mol) of CuCl in 40 mL of dioxane. After an additional 1.5-h reflux, the reaction mixture was diluted with pentane and filtered through Celite, the solids were reextracted with pentane, and the combined filtrates were washed with NH$_4$Cl solution and water (3×). Workup gave 1.30 g (68%) of **12**: bp 58–70 °C (130 mm); IR 1270, 1255, 1045, 870, 845, 755 cm^{-1}; ^{1}H NMR δ 0.11 (s, 9 H), 0.37 (m, 2 H), 0.71 (m, 2 H), 1.37 (s, 3 H).

Anal. Calcd for C$_7$H$_{16}$OSi: C, 58.28; H, 11.18. Found: C, 58.16; H, 11.20.

FVP of **12** at 625 °C (10 mm) gave partial conversion to a mixture of products. NMR analysis indicated the major components of this mixture to be **4**, 3-(trimethylsiloxy)-1-butene (**13**), and butanone in approximately equimolar amounts.

Preparation and Thermolysis of 1-Ethoxy-1-(trimethylsilyl)cyclopropane (14). A 6.4-g (0.044-mol) sample of 1-ethoxy-1-(trimethylsilyl)ethene[2] was cyclopropanated as in the preparation of **1**[2] to give 5.3 g (76%) of **14**: bp 63–65 °C (40 mm); IR 1250, 1195, 1125, 1070, 1020, 900, 840, 755 cm^{-1}; ^{1}H NMR δ 0.04 (s, 9 H), 0.39 (m, 2 H), 0.69 (m, 2 H), 1.08 (t, 3 H, J = 7 Hz), 3.33 (q, 2 H, J = 7 Hz).

Anal. Calcd for C$_8$H$_{18}$OSi: C, 60.70; H, 11.46. Found: C, 60.68; H, 11.30.

FVP of 0.206 g of **14** led to complete conversion to 0.120 g of water-white condensate which VPC showed consisted of many components. The largest of these with retention time just lower than that of **14** was collected and identified as 3-(trimethylsilyl)propanal:[16] ^{1}H NMR δ 0.00 (s, 9 H), 0.74 (m, 2 H), 2.37 (m, 2 H), 9.74 (t, 1 H, J = 2 Hz).

Preparation and Thermolysis of 1-Acetoxy-1-(trimethylsilyl)cyclopropane (17).[2] A solution of 0.96 g (0.0074 mol) of 1-(trimethylsilyl)cyclopropanol,[2] 1.51 g (0.0148 mol) of acetic anhydride, and a trace of 4-(dimethylamino)pyridine in 30 mL of ether was allowed to stand at 25 °C for 30 h. After the solution was washed with dilute HCl, NaHCO$_3$ solution, and water, workup gave 1.16 g (91%) of **17**, bp 60–72 °C (20 mm).

FVP of **17** at 600 °C (2 mm) led to recovery of some **17** and the formation of 3-acetoxy-2-(trimethylsilyl)propene (**20**) as the only significant product.[19] VPC collection gave pure **20**: IR 1743, 1250, 1231, 1032, 840 cm^{-1}; ^{1}H NMR δ 0.11 (s, 9 H), 2.07 (s, 3 H), 4.67 (m, 2 H), 5.44 (m, 1 H), 5.75 (m, 1 H).

Anal. Calcd for C$_8$H$_{16}$O$_2$Si: C, 55.77; H, 9.36. Found: C, 55.90; H, 9.47.

For comparison purposes, an authentic sample of **20** was prepared as follows. A solution of 1.89 g (0.010 mol) of 1-bromo-1-(trimethylsilyl)ethene in 25 mL of THF at −78 °C was treated dropwise with 9.5 mL of 2.3 N *tert*-butyllithium in pentane (0.022 mol). After 25 min at −78 °C, 0.64 g (0.21 mol) of dry paraformaldehyde was added at once and the cooling bath removed. The reaction mixture eventually reached 40–45 °C spontaneously. Five minutes later, the water-white solution was poured into NH$_4$Cl solution and worked up. Distillation gave 0.92 g (71%) of 2-(trimethylsilyl)-2-propen-1-ol: bp 60–72 °C (20 mm); IR 3320 (br), 1245, 1025, 835 cm^{-1}; ^{1}H NMR δ 0.10 (s, 9 H), 1.35 (t, 1 H), 4.45 (m, 2 H), 5.39 (m, 1 H), 7.69 (m, 1 H).

Anal. Calcd for C$_6$H$_{14}$OSi: C, 55.31; H, 10.83. Found: C, 55.41; H, 10.95.

A mixture of 0.26 g (0.020 mol) of the above alcohol, 0.22 g (0.022 mol) of acetic anhydride, and 0.20 g (0.020 mol) of triethylamine in 5 mL of ether gave, upon standing several days at 25 °C, a sample of **20** identical with that obtained above.

Registry No. **1**, 98720-91-3; **4**, 107-46-0; **5c**, 98720-92-4; **5t**, 56919-88-1; **6**, 64299-50-9; **7**, 98720-93-5; **8**, 2652-41-7; **9c**, 98720-94-6; **9t**, 98720-95-7; **11b**, 66662-18-8; **12**, 98720-97-9; **13**, 18269-41-5; **14**, 98720-98-0; **17**, 98720-99-1; **20**, 98721-01-8; CH$_2$I$_2$, 75-11-6; chlorotriethylsilane, 994-30-9; (allyloxy)trimethylsilane, 18146-00-4; *cis*-3-(triethylsilyl)-1-(trimethylsiloxy)propene, 98720-96-8; 2-(trimethylsiloxy)propene, 1833-53-0; 2-butanone, 78-93-3; 1-ethoxy-1-(trimethylsilyl)ethene, 81177-92-6; 1-(trimethylsilyl)cyclopropanol, 98721-00-7; 1-bromo-1-(trimethylsilyl)ethene, 13683-41-5; paraformaldehyde, 30525-89-4; 2-(trimethylsilyl)-2-propen-1-ol, 55287-89-3; 3-(trimethylsilyl)propanol, 2917-47-7.

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(19) The author thanks Mr. C. P. Kuan for carrying out this experiment.

