$Ph_2PC_6H_4CO_2H$, 17261-28-8; r$\overline{\mathrm{IrH(PCO}}\mathrm{_2)Cl(CO)(PPh_3)}$, 80062-96-0; *o*-$Ph_2PC_6H_4OH$, 90254-10-6; $\overline{\mathrm{IrH(PO}}\mathrm{_2)Cl(CO)(PPh_3)}$, 80062-97-1; $IrCl(CO)_2$(*P*-NH_2-$C_6H_4CH_3$), 14243-22-2; *o*-$Ph(P(C_6H_4CHO)_2$, 65654-64-0; *trans*-$\overline{\mathrm{IrH}}$-$\overline{\mathrm{[}o\mathrm{-Ph_2PC_6H_4C}}\mathrm{(O)]Cl(CO(AsPh_3)}$, 80062-94-8; *trans*-$\overline{\mathrm{IrH}}$[*o*-$\overline{\mathrm{Ph_2A_5C_6H_4C}}\mathrm{(o)]Cl(CO)(A_5Ph_3)}$, 80062-95-9; *o*-$Ph_2AsC_6H_a4CHO$, 80049-10-1; $IrH_3(CO)(PPh_3)_2$, 16971-53-2; $\overline{\mathrm{IrD(PCO}}\mathrm{_2)Cl(CO)(PPh_3)}$, 80062-93-7.

Supplementary Material Available: Tables of bond angles, least-squares planes, analytical data, fractional coordinates, and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Tellurium-125 Chemical Shifts of Symmetric and Unsymmetric Dialkyl Ditellurides

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The proton-noise-decoupled tellurium-125 NMR spectra of symmetric dialkyl ditellurides R_2Te_2 [R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, *t*-Bu, *n*-Pent, neo-Pent, *i*-Pent, and *n*-C_nH_{2n+1} (n = 6, 7, 8, 9, 11, and 18)] and 36 unsymmetric dialkyl ditellurides (R = all alkyl isomers C_1–C_4 and neopentyl) are reported. The unsymmetric dialkyl ditellurides were prepared in situ by mixing chloroform solutions of two symmetric ditellurides. Equilibration took place but exchange was slow on the tellurium-125 NMR time scale and the spectra contained four Te resonances, one each for the two symmetric ditellurides and two for the unsymmetric ditelluride. The effect of alkyl substitution on tellurium chemical shifts was found to be additive. The magnitude of the effect diminishes as the substitution site moves away from the tellurium atoms and becomes negligible at the fourth atom.

Introduction

Recent investigations have shown that organic tellurium compounds have considerable potential as agents in nuclear medicine. Telluracarboxylic acids are attractive candidates for myocardial imaging,[1–4] tellurium-containing steroids show preferential uptake by the adrenal gland,[5–7] and alkyltellurobarbiturates show promise as reagents for the determination of regional cerebral blood perfusion.[8,9] Because of the large number of resonances and complex

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