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Addition Reactions and Crystal Structure of *trans*-$CH_3Ir(CO)(PPh_3)_2$

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The complex *trans*-$MeIr(CO)(PPh_3)_2$ readily undergoes addition reactions with a variety of small molecules such as H_2, CO, $MeO_2CCH{=}CHCO_2Me$, $MeO_2CC{\equiv}CCO_2Me$, O_2, CH_3I, and $H_2C(O)$ to yield well-characterized products. Further reactions of the addition complexes are noted in most cases. The species *trans*-$MeIr(CO)(PPh_3)_2$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 9.2497$ (9) Å, $b = 9.6080$ (11) Å, $c = 10.4855$ (14) Å, $\alpha = 72.390$ (10)°, $\beta = 88.990$ (9)°, $\gamma = 69.224$ (8)°, $V = 826.22$ (16) Å^3, $Z = 1$, and D(calcd) = 1.53 g cm^{-3} for mol wt 759.9. Diffraction data (Mo Kα, $2\theta = 4.5$–$50.0°$) were collected with a Syntex $P2_1$ automated four-circle diffractometer and refined to $R_F = 1.8\%$ and $R_{wF} = 2.1\%$ for the 2922 independent reflections (none rejected). The molecule lies on a center of symmetry and is disordered with CO and Me ligands occupying square-planar sites rigorously coplanar with the iridium atom. The Ir–P distances are each 2.300 (1) Å; estimated Ir–CO and Ir–Me distances are ~1.835 and ~2.17 Å, respectively.

Introduction

The square-planar complexes of Rh(I) and Ir(I) have been very important to the understanding of organometallic reactions. Oxidative addition and reductive elimination were first observed on these complexes and have subsequently formed an important part of homogeneous catalysis.[2-8] Several analogues of *trans*-$Ir(CO)(PPh_3)_2Cl$ have been prepared and their reactions investigated.[5-11] The reactivity of an important analogue, *trans*-$CH_3Ir(CO)(PPh_3)_2$, has not been previously investigated and is the subject of this report.

One of the first organometallic complexes to be extensively investigated was *trans*-$Ir(CO)(PPh_3)_2Cl$. Although this complex functions as a catalyst for hydrogenation reactions, the stoichiometric reactions have been of more value in understanding organometallic reaction mechanisms.[5-11] *trans*-$Ir(CO)L_2X$ complexes undergo a number of oxidative-addition reactions with species such as H_2, O_2, etc.[2] Alkenes and alkynes also bind to *trans*-$Ir(CO)(PPh_3)_2Cl$ (eq 1 and 2).[5,6] The electron-withdrawing ability

$$trans\text{-}Ir(CO)(PPh_3)_2Cl + \text{alkene} \rightleftarrows Ir(CO)(\text{alkene})(PPh_3)_2Cl \quad (1)$$

$$trans\text{-}Ir(CO)(PPh_3)_2Cl + \text{alkyne} \rightarrow Ir(CO)(\text{alkyne})(PPh_3)_2Cl \quad (2)$$

of the alkene seems to be the predominant factor in alkene bonding.

Table I. Spectroscopic Properties of Prepared Compounds

compound	ν(CO), cm^{-1}	^{1}H NMR^a δ
trans-$Ir(CO)(PPh_3)_2Cl$	1955^b	
trans-$CH_3Ir(CO)(PPh_3)_2$	1937^b	0.63 (t, J_{P-H} = 9.0 Hz)
$CH_3Ir(CO)_2(PPh_3)_2$	1961 (s), 1904 (vs)^c	
$CH_3C(O)Ir(CO)_2(PPh_3)_2$	1975 (s), 1916 (vs), 1612 (m)^c	2.5 (s)
$H_3Ir(CO)(PPh_3)_2$	2108 (m), 2070 (vs), 1960 (s), 1953 (vs),^{b} 1776 (m br) (Ir–H)	
$CH_3Ir(O_2)(CO)(PPh_3)_2$	1967, ν_{O-O} = 827^c	1.48 (t, J_{P-H} = 4.8 Hz)
$CH_3Ir(MeO_2CCH{=}CHCO_2Me)(CO)(PPh_3)_2$	1998^c	0.23 (t, J_{P-H} = 8.7 Hz), 3.04 (s), 3.50 (s)
$CH_3Ir(MeO_2CC{\equiv}CCO_2Me)(CO)(PPh_3)_2$	1943^c	0.87 (dd, J_{P-H} = 5.5 Hz, J_{P-H} =7.9 Hz), 3.45 (s), 3.60 (s)
$(CH_3)_2Ir(CO)(PPh_3)_2I$	1993^b	0.51 (t, J_{P-H} = 4.9 Hz), 1.02 (t, J_{P-H} = 7.6 Hz)

^{a}The phenyl groups are not included in this table. ^{b}Benzene solution. ^{c}KBr.