Formation of Carboalkoxyiridium Complexes by Carbonylation of Alkoxyiridium Complexes and the Crystal Structure of *trans*-PhOIr(CO)(PPh$_3$)$_2$

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The preparation of iridium alkoxide complexes *trans*-ROIr(CO)(PPh$_3$)$_2$ and their carbonylation to carboalkoxy complexes ROC(O)Ir(CO)$_2$(PPh$_3$)$_2$ are described for R = Me, n-Pr, t-Bu, and Ph. The preparations involve metathetical reactions between *trans*-Ir(CO)(PPh$_3$)$_2$Cl and NaOR. In the carbonylation an intermediate can be identified by infrared and conductivity studies as [Ir(CO)$_3$(PPh$_3$)$_2^+$][OR$^-$]. Thus a mechanism involving alkoxide displacement by CO and subsequent nucleophilic attack of alkoxide on a CO of the cation is indicated. The complex *trans*-PhOIr(CO)(PPh$_3$)$_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (no. 14) with a = 15.790 (3) Å, b = 11.461 (3), c = 19.986 (5) Å, β = 100.326 (18)°, V = 3558 (2) Å^3, and Z = 4. Diffraction data (Mo Kα, 2θ = 5–55°) were collected with a Syntex P2$_1$ automated four-circle diffractometer, and the structure was solved and refined to R_F = 6.2% and R_{wF} = 4.6% for all 8220 reflections (R_F = 3.8% and R_{wF} = 4.1% for those 5981 reflections with $|F_0| > 6\sigma(|F_0|)$). The iridium atom has the expected square-planar geometry with Ir–P(1) = 2.328 (1) Å, Ir–P(2) = 2.344 (1) Å, Ir–CO = 1.795 (5) Å, and Ir–OPh = 2.049 (4) Å. The phenoxide ligand is "bent" with ⟨Ir–O–C(ipso) = 126.5 (3)°.

Alkoxy compounds have formed a part of inorganic chemistry for a number of years.[1-3] Alkoxy complexes of low oxidation state metals are not common, although a number of important reactions in methanol may involve alkoxy compounds. Among the important reactions are those that involve the use of palladium catalysts to effect the conversion of alkenes, CO, and methanol to esters, the

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carboalkoxylation of alkenes.[4-8] In the course of our studies on Ir(I) complexes, we have examined the carbonylation of *trans*-ROIr(CO)$(PPh_3)_2$.[9,10]

Square-planar complexes of Rh(I) and Ir(I) such as *trans*-Ir(CO)$(PPh_3)_2$Cl and Rh$(PPh_3)_3$Cl undergo an array of reactions which have considerably advanced our understanding of organometallic reactivity.[11] A number of analogues of *trans*-Ir(CO)$(PPh_3)_2$Cl have been prepared and shown to undergo an array of reactions.[9,10,12-25] There appears to be only one brief report of an alkoxy analogue, MeOIr(CO)$(PPh_3)_2$.[26] Earlier attempts to prepare alkoxy complexes may have failed because of improperly dried reagents. Conversion of the alkoxy complexes to *trans*-HOIr(CO)$(PPh_3)_2$ and *trans*-DOIr(CO)$(PPh_3)_2$ can be readily achieved by treatment with H_2O and D_2O, respectively.[9]

Although there have been several reports of the use of catalysts for the carboalkoxylation of alkenes, a reaction which may involve carbonylation of an intermediate palladium alkoxy complex, there have been only a few reports of the stoichiometric carbonylation of transition metal alkoxides.[9,27-29] The preparation of a platinum diester complex (eq 1). almost certainly involves carbonylation of

$$(PPh_3)_2PtCl_2 + 2KOH + 2CH_3OH + 2CO \rightarrow 2KCl + 2H_2O + (PPh_3)_2Pt(CO_2CH_3)_2 \quad (1)$$

Pt–OMe bonds.[27] Similarly a rapid carbonylation of $BuOCo(CO)_4$ has been reported (eq 2).[28] No mechanistic

$$BuOCo(CO)_4 \xrightarrow{CO} BuOC(O)Co(CO)_4 \quad (2)$$

data were reported for either reaction 1 or 2. The carbonylation of Pt(dppe)$(CH_3)(OCH_3)$ was reported to occur by an associative process (eq 3). Thus the methoxy group

$$Pt(dppe)(CH_3)(OCH_3) + CO \rightarrow Pt(dppe)(CH_3)(C(O)OMe) \quad (3)$$

is carbonylated in preference to the methyl group. The Pt(dppe)$(CH_3)(OCH_3)$ complex also reacts with C_2F_4 (eq 4).[30] This reaction also occurred through an associative mechanism.

$$Pt(dppe)(CH_3)(OCH_3) + C_2F_4 \rightarrow Pt(dppe)(CH_3)(CF_2CF_2OCH_3) \quad (4)$$

Table I. Infrared Spectroscopic Data (cm^{-1})

trans-ROIr(CO)$(PPh_3)_2$

R	C_6H_6	C_6H_{12}
CH_3	1935	1951
n-propyl	1937	1950
tert-butyl	1936	1951
Ph	1941	1958

ROC(O)Ir$(CO)_2(PPh_3)_2$

R	C_6H_6	KBr
CH_3	1994 (s), 1939 (vs), 1636 (m)	1982 (s), 1935 (vs), 1636 (m)
n-propyl	1994 (s), 1937 (vs), 1635 (m)	1983 (s), 1934 (vs), 1640 (m)
tert-butyl	1995 (s), 1941 (vs), 1643 (m)	1993 (s), 1941 (vs), 1633 (m)
Ph		1985 (vs), 1938 (vs), 1675 (m)

Table II. NMR Spectroscopic Data (δ)[a]

(A) *trans*-ROIr(CO)$(PPh_3)_2$	
CH_3	3.4 (s)[b]
n-propyl	3.65 (t), 1.16 (m), 0.60 (t)[c]
tert-butyl	0.89 (s)[b]
(B) ROC(O)Ir$(CO)_2(PPh_3)_2$	
CH_3	3.00 (s)[b]
n-propyl	3.57 (t), 1.3 (m), 0.81 (t)[c]
tert-butyl	1.13 (s)[b]

[a] In addition all spectra contain a multiplet at δ ~7.0 for phenyl resonances. [b] Toluene-d_8. [c] Benzene-d_6.

Structural studies have been reported for a number of alkoxides.[1-3,31-33] Many of these studies have focused on the common oligomerization products of the simple transition-metal alkoxides.[1-3,31] The alkoxides demonstrate both σ- and π-donor capabilities.

We have developed syntheses for a number of alkoxy complexes, *trans*-ROIr(CO)$(PPh_3)_2$ (R = Me, Pr, *t*-Bu, Ph), and have studied their reactions with CO (see eq 5). An

$$trans\text{-}ROIr(CO)(PPh_3)_2 + 2CO \rightarrow ROC(O)Ir(CO)_2(PPh_3)_2 \quad (5)$$

intermediate is detectable en route to the carboalkoxy complex and has been identified as $[Ir(CO)_3(PPh_3)_2{}^+][OR^-]$. To define this reaction we have investigated the reaction by IR and NMR spectroscopy, conductivity studies and an X-ray diffraction study of *trans*-PhOIr(CO)$(PPh_3)_2$.

Experimental Section

Iridium trichloride, $IrCl_3 \cdot xH_2O$, was loaned by Johnson Matthey Inc. All solvents were dried and degassed prior to use. All syntheses were accomplished under a nitrogen or argon atmosphere. Infrared spectra were recorded on a Beckman 4240 or a Perkin-Elmer 683 infrared spectrophotometer, and ^1H NMR spectra were recorded on a Varian EM390 or on a Joelco FX90Q.

Preparations. ***trans*-Ir(CO)$(PPh_3)_2$Cl** was prepared as previously described.[34] Aliphatic alcohols were dried with finely

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divided CaH_2 and then vacuum distilled onto freshly cut sodium to produce the sodium alkoxides. Sodium phenoxide was prepared by reaction of phenol with freshly cut sodium in a THF solution. The crude sodium alkoxide or phenoxide was purified in an inert-atmosphere glovebox by extraction into THF and vacuum removal of the THF. The sodium alkoxide and phenoxide products were stored in the inert-atmosphere glovebox until used.

***trans*-$CH_3OIr(CO)(PPh_3)_2$.** In an inert-atmosphere glovebox 1.0 g of *trans*-$Ir(CO)(PPh_3)_2Cl$ and 0.5 g of CH_3ONa were suspended in 75 mL of THF. This mixture was stirred for 14 h at room temperature followed by THF removal under vacuum. To remove any traces of THF, 15 mL of benzene was added and the suspension stirred for a few minutes, and then the benzene was removed in vacuo. The solid was then extracted with 40 mL of benzene to give a deep yellow solution. Evaporation produced 0.93 g of a yellow powder (94% yield). The infrared and NMR spectra are reported in Tables I and II, respectively.

***trans*-(*n*-PrO)$Ir(CO)(PPh_3)_2$.** In an inert-atmosphere glovebox 1.0 g of *trans*-$Ir(CO)(PPh_3)_2Cl$ and 0.40 g of *n*-PrONa were suspended in 50 mL of THF. The mixture was stirred for 14 h at room temperature followed by solvent removal under vacuum. To remove traces of THF, 10 mL of C_6H_6 was added and the suspension stirred for a few minutes. The benzene was then removed in vacuo. The resulting solid was extracted with 20 mL of C_6H_6 and filtered (fine fritte) and the filtrate evaporated under vacuum to produce 0.91 g (90%) of a yellow powder. The infrared and NMR spectra are reported in Tables I and II.

***trans*-(*t*-BuO)$Ir(CO)(PPh_3)_2$.** A suspension of 0.80 g of *trans*-$Ir(CO)(PPh_3)_2Cl$ and 0.10 g of *t*-BuONa were stirred in 75 mL of THF for 14 h at room temperature. The THF was removed in vacuo and cyclohexane added (20 mL), stirred for a few minutes, and removed under vacuum. Cyclohexane (100 mL) was added and the mixture refluxed for 2 min, allowed to cool for 5 min, and filtered through a medium, sintered-glass filter. The cyclohexane was allowed to evaporate for 3 days to yield 0.58 g (70% yield) of deep yellow crystals. Anal. Calcd: C, 60.21; H, 4.77; P, 7.59. Found: C, 60.12; H, 4.97; P, 7.67. The infrared and NMR spectra are reported in Tables I and II.

***trans*-$PhOIr(CO)(PPh_3)_2$.** A THF (50-mL) suspension of 1.0 g of *trans*-$Ir(CO(PPh_3)_2Cl$ and 0.60 g of PhONa were stirred at room temperature for 14 h. The THF was evaporated and the yellow solid extracted with 20 mL of benzene. The resulting suspension was filtered through a fine, sintered-glass filter. The filtrate was evaporated to dryness and the yellow powder extracted into 100 mL of cyclohexane which was refluxed for 5 min and filtered. Evaporation of the filtrate for 3 days produced 0.86 g of bright yellow crystals (80% yield). Anal. Calcd: C, 61.63; H, 4.22; P, 7.39. Found: C, 62.36; H, 4.69; P, 7.28. The infrared spectrum is reported in Table I.

$CH_3OC(O)Ir(CO)_2(PPh_3)_2$. A solution of 0.20 g of *trans*-$CH_3OIr(CO)(PPh_3)_2$ in 20 mL of toluene was prepared in an inert-atmosphere glovebox and transferred to a pressure bottle. The pressure bottle was sealed, removed from the glovebox, flushed, charged with CO (50 psi), and allowed to stir at room temperature for 2 days. The solution was filtered and transferred to a vapor diffusion crystallization apparatus charged with pentane and stored under CO for 5 days yielding 0.13 g of pale yellow crystals (61% yield). Anal. Calcd: C, 57.75; H, 3.97; P, 7.46. Found: C, 57.65; H, 3.82; P, 7.37. The infrared and NMR spectra are reported in Tables I and II.

***n*-PrOC(O)$Ir(CO)_2(PPh_3)_2$.** A toluene solution (15 mL) of 0.15 g of *trans*-*n*-$PrOIr(CO)(PPh_3)_2$ is carbonylated and crystallized as described for the methoxy analogue yielding 0.095 g (59%) of pale yellow crystals. The infrared and NMR spectra are reported in Tables I and II.

***t*-BuOC(O)$Ir(CO)_2(PPh_3)_2$.** A toluene solution (10 mL) of 0.20 g of *trans*-*t*-$BuOIr(CO)(PPh_3)_2$ is carbonylated and crystallized as described above for the methoxy analogue. The yield is 0.18 g (84%). Anal. Calcd: C, 59.09; H, 4.47; P, 7.10. Found: C, 59.18; H, 4.31; P, 6.81. The infrared and NMR spectral data are reported in Tables I and II.

$PhOC(O)Ir(CO)_2(PPh_3)_2$. A 30-mL solution of *trans*-$PhOIr(CO)(PPh_3)_2$ in toluene was prepared in a Schlenk flask in an inert-atmosphere glovebox. The flask was removed, placed under a CO atmosphere for 90 min at room temperature, and then stored at −20 °C overnight. The pale yellow solid was collected by decanting the solution and drying the solid with a stream of CO. The infrared spectrum is reported in Table I.

Table III. Conductivity Data for Carbonylation of *trans*-$PhOIr(CO)(PPh_3)_2$

sol	*I*, Ω^{-1} cm^{-1}
THF	*a*
THF, CO	*a*
trans-$PhOIr(CO)(PPh_3)_2$	*a*
$Ir(CO)_3(PPh_3)_2{}^+BPh_4{}^-$	9.46×10^{-5}
trans-$PhOIr(CO)(PPh_3)_2$,CO	1.95×10^{-6}

[a] Below 9×10^{-8} which is the limit of detection for the instrument.

$[Ir(CO)_3(PPh_3)_2{}^+][ClO_4{}^-]$. A modified procedure of that previously described was used for preparation of this complex.[35] A solution of 0.20 g of *trans*-$Ir(CO)(PPh_3)_2Cl$ in 25 mL of THF was stirred under CO for 30 min. With CO flushing over the solution, 0.055 g of $AgClO_4$ (finely ground) was added. The solution was stirred for 20 min, the solvent was removed under vacuum, and the resulting white solid was extracted with 10 mL of CH_2Cl_2. Addition of 10 mL of pentane caused precipitation of a white microcrystalline product which can be recrystallized from CH_2Cl_2/pentane to yield 0.18 g (78%) of white crystalline product. The infrared spectrum in KBr shows 2077 (w), 2020 (s), and 1997 (s) cm^{-1}.