The studies of the addition of small molecules to *trans*-$Ir(CO)(PPh_3)_2Cl$ have been central to the development of organometallic chemistry.[2-14] Analogues, *trans*-$RIr(CO)(PPh_3)_2$ (where R is an alkyl group which may be involved in reactions) have not been investigated as thoroughly.[15-25] An electrochemical route to alkyl and aryl

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[17] In one case crystalline product was produced although no experimental detail was provided. In another case the product of CH_3Li was reported to be unstable.[17-19]

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derivatives has been reported (eq 3 and 4), although no

$$M(CO)(PPh_3)_2Cl \xrightarrow{RX} RM(CO)(PPh_3)_2XCl \xrightarrow{2e^-} RM(CO)(PPh_3)_2 + X^- + Cl^- \quad (3)$$

$$M(CO)(PPh_3)_2Cl \xrightarrow[-Cl^-]{e^-} M(CO)(PPh_3)_2^- \xrightarrow{RX} RM(CO)(PPh_3)_2 + X^- \quad (4)$$

M = Rh, Ir; R =
Me, Ph, *p*-tolyl, *p*-methoxyphenyl, C_6F_5, CPh_3

subsequent reactions were investigated.[15,16] Reaction of alkyllithium reagents with *trans*-$Ir(CO)(PPh_3)_2X$ complexes have been reported. The in situ preparation of (octyl)$Ir(CO)(PPh_3)_2$ by this method allowed evaluation of the deuterium isotope effect for β-elimination.[21] Several stable aryl complexes, $ArIr(CO)(PPh_3)_2$ (Ar = aryl), have been previously reported from reaction of LiAr with *trans*-$Ir(CO)(PPh_3)_2Cl$.[22-25] For the aryl complexes cis-trans isomerization, oxidative addition of HCl and formation of the O_2 adduct have been reported.[22-25] Methyl complexes $CH_3M(PPh_3)_3$ undergo ortho metalation and reductive elimination of CH_4 to form $M(C_6H_4PPh_2)(PPh_3)_2$.[26,27] Thus the reactivity of 16-electron alkyl complexes of rhodium and iridium is largely unexplored.

Experimental Section

Iridium trichloride was generously loaned by Johnson Matthey Inc. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer, and ^1H NMR spectra were recorded on a Varian EM 390 or on a Jeolco FX 90Q. *trans*-$Ir(PPh_3)_2(CO)Cl$ was prepared as previously described.[28] The CO stretching frequency is given in Table I.

Preparations. *trans*-$CH_3Ir(CO)(PPh_3)_2$ was prepared by the addition of CH_3Li to *trans*-$Ir(CO)(PPh_3)_2Cl$ by the following procedure: *trans*-$Ir(CO)(PPh_3)_2Cl$ (1.0 g) was suspended in 20 mL THF and 10 mL of a CH_3Li solution (1.5 M in Et_2O) were added in an inert-atmosphere glovebox. The solution was stirred until it becomes deep orange-red in color (30 min to 1 h). At this time the remaining CH_3Li was decomposed by addition of Florisil which was added until obvious reaction with MeLi has ceased. The mixture was filtered through a coarse-sintered glass filter and the Florisil washed with THF (3 × 10 mL). The filtrate was again filtered (fine filter), the volume reduced to 25 mL, and 70 mL of hexanes added to induce precipitation. The deep yellow precipitate was collected by suction filtration and washed with hexanes (2 × 5 mL), yielding 0.8 g (82%). The CO stretching frequency (1937 cm^{-1}) and ^1H NMR (δ 0.63 (t, $J_{P-H} = 9.0$ Hz), 7.1 (m)) are consistent with the formulation *trans*-$CH_3Ir(CO)(PPh_3)_2$. Crystals suitable for crystallographic analysis were grown by slow evaporation of a saturated benzene solution of $CH_3Ir(CO)(PPh_3)_2$ in the glovebox. The compound reacted rapidly with O_2 but was otherwise quite stable.

$CH_3Ir(CO)_2(PPh_3)_2$. A solution of 0.8 g of *trans*-$CH_3Ir(CO)(PPh_3)_2$ in 25 mL of THF was placed under a CO atmosphere at −78 °C for 30 min. Addition of 125 mL of chilled pentane and continued stirring at −78 °C under CO for 2 h resulted in an air-stable pale yellow precipitate which was collected by suction filtration; 0.7 g (84%). In solution this complex rapidly reverted to the 16-electron complex. The KBr IR spectrum shows absorptions at 1961 (s) and 1904 (vs) cm^{-1}.

$CH_3C(O)Ir(CO)_2(PPh_3)_2$.[19-21] A suspension of 0.50 g of $CH_3Ir(CO)(PPh_3)_2$ in 30 mL of pentane was reacted with CO at 1000 psi and 70 °C for 48 h. Upon cooling, the air-stable, white precipitate could be collected by suction filtration (0.48 g, 93%). The infrared spectrum (KBr) 1975 (s), 1916 (vs), and 1612 (m) cm^{-1} and ^1H NMR (δ 2.5 (s) and 6.9 (m)) were consistent with the formulation.

Reaction of $CH_3Ir(CO)(PPh_3)_2$ with H_2 or D_2 at Room Temperature. A 0.05-g sample of $CH_3Ir(CO)(PPh_3)_2$ was suspended in 25 mL of cyclohexane in a Schlenk flask, sealed, and brought out of the drybox. H_2 (or D_2) gas dispersion was carried out for a period of 15–30 min after which time a clear solution resulted. The IR spectra in cyclohexane were as follows: H_2, 2085 (s), 1974 (vs), 1782 (mbr); D_2, 2010 (vs) cm^{-1}. The solvent was evaporated to yield white powders with IR spectra (in KBr) as follows; H_2, 2108 (m), 2070 (vs), 1960 (s), 1953 (vs), 1776 (mbr); D_2, 1992 (vs), 1985 (vs) cm^{-1}.

Reaction of $CH_3Ir(CO)(PPh_3)_2$ with H_2 at Low Temperature. A solution of 0.10 g of $CH_3Ir(CO)(PPh_3)_2$ in 15 mL of toluene was transferred to a 100-mL gas tube (Teflon stopper and stopcock) and brought out of the drybox. The gas tube was placed on a vacuum line, chilled to −78 °C, then evacuated, and backfilled with 0.9 atm of H_2. The solution was stirred and kept in a cold bath while gas samples were withdrawn at various intervals for GC analysis (Varian 2440, Poropak Q $^1/_8$ × 6 ft column at 130 °C). Methane evolution was noted at −40 °C and became rapid at temperatures of −20 °C.

$CH_3Ir(O_2)(CO)(PPh_3)_2$. A 0.30-g sample of *trans*-$CH_3Ir(CO)(PPh_3)_2$ was dissolved in 40 mL of toluene and placed under 1 atm of O_2 for 25 min. The solution was then cooled in an ice bath and 20 mL of pentane added. After 15 min the light yellow air-stable product was collected by suction filtration, yielding 0.27 g (87%). The ν_{CO}, 1967 (vs), ν_{O-O}, 827 (m), and ^1H NMR, (t, 1.48 $J_{P-H} = 4.8$ Hz) and 7.1 (m), were consistent with the suggested composition. Microanal. Calcd: C, 52.73; H, 4.17; P, 7.84. Found: C, 57.46; H, 4.05; P, 7.59.

CH_3Ir(dimethyl maleate)$(CO)(PPh_3)_2$. In a glovebox 0.15 g of $CH_3Ir(CO)(PPh_3)_2$ is suspended in 7 mL of benzene. To this was added 0.25 mL of dimethylmaleate dropwise with stirring to produce a pale yellow solution. After being stirred for 5 min, 30 mL of hexane was added to produce a cream precipitate which was collected via suction filtration to yield 0.16 g (98% yield based on iridium) of an air-stable cream powder. Spectroscopic data are reported in Table I. Microanal. Calcd: C, 58.46; H, 4.54; P, 6.87. Found: C, 58.27; H, 4.55; P, 6.65.