$[Ir(CO)_3(PPh_3)_2{}^+][BPh_4{}^-]$. The $BPh_4{}^-$ analogue was prepared by modification of a previously reported procedure.[36] A portion (0.50 g) of $NaBPh_4$ was added to a solution of *trans*-$Ir(CO)(PPh_3)_2Cl$ in 75 mL of THF that has been saturated with CO. This mixture was stirred for 30 min and the THF removed. The resulting pale yellow solid was extracted with CH_2Cl_2, filtered into a Schlenk flask, and stirred under CO for 15 min. Pentane was added to form a white microcrystalline solid which can be recrystallized from CH_2Cl_2/pentane to give 1.4 g (100%) of white crystalline product. The infrared spectrum in KBr shows three sharp absorptions, 2070 (w), 2015 (s), and 1997 (s) cm^{-1}, although in THF solution only one absorption (2010 cm^{-1}) is observed.

Conductivity Studies. Conductivity of the carbonylation reaction mixture was measured by a platinum black dipping electrode with a Sybrom/Barnstead conductivity bridge (Model PM-70CB). All glassware was cleaned in EtOH/KOH and dilute HCl baths followed by 48-h soaking in distilled H_2O and rinsing with distilled H_2O, drying at 110 °C, and rinsing repeatedly with freshly dried and distilled THF. The cell constant for the electrode was calculated by using 0.020 N KCl ($\Omega(H_2O) = 1.68 \times 10^6$ Ω, Ω (0.020 N KCl) = 352 Ω) as $K = 0.974$. The data in Table III were collected for 5×10^{-3} M solutions of iridium complexes at 25 °C. The reaction mixture (*trans*-$PhOIr(CO)(PPh_3)_2$ + CO) was evaluated after 90 min.

Carbonylation of *trans*-$PhOIr(CO)(PPh_3)_2$ in the Presence of $NaBPh_4$. A solution of 0.10 g of *trans*-$PhOIr(CO)(PPh_3)_2$ in 30 mL of THF was prepared in an inert-atmosphere glovebox and carbonylated for 2 h. Then 0.8 g of $NaBPh_4$ (20 equiv) were added and carbonylation continued. Infrared spectra recorded at various times are shown in Figure 1.

Collection of Diffraction Data for *trans*-$PhOIr(CO)(PPh_3)_2$. The crystal selected was a well-formed yellow parallelepiped of approximate dimensions 0.3 × 0.3 × 0.5 mm^3. It was sealed in a thin-walled glass capillary and aligned accurately on our Syntex $P2_1$ automated four-circle diffractometer. Subsequent set-up operations (determination of accurate cell dimensions and orientation matrix) and collection of the intensity data were carried out as described previously;[37] details appear in Table IV. The observed $2/m$ (C_{2h}) diffraction symmetry, along with the systematic absences of $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$,

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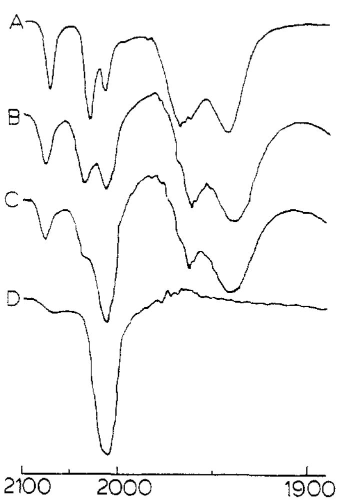

Figure 1. Infrared spectra resulting from addition of a 20-fold excess of $NaBPh_4$ to the carbonylation equilibrium for *trans*-PhOIr(CO)$(PPh_3)_2$. A is before $NaBPh_4$ addition; B is 6 h after $NaBPh_4$ addition; C is 24 h after $NaBPh_4$ addition; and D is $[Ir(CO)_3(PPh_3)_2{}^+][BPh_4{}^-]$ in THF.

Table IV. Experimental Data for the X-Ray Diffraction Study of *trans*-PhOIr(CO)$(PPh_3)_2$

(A) Unit Cell Parameters[a] at 24 °C (297 K)

cryst system: monoclinic	$V = 3558$ (2) Å^3
space group: $P2_1/c$ [C^5_{2h}; NO. 14]	$Z = 4$
$a = 15.790$ (3) Å	formula: $C_{43}H_{35}IrO_2P_2$
$b = 11.461$ (3) Å	mol wt = 837.92
$c = 19.986$ (5) Å	D(calcd) = 1.564 g cm^{-3}
$\beta = 100.326$ (18)°	μ(Mo Kα) = 41.1 cm^{-1}

(B) Data Collection

diffractometer: Syntex $P2_1$
radiation: Mo K$\bar{\alpha}$ ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly oriented (pyrolitic) graphite; equatorial mode with 2θ(m) = 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction
reflections measured: $+h,+k,\pm l$ for 2θ = 5.0–55.0°; 9221 reflections collected and marged to 8220 unique data
scan type: coupled θ(crystal)–2θ(counter)
scan range: $[2\theta(K\alpha_1) - 1.0]° \rightarrow [2\theta(K\alpha_2) + 1.0]°$
scan speed: 3.0 deg/min (in 2θ)
backgrounds: stationary crystal and counter at the two ends of the scan range, each for one-fourth total scan time
standard reflections: (3) approximately mutual orthogonal reflections collected after every 97 data points; no significant fluctuations or decay observed
absorption correction: empirical, based upon interpolation (in 2θ and ϕ) between normalized ψ scans of four close-to-axial reflections (min/max transmission = 0.72)

[a] Based upon refinement of the setting angels of 25 unresolved (Mo K$\bar{\alpha}$) reflections with 2θ = 20–30°.

indicated that the crystal belonged to the centrosymmetric monoclinic space group $P2_1/c$.

All data were corrected for the effects of absorption and the Lorentz and polarization factors; they were converted to unscaled $|F_0|$ values. Symmetry-equivalent reflections were averaged ($R(I)$ = 4.8% for 290 pairs of reflections). Any reflection with I(net) < 0 was assigned the value $|F_0| = 0$. Data were placed on an approximately absolute scale by means of a Wilson plot, which also gave the value of $\bar{B}$ = 2.51 Å^2 for the average overall isotropic thermal parameter.