$CH_3Ir(CO)(CH_3CO_2C{\equiv}CCO_2CH_3)(CO)(PPh_3)_2$. To 0.20 g of *trans*-$CH_3Ir(CO)(PPh_3)_2$ was added 4.0 mL of a 0.07 M solution of dimethyl acetylenedicarboxylate ($CH_3CO_2C{\equiv}CCO_2CH_3$) in benzene. After 5 min hexane (5 mL) was added to the light yellow solution producing a pale yellow slurry from which a pale yellow, air-stable solid was isolated by suction filtration. The yield was 0.15 g (63%) with $\nu_{CO} = 1943$ cm^{-1} and ^1H NMR (CH_3Ir, δ 0.87 (dd, $J_{P-H} = 5.5$ Hz, $J_{P-H} = 7.9$ Hz O-CH_3, δ 3.45 (s); OCH_3, δ 3.60 (s); PPh_3, δ 7.1 (m)). Microanal. Calcd: C, 58.59; H, 4.33; P, 6.88. Found: C, 58.48; H, 4.37; P, 6.94.

$(CH_3)_2Ir(CO)(PPh_3)_2I$. A suspension of 0.20 g of *trans*-$CH_3Ir(CO)(PPh_3)_2$ in 10 mL of benzene was treated with 0.84 mL of a solution of CH_3I in benzene (0.34 M) and allowed to stir for 10 min. Addition of 10 mL of hexane caused the precipitation of the pale yellow air-stable product which was collected and washed with hexane (2 × 3 mL). Crystals of $(CH_3)_2Ir(I)(CO)(PPh_3)_2$ can be produced by recrystallization of the crude product from a refluxing saturated solution of the crude product in C_6H_6. The ν_{CO} in benzene was 1993 cm^{-1} and in KBr, 1990 cm^{-1}. The ^1H NMR showed inequivalent CH_3 groups, δ 0.51 (t, $J_{P-H} = 4.9$ Hz) and 1.02 (t, $J_{P-H} = 7.6$ Hz). Microanal. Calcd: C, 51.94; H, 4.00; P, 6.88; I, 14.08. Found: C, 52.19; H, 4.31; P, 6.74; I, 14.19.

Reaction of *trans*-$CH_3Ir(CO)(PPh_3)_2$ with Paraformaldehyde. *trans*-$CH_3Ir(CO)(PPh_3)_2$ (0.10 g) and paraformaldehyde (0.02 g) were dissolved in THF and allowed to stir for 16 h at room temperature under argon. Evaporation of solvent gave a pale yellow solid which was chromatographed (Florosil, cyclohexane), yielding $HIr(CO)_2(PPh_3)_2$ (IR (cyclohexane) 2085 (m, br), 1993 (s), 1983 (m, sh), 1945 (vs), 1935 (s) m^{-1}).[29]

Collection of the X-ray Diffraction Data for $MeIr(CO)(PPh_3)_2$. A light yellow crystalline parallelepiped of approximate dimensions 0.13 × 0.17 × 0.20 mm was selected for the structural analysis. Since we believed that the crystal might be

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Table II. Experimental Data for the X-ray Diffraction Study of *trans*-MeIr(CO)(PPh$_3$)$_2$

(A) Crystallographic Parameters

cryst system: triclinic
a = 9.2497 (9) Å
b = 9.6080 (11) Å
c = 10.4855 (14) Å
α = 72.390 (10)°
β = 88.990 (9)°
γ = 69.224 (8)°
V = 826.22 (16) Å^3

space group: $P\bar{1}$ (C_i^1; No. 2)
formula: $C_{38}H_{33}IrOP_2$
mol wt: 759.9 amu
Z = 1
D(calcd) = 1.53 g/cm^3
T = 23 °C (296 K)

(B) Data Collection

diffractometer:	Syntex P2$_1$
radiation:	Mo Kα ($\bar{\lambda}$ = 0.710730 Å)
monochromator:	highly oriented graphite, equatorial geometry, $2\theta_m$ = 12.2°, assumed 50% perfect
reflctns measd:	entire shell (i.e., $\pm h$, $\pm k$, $\pm l$) for 2θ = 4.5–50.0°
scan type:	coupled θ(crystal)–2θ(counter)
scan width:	symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]$°
scan speed:	2.5 deg/min (in 2θ)
bkgd measd:	stationary-crystal, stationary-counter at beginning and end of 2θ scan; each for one-half of total scan time
std reflctns:	3 check reflectns remeasd after each 97 reflectns: a minor decay in the standards (to 98% initial values) was observed and corrected for
reflctns collected:	6238 total; merged to 2922 unique data (file name IRFR-172)
μ(Mo Kα):	44.1 cm^{-1}; empirical correction made, based upon interpolation (in 2θ and ϕ) between close-to-axial ψ-scans

Table III. Atomic Coordinates for *trans*-MeIr (CO)(PPh$_3$)$_2$[a]

atom	x	y	z
Ir	0.000 00 (0)	0.000 00 (0)	0.000 00 (0)
P	0.021 20 (7)	−0.20351 (8)	0.192 51 (7)
O	−0.262 27 (90)	0.20474 (83)	0.106 55 (75)
C	−0.171 56 (46)	0.13906 (45)	0.075 16 (39)
C10	0.114 63 (31)	−0.19520 (35)	0.340 43 (30)
C11	0.125 65 (36)	−0.05441 (41)	0.338 24 (38)
C12	0.194 95 (45)	−0.04219 (56)	0.447 57 (49)
C13	0.254 35 (46)	−0.16792 (65)	0.559 84 (45)
C14	0.244 48 (57)	−0.30753 (67)	0.564 72 (44)
C15	0.174 37 (47)	−0.32247 (47)	0.455 62 (38)
C20	0.132 63 (36)	−0.40341 (34)	0.191 75 (33)
C21	0.292 19 (40)	−0.44990 (42)	0.189 31 (43)
C22	0.378 49 (52)	−0.59754 (53)	0.180 88 (49)
C23	0.309 49 (81)	−0.69732 (54)	0.173 87 (62)
C24	0.152 31 (85)	−0.65254 (62)	0.174 38 (78)
C25	0.062 66 (52)	−0.50600 (47)	0.182 79 (56)
C30	−0.168 29 (32)	−0.21025 (35)	0.241 05 (33)
C31	−0.279 68 (43)	−0.17866 (56)	0.139 33 (42)
C32	−0.424 41 (47)	−0.18461 (65)	0.169 52 (56)
C33	−0.458 70 (46)	−0.21784 (59)	0.300 37 (58)
C34	−0.350 63 (51)	−0.24605 (56)	0.401 22 (50)
C35	−0.204 83 (40)	−0.24354 (43)	0.372 13 (37)
H11[b]	0.084 90	0.03488	0.260 35
H12	0.201 16	0.05543	0.444 23
H13	0.302 52	−0.15871	0.634 57
H14	0.285 85	−0.39568	0.643 38
H15	0.167 63	−0.42028	0.460 43
H21	0.342 74	−0.38061	0.193 42
H22	0.488 03	−0.62861	0.180 05
H23	0.369 91	−0.79824	0.168 61
H24	0.103 46	−0.72271	0.168 88
H25	−0.046 91	−0.47610	0.182 41
H31	−0.256 98	−0.15275	0.048 35
H32	−0.499 62	−0.16567	0.099 56
H33	−0.558 06	−0.22127	0.320 99
H34	−0.375 52	−0.26747	0.491 66
H35	−0.129 54	−0.26489	0.442 90

[a] The molecule lies on the center of symmetry at (0, 0, 0). Atoms in the "other half" of the molecule are labeled with a prime (′) and are related to the basic asymmetric unit by the transformation (x', y', z') = ($-x$, $-y$, $-z$). [b] B = 6.0 Å^2 for all hydrogen atoms.

sensitive to air and/or moisture, it was sealed under argon in a thin-walled capillary, which was then set (with bees' wax) into an aluminum pin or a eucentric goniometer. The crystal was then accurately centered on a Syntex P2$_1$ automated four-circle diffractometer. Determination of the crystal's orientation matrix and accurate unit cell parameters were carried out as described previously (see Table II).[30] The crystal was found to belong to the triclinic crystal system (diffraction symmetry $\bar{1}$; no systematic absences). Possible space groups were the noncentrosymmetric space group $P1$ (C_1^1; No. 1) or the centrosymmetric space group $P\bar{1}$ (C_i^1; No. 2). With a unit cell volume of 826.22 (16) Å^3, the assumption of Z = 1 gave a volume of 11.0 A^3 per atom (a typical value). Thus there was either one ordered molecule per unit cell in space group $P1$ or one disordered molecule (with averaged $\bar{1}$ symmetry) in space group $P\bar{1}$. [The latter was later found to be the appropriate choice.] We elected, therefore, to collect a complete shell of data for 2θ = 4.5–50.0° (Mo Kα).