Solution and Refinement of the Structure for *trans*-PhOIr(CO)$(PPh_3)_2$. All subsequent calculations were performed by using our locally modified version of the Syntex XTL interaction crystallographic program package.[38] The structure was solved by direct methods using the program MULTAN; it was found necessary to normalize each parity group individually because of uneven intensity distribution (e.g., $\langle E^2\rangle = 0.688$ for EOE vs. $\langle E^2\rangle = 1.241$ for EEO). The iridium atom (with a y coordinate close to $^1/_2$) and two phosphorus atoms were located from an "E map". All remaining non-hydrogen atoms were located by use of difference Fourier maps. The structure was optimized by full-matrix least-squares refinement, minimizing the function $\sum w(|F_0| - |F_c|)^2$ where $1/w = \{[\sigma(|F_0|)]^2 + [0.015|F_0|]^2\}$. All hydrogen atoms were included in their idealized positions, based upon d(C–H) = 0.95 Å;[39] these positions were updated, but not refined. Anisotropic thermal parameters were used for atoms in the OIr(CO)P_2 core of the molecule; isotropic thermal parameters were used for all carbon atoms of the phenyl rings. Final convergence was reached with[40] R_F = 6.2%, R_{wF} = 4.6%, and GOF = 1.54 for all 8220 reflections [R_F = 4.6% and R_{wF} = 4.4% for those 6777 reflections with $|F_0| > 3\sigma(|F_0|)$; R_F = 3.8% and R_{wF} = 4.1% for those 5981 reflections with $|F_0| > 6\sigma(|F_0|)$]. A final difference-Fourier map showed no unexpected features; the structure is thus both correct and complete. Final atomic parameters are collected in Table V.

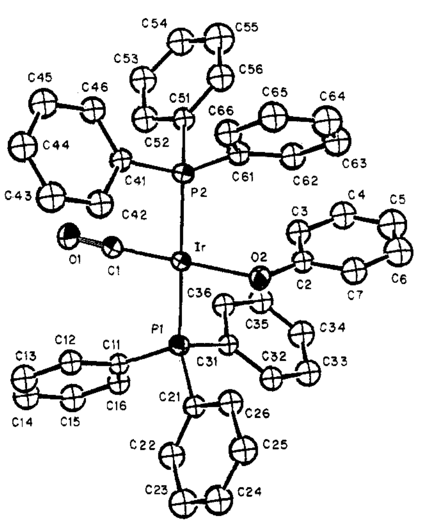

Figure 2. Labeling diagram for *trans*-PhOIr(CO)$(PPh_3)_2$ (ORTEP-II diagram; 30% probability ellipsoids).

Throughout the analysis the calculated structure factors were based upon the analytical expression for the neutral atoms' form factors; both the real imaginary components of anomalous dispersion were included for all non-hydrogen atoms.[41]

Results and Discussion

The syntheses of the alkoxy complexes *trans*-ROIr(CO)$(PPh_3)_2$ involves a straightforward metathetical reaction between *trans*-Ir(CO)$(PPh_3)_2$Cl and NaOR (eq 6).

$$trans\text{-}Ir(CO)(PPh_3)_2Cl + NaOR \rightarrow trans\text{-}ROIr(CO)(PPh_3)_2 + NaCl \quad (6)$$

The primary impurity NaOR may be removed by careful recrystallization or extraction with solvents such as cyclohexane or benzene. The IR and NMR characterization are consistent with the products being square-planar, 16-electron complexes. The carbonyl stretching frequencies indicate that the PhO^- group is a weaker donor than the alkoxides, as expected. In each case the NMR integration was consistent with the formulation and indicated no remaining NaOR impurity. The purity of the complexes was ascertained by microanalysis.

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(38) "Syntex XTL Operations Manual"; Syntex Analytical Instruments, Cupertino, CA, 1976.

(39) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(40) R_F (%) = $100\sum||F_0| - |F_0||/\sum|F_0|$; R_{wF} (%) = $100[\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$; GOF = $[\sum w(|F_0| - |F_0|)^2/(NO - NV)]^{1/2}$, where NO = *number of observations and* NV = *number of variables.*

(41) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

Table V. Final Atomic Parameters (with Esd's) for *trans*-PhOIr(CO)(PPh$_3$)$_2$

atom	*x*	*y*	*z*	*B*(iso), Å^2	atom	*x*	*y*	*z*	*B*(iso), Å^2
Ir	0.261 28 (1)	0.479 78 (2)	0.244 02 (1)		C(61)	0.446 49 (33)	0.599 95 (47)	0.357 00 (26)	3.266 (95)
P(1)	0.161 47 (8)	0.467 50 (12)	0.143 27 (6)		C(62)	0.427 91 (38)	0.717 59 (54)	0.347 27 (29)	4.17 (11)
P(2)	0.358 16 (8)	0.493 90 (11)	0.347 29 (6)		C(63)	0.493 99 (44)	0.799 79 (61)	0.354 55 (33)	5.17 (14)
C(1)	0.232 56 (35)	0.339 67 (47)	0.273 27 (25)		C(64)	0.578 19 (46)	0.764 29 (65)	0.372 98 (35)	5.61 (15)
O(1)	0.213 53 (29)	0.251 40 (37)	0.295 09 (20)		C(65)	0.597 34 (42)	0.650 05 (61)	0.384 33 (33)	5.13 (14)
O(2)	0.296 47 (24)	0.637 11 (31)	0.208 77 (18)		C(66)	0.532 66 (38)	0.566 34 (55)	0.376 08 (29)	4.20 (11)
C(2)	0.269 92 (32)	0.741 43 (47)	0.224 68 (26)	3.183 (93)	H(3)	0.1815	0.6919	0.2824	6.0
C(3)	0.207 55 (38)	0.757 94 (53)	0.265 65 (29)	4.02 (11)	H(4)	0.1394	0.8790	0.3087	6.0
C(4)	0.183 10 (44)	0.869 49 (62)	0.282 02 (35)	5.25 (14)	H(5)	0.2043	1.0415	0.2711	6.0
C(5)	0.221 27 (50)	0.965 57 (71)	0.259 79 (38)	6.27 (17)	H(6)	0.3112	1.0184	0.2067	6.0
C(6)	0.283 81 (49)	0.951 68 (67)	0.221 30 (39)	6.00 (16)	H(7)	0.3516	0.8322	0.1756	6.0
C(7)	0.308 46 (41)	0.840 31 (59)	0.203 01 (32)	4.76 (13)	H(12)	0.1894	0.2203	0.1536	6.0
C(11)	0.091 92 (32)	0.338 77 (45)	0.130 64 (25)	2.984 (89)	H(13)	0.1031	0.0536	0.1350	6.0
C(12)	0.128 85 (36)	0.228 00 (51)	0.139 83 (28)	3.85 (11)	H(14)	−0.0436	0.0705	0.1032	6.0
C(13)	0.077 46 (43)	0.128 92 (60)	0.128 98 (34)	5.07 (14)	H(15)	−0.1078	0.2514	0.0852	6.0
C(14)	−0.009 06 (44)	0.138 97 (62)	0.109 76 (35)	5.28 (14)	H(16)	−0.0245	0.4213	0.1038	6.0
C(15)	−0.047 20 (43)	0.245 87 (62)	0.099 64 (33)	5.19 (14)	H(22)	0.3053	0.5769	0.0995	6.0
C(16)	0.002 31 (36)	0.346 87 (50)	0.110 30 (28)	3.79 (11)	H(23)	0.3586	0.5869	−0.0020	6.0
C(21)	0.203 82 (32)	0.471 99 (46)	0.063 54 (25)	3.143 (87)	H(24)	0.2931	0.4827	−0.0964	6.0
C(22)	0.276 94 (38)	0.536 10 (53)	0.060 42 (30)	4.17 (11)	H(25)	0.1700	0.3770	−0.0928	6.0
C(23)	0.309 06 (44)	0.541 08 (60)	0.000 27 (34)	5.10 (14)	H(26)	0.1135	0.3692	0.0080	6.0
C(24)	0.269 84 (44)	0.480 79 (61)	−0.055 80 (35)	5.19 (14)	H(32)	0.1121	0.6690	0.0530	6.0
C(25)	0.197 81 (44)	0.417 92 (64)	−0.053 62 (34)	5.46 (15)	H(33)	0.0224	0.8297	0.0575	6.0
C(26)	0.164 24 (40)	0.413 39 (56)	0.006 65 (31)	4.56 (12)	H(34)	−0.0545	0.8476	0.1455	6.0
C(31)	0.087 29 (32)	0.589 87 (44)	0.138 36 (25)	2.956 (89)	H(35)	−0.0459	0.7057	0.2286	6.0
C(32)	0.080 43 (36)	0.675 68 (51)	0.089 01 (28)	3.86 (11)	H(36)	0.0450	0.5449	0.2263	6.0
C(33)	0.027 17 (42)	0.771 25 (59)	0.091 73 (32)	4.94 (13)	H(42)	0.4278	0.3236	0.2707	6.0
C(34)	−0.018 57 (43)	0.781 54 (62)	0.143 89 (34)	5.23 (14)	H(43)	0.4991	0.1474	0.2920	6.0
C(35)	−0.013 24 (40)	0.698 21 (56)	0.193 26 (31)	4.60 (12)	H(44)	0.5236	0.0679	0.4011	6.0
C(36)	0.040 23 (36)	0.602 29 (50)	0.191 48 (28)	3.76 (10)	H(45)	0.4786	0.1689	0.4890	6.0
C(41)	0.412 61 (32)	0.354 82 (44)	0.368 17 (25)	2.949 (88)	H(46)	0.4122	0.3499	0.4696	6.0
C(42)	0.438 83 (39)	0.293 01 (55)	0.315 68 (31)	4.42 (12)	H(52)	0.2226	0.3884	0.4014	6.0
C(43)	0.480 43 (44)	0.188 10 (62)	0.328 26 (35)	5.35 (14)	H(53)	0.1541	0.4153	0.4940	6.0
C(44)	0.495 42 (43)	0.141 07 (61)	0.392 71 (35)	5.21 (14)	H(54)	0.1887	0.5758	0.5642	6.0
C(45)	0.469 18 (43)	0.201 24 (60)	0.444 40 (33)	5.11 (14)	H(55)	0.3018	0.6941	0.5503	6.0
C(46)	0.428 82 (36)	0.308 35 (52)	0.432 90 (29)	4.02 (11)	H(56)	0.3749	0.6635	0.4593	6.0
C(51)	0.305 36 (33)	0.523 52 (47)	0.420 02 (26)	3.201 (88)	H(62)	0.3696	0.7424	0.3355	6.0
C(52)	0.239 74 (41)	0.451 67 (58)	0.431 76 (33)	4.78 (13)	H(63)	0.4809	0.8802	0.3467	6.0
C(53)	0.197 83 (45)	0.468 20 (61)	0.486 28 (36)	5.26 (14)	H(64)	0.6233	0.8202	0.3777	6.0
C(54)	0.219 60 (44)	0.560 71 (65)	0.528 47 (35)	5.44 (14)	H(65)	0.6556	0.6267	0.3980	6.0
C(55)	0.285 04 (53)	0.631 59 (73)	0.519 55 (42)	6.87 (19)	H(66)	0.5470	0.4861	0.3834	6.0
C(56)	0.328 82 (42)	0.613 37 (59)	0.465 06 (33)	5.04 (14)					

Table VI. Interatomic Distances (Å) for *trans*-PhOIr(CO)(PPh$_3$)$_2$

(A) Iridium–Ligand Distances			
Ir–P(1)	2.328 (1)	Ir–O(2)	2.049 (4)
Ir–P(2)	2.344 (1)	Ir–C(1)	1.795 (5)
(B) Phosphorus–Carbon Distances			
P(1)–C(11)	1.829 (5)	P(2)–C(41)	1.824 (5)
P(1)–C(21)	1.836 (5)	P(2)–C(51)	1.832 (5)
P(1)–C(31)	1.819 (5)	P(2)–C(61)	1.834 (5)
(C) Oxygen–Carbon Distances			
O(1)–C(1)	1.162 (7)	O(2)–C(2)	1.324 (6)

Table VII. Interatomic Angles (deg) for *trans*-PhOIr(CO)(PPh$_3$)$_2$

(A) Angles about the Iridium Atom			
P(1)–Ir–P(2)	178.15 (4)	P(2)–Ir–C(1)	86.45 (17)
P(1)–Ir–C(1)	93.22 (17)	P(2)–Ir–O(2)	93.88 (11)
P(1)–Ir–O(2)	86.51 (11)	C(1)–Ir–O(2)	178.19 (20)
(B) Ir–P–C and C–P–C Angles			
Ir–P(1)–C(11)	117.68 (17)	C(11)–P(1)–C(21)	101.88 (23)
Ir–P(1)–C(21)	116.97 (17)	C(11)–P(1)–C(31)	104.46 (23)
Ir–P(1)–C(31)	109.24 (17)	C(21)–P(1)–C(31)	105.24 (23)
Ir–P(2)–C(41)	110.35 (17)	C(41)–P(2)–C(51)	104.08 (23)
Ir–P(2)–C(51)	113.17 (17)	C(41)–P(2)–C(61)	103.69 (24)
Ir–P(2)–C(61)	120.19 (18)	C(51)–P(2)–C(61)	103.81 (24)
(C) Ir–O–C, O–C–C, and Ir–C–O Angles			
Ir–O(2)–C(2)	126.5 (3)	O(2)–C(2)–C(3)	123.2 (5)
Ir–C(1)–O(1)	176.8 (5)	O(2)–C(2)–C(7)	119.0 (5)
(D) P–C–C Angles			
P(1)–C(11)–C(12)	119.3 (4)	P(2)–C(41)–C(42)	117.7 (4)
P(1)–C(11)–C(16)	122.4 (4)	P(2)–C(41)–C(46)	123.6 (4)
P(1)–C(21)–C(22)	119.5 (4)	P(2)–C(51)–C(52)	119.2 (4)
P(1)–C(21)–C(26)	121.6 (4)	P(2)–C(51)–C(56)	123.4 (4)
P(1)–C(31)–C(32)	123.7 (4)	P(2)–C(61)–C(62)	119.5 (4)
P(1)–C(31)–C(36)	117.3 (4)	P(2)–C(61)–C(66)	122.0 (4)

Description of the Molecular Geometry of *trans*-PhOIr(CO)(PPh$_3$)$_2$. The complex crystallizes as discrete molecular units, separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. The scheme used for labeling atoms is illustrated in Figure 2, while Figure 3 provides a clear stereoscopic view of the molecular structure. Interatomic distances and angles are compiled in Tables VI and VII.

The central d^8 iridium(I) atom has the expected square-planar stereochemistry. The two trans angles are P(1)–Ir–P(2) = 178.15 (4)° and C(1)–Ir–O(2) = 178.19 (20)°; the various cis angles range from P(2)–Ir–C(1) = 86.45 (17)° through P(2)–Ir–O(2) = 93.88 (11)°. The two independent iridium–phosphorus distances are Ir–P(1) = 2.328 (1) Å and Ir–P(2) = 2.344 (1) Å; the average value of 2.336 Å is rather longer than the Ir–P distance of 2.300 (1) Å found in the related species *trans*-MeIr(CO)(PPh$_3$)$_2$.[10]

Distances and angles within the PPh$_3$ ligands are normal, with P–C = 1.819 (5)–1.836 (5) Å, ⟨Ir–P–C = 109.24 (17)–120.19 (18)°, and ⟨C–P–C = 101.88 (23)–105.24 (23)°. The carbon atom skeletons of the phenyl groups of the

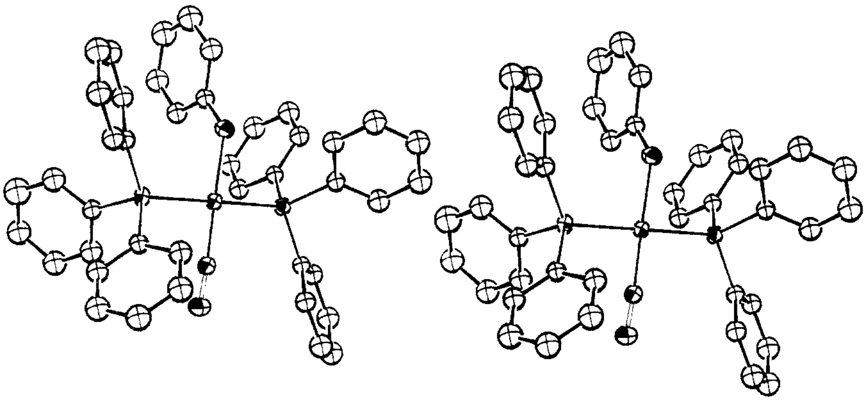

Figure 3. Stereoscopic view of the *trans*-PhOIr(CO)(PPh$_3$)$_2$ molecule.

PPh$_3$ ligand show the usual slight distortions[42] from D_{6h} toward C_{2v} symmetry, with C(α)–C(ipso)–C(α′) angles of 118.3 (5)°, 119.0 (5)°, 118.8 (5)°, 118.8 (5), 117.4 (5)°, and 118.5 (5)° sequentially. The Ir–C–O system is approximately linear with ∠Ir–C(1)–O(1) = 176.8 (5)°, Ir–C(1) = 1.795 (5) Å, and C(1)–O(1) = 1.162 (7) Å.

The phenoxide ligand is bent, with ∠Ir–O(2)–C(2) = 126.5 (3)°. The Ir–O(2) distance of 2.049 (4) Å and the O(2)–C(2) distance of 1.324 (6) Å are indicative of some multiple-bond character in these linkages. The internal angle at the ipso carbon of the phenoxide ligand, ∠C(3)–C(2)–C(7) = 117.7 (5)°, is reduced in the expected manner from the typical benzenoid angle of 120.0°.[42]

Carbonylation of *trans*-ROIr(CO)(PPh$_3$)$_2$. Each of the iridium alkoxides undergoes carbonylation at moderate conditions to the dicarbonyl carboalkoxy complexes ROC(O)Ir(CO)$_2$(PPh$_3$)$_2$ (reaction 5). The products show the expected spectroscopic characteristics for the suggested formulation (Tables I and II). Each shows a C=O at ~1640 cm^{-1} and two additional C≡O stretches in the 1900's cm^{-1}, very similar to the complexes RC(O)Ir(CO)$_2$(PPh$_3$)$_2$.[10] The characterization of CH$_3$OC(O)Ir(CO)$_2$(PPh$_3$)$_2$ is completely consistent with that previously reported for this species formed by methoxide attack on [Ir(CO)$_3$(PPh$_3$)$_2^+$].[43]

Infrared spectra taken during the course of the carbonylation reaction show the growth and then loss of very sharp absorptions at ~2075 and ~2035 cm^{-1}, suggesting the formation of an intermediate. A sample spectrum is shown in Figure 4. The high frequency and sharpness indicate [Ir(CO)$_3$(PPh$_3$)$_2^+$] which was prepared as described in the Experimental Section. The infrared spectra are similar, but not identical.[9] Although the effect of cations on the infrared spectrum of metal carbonyl anions has been often studied, the possible influence of a counteranion on the infrared spectrum of metal carbonyl cations are not well understood. To verify the existence of [Ir(CO)$_3$(PPh$_3$)$_2^+$] in the carbonylation mixture, we carbonylated *trans*-PhOIr(CO)(PPh$_3$)$_2$ for 2 h at room temperature and added a 20-fold excess of NaBPh$_4$. The infrared spectra which result from this are shown in Figure 1. The formation of [Ir(CO)$_3$(PPh$_3$)$_2^+$][BPh$_4^-$] (a single absorption at 2010 cm^{-1}) is clearly shown.

Conductivity studies also show the formation of charged species upon carbonylation of *trans*-PhOIr(CO)(PPh$_3$)$_2$. The conductivity of THF solutions of CO or *trans*-PhOIr(CO)(PPh$_3$)$_2$ is smaller than that can be detected. Conductivity of [Ir(CO)$_3$(PPh$_3$)$_2^+$][BPh$_4^-$] is 9.46 × 10^{-5} Ω^{-1} cm^{-1}. The conductivity of the carbonylation mixture (after 1 h) is lower than that for the pure ionic complex (1.95 × 10^{-6} Ω^{-1} cm^{-1}), as is expected for formation of *some* [Ir(CO)$_3$(PPh$_3$)$_2^+$] in the reaction. Certainly the conductivity combined with the infrared studies confirm the formation of [Ir(CO)$_3$(PPh$_3$)$_2^+$] as an intermediate in the carbonylation of *trans*-ROIr(CO)(PPh$_3$)$_2$.

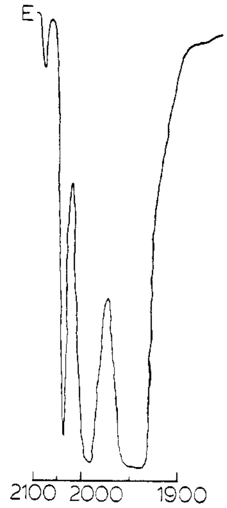

Figure 4. A spectrum recorded after 45 min of carbonylation of *trans*-*n*-PrOIr(CO)(PPh$_3$)$_2$ in toluene showing the sharp absorptions due to [Ir(CO)$_3$(PPh$_3$)$_2^+$] above 2000 cm^{-1}.

The weakest of the alkoxide nucleophiles PhO$^-$ leads to an equilibrium between [Ir(CO)$_3$(PPh$_3$)$_2^+$][OPh$^-$] and PhOC(O)Ir(CO)$_2$(PPh$_3$)$_2$. The equilibrium mixture can be reached by either carbonylation of *trans*-PhOIr(CO)(PPh$_3$)$_2$ or by addition of NaOPh to [Ir(CO)$_3$(PPh$_3$)$_2^+$][BPh$_4^-$]. The approximate unit value of the equilibrium constant indicates very little energy difference between the ion pair and the carbophenoxy complex. With more nucleophilic alkoxides no trace of [Ir(CO)$_3$(PPh$_3$)$_2^+$] is evident at completion although it is detectable as an intermediate. The equilibrium of the phenoxide as a free ion or coordinated to CO is very similar to the equilibrium reported for a platinum carboxylic acid (see eq 7).[44]

$$\mathrm{Pt(CO_2H)(C_6H_9)(dppe)} \rightleftarrows [\mathrm{Pt(C_6H_9)(CO)(dppe)^+}][\mathrm{OH^-}] \quad (7)$$

The conductivity and infrared data indicate the formation of Ir(CO)$_3$(PPh$_3$)$_2^+$OR$^-$ in the carbonylation of *trans*-ROIr(CO)(PPh$_3$)$_2$. This species is formed upon addition of carbon monoxide to *trans*-ROIr(CO)(PPh$_3$)$_2$. The lifetime for these intermediates is strongly dependent on the nucleophilicity of OR$^-$. For R = Me the infrared absorptions of Ir(CO)$_3$(PPh$_3$)$_2^+$OR$^-$ appear very rapidly and

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[42] Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1630.

[43] Angoletta, M.; Caglio, G.; Malatesta, L. *J. Chem. Soc.* **1965**, 6974.

[44] Bennett, M. A.; Rokicki, A. *Organometallics* **1985**, *4*, 180.

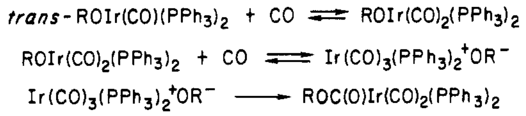

Figure 5. Suggested scheme for the carbonylation of iridium alkoxides.

then disappear as the reaction continues with formation of $CH_3OC(O)Ir(CO)_2(PPh_3)_2$ in near quantitative yield. For R = Ph some $Ir(CO)_3(PPh_3)_2{}^+OPh^-$ remains after 24 h, and for R = C_6F_5 only the ion pair is formed.

Mechanism of Carbonylation. Clearly the first step anticipated for reaction of a 16-electron, square-planar complex with a molecule such as CO is addition, as shown in the suggested scheme (Figure 5). Such a reaction is consistent with our results and the first-order dependence on [CO] observed in reaction of $Pt(dppe)(CH_3)(OCH_3)$ with CO.[29,30] The suggestions for the mechanism of carbonylation of *trans*-$MeOIr(CO)(PPh_3)_2$ and $Pt(dppe)(CH_3)(OCH_3)$ diverge after this initial carbonylation. Our observation of $[Ir(CO)_3(PPh_3)_2]^+[OR]^-$ by infrared and conductivity studies indicates a second step of OR^- displacement by a second CO. Although we have no direct evidence, a dissociation of OR^- from the 18-electron complex seems most likely. Once the cation, anion pair is formed, a rapid nucleophilic attack of OR^- on a carbon occurs leading to the carboalkoxy product as shown in step 3 of Figure 5. This reaction has been previously reported for OMe^-, and we have independently confirmed that it occurs readily.

The only piece of data which has been cited to exclude a similar mechanism for the platinum complex, is the fairly small incorporation (10%) of OCD_3 in the product when the reaction is accomplished in the presence of CD_3OD.[29,30] Presuming that $[Pt(dppe)(CH_3)(CO)_{1or2}]^+[OMe]^-$ is formed, the amount of OCD_3^- incorporation would depend on the relative rate of breakup of the ion pair compared to the rate of nucleophilic attack of OCH_3^- on coordinated CO. In a weakly solvating solvent, where the ion pair would be tight and OCH_3^- would not be extensively solvated, the incorporation of OCD_3 could be quite small. Thus it is possible that the alkoxy dissociation, nucleophilic attack mechanism observed for *trans*-$ROIr(CO)(PPh_3)_2$ pertains also to $Pt(dppe)(CH_3)(OCH_3)$.

Conclusion. The carbonylation of alkoxyiridium complexes, *trans*-$ROIr(CO)(PPh_3)_2$, occurs by displacement of OR^- from the coordination sphere of iridium and subsequent nucleophilic attack of the alkoxide on a carbon of the cationic carbonyl. This mechanism may have important consequences for similar reactions of hydroxide with coordinated alkenes. A recent theoretical study has suggested that cis migration of hydroxide to an alkene is impossible for a palladium complex.[45]

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Registry No. *trans*-$CH_3OIr(CO)(PPh_3)_2$, 94070-38-9; *trans*-*n*-$PrOIr(CO)(PPh_3)_2$, 94070-39-0; *trans*-*t*-$BuOIr(CO)(PPh_3)_2$, 98720-65-1; *trans*-$PhOIr(CO)(PPh_3)_2$, 94070-40-3; $CH_3OC(O)Ir(CO)_2(PPh_3)_2$, 15522-78-8; *n*-$PrOC(O)Ir(CO)_2(PPh_3)_2$, 63397-73-9; *t*-$BuOC(O)Ir(CO)_2(PPh_3)_2$, 98735-49-0; $PhOC(O)Ir(CO)_2(PPh_3)_2$, 94070-41-4; $Ir(CO)(PPh_3)_2Cl$, 15318-31-7; $[Ir(CO)_3(PPh_3)_2{}^+][ClO_4^-]$, 15738-08-6; $[Ir(CO)_3(PPh_3)_2{}^+][BPh_4^-]$, 59809-88-0; $[Ir(CO)_3(PPh_3)_2{}^+]$, 47855-02-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances and angles, and observed and calculated structure factor amplitudes for *trans*-$PhOIr(CO)(PPh_3)_2$ (42 pages). Ordering information is given on any current masthead page.

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