Data were corrected for the effects of absorption (by an empirical method, based on interpolation in 2θ and ϕ between a set of ψ scans of close-to-axial reflections) and for Lorentz and polarization effects. Symmetry-equivalent data were averaged ($R(I)$ = 0.7%, $R_w(I)$ = 1.7%) and were converted to unscaled $|F_o|$ values. Any reflection with I(net) < 0 was assigned a value of $|F_o|$ = 0. Data were placed on an approximately absolute scale by means of a Wilson plot, which also provided the overall isotropic thermal parameter ($\bar{B}$ = 2.84 Å^2).

Solution and Refinement of the Structure of *trans*-MeIr(CO)(PPh$_3$)$_2$. The structure was solved by using the SUNY—Buffalo modified version of the Syntex XTL interactive crystallographic program package on our in-house NOVA 1200 computer.[31] Scattering factors for neutral atoms (Ir, P, O, C, H) were used in their analytical form; the contributions of all non-hydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[32] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$; the weights used (w) are derived from the stochastic $\sigma(|F_o|)$ values modified by an "ignorance factor" (p) of 0.015; viz., $w = \{[\sigma(|F_o|)]^2 + (0.015|F_o|)^2\}^{-1}$.

The structure was solved by setting the iridium atom at 0, 0, 0. A difference-Fourier synthesis phased by this single atom (R_F = 24%)[33] revealed the two equivalent phosphorus atoms. A second such synthesis phased by the IrP$_2$ moiety (R_F = 17%) revealed all of the carbon atoms of the phenyl groups. Three cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters of the Ir[P(C$_6$)$_3$]$_2$ moiety converged with R_F = 5.0%. A further difference-Fourier synthesis revealed the remaining (disordered) carbonyl and methyl groups; the disordered carbon atom of the methyl or carbonyl group was treated as a composite atom of unit occupancy, while the oxygen atom was given half occupancy in subsequent calculations. Continued full-matrix least-squares refinement of positional and anisotropic thermal parameters led to convergence with R_F = 2.3%, R_{wF} = 2.8%, and GOF = 1.04.[33] Hydrogen atoms of the phenyl groups were now included in their idealized externally bisecting positions with d(C–H) = 0.95 Å[34] and B = 6.0 Å^2; their positions were not refined but were updated. Continued refinement led to final convergence with the encouragingly low residuals of R_F = 1.8%, R_{wF} = 2.1%, and GOF = 0.79 for all 2922 independent reflections (none rejected). Contributions from hydrogen atoms belonging to the methyl group were not included in the calculations. A final difference-Fourier synthesis showed no significant features; the structure is thus both correct and complete. Final positional parameters are collected in Table III; anisotropic thermal parameters are deposited as Table IIIS.

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

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

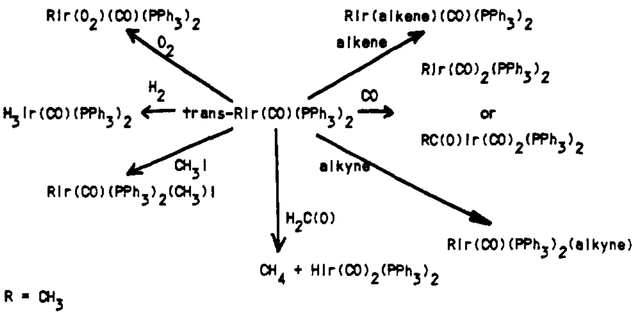

Figure 1. Summary of the addition reactions of *trans*-$CH_3Ir(CO)(PPh_3)_2$.

Table IV. Interatomic Distances (Å) for *trans*-MeIr(CO)$(PPh_3)_2$

(A) Distances from the Iridium Atom			
Ir–P(1)	2.300 (1)	Ir···O	2.975 (8)
Ir–C[a]	2.003 (4)	C–O[a]	0.975 (9)
(B) Phosphorus–Carbon Distances			
P(1)–C(10)	1.825 (3)	P(1)–C(30)	1.834 (3)
P(1)–C(20)	1.832 (3)		
(C) C–C(phenyl)			
C(10)–C(11)	1.386 (5)	C(13)–C(14)	1.362 (8)
C(11)–C(12)	1.378 (6)	C(14)–C(15)	1.393 (7)
C(12)–C(13)	1.356 (7)	C(15)–C(10)	1.382 (5)
C(20)–C(21)	1.384 (5)	C(23)–C(24)	1.362 (11)
C(21)–C(22)	1.388 (6)	C(24)–C(25)	1.386 (8)
C(22)–C(23)	1.345 (8)	C(25)–C(20)	1.382 (6)
C(30)–C(31)	1.383 (5)	C(33)–C(34)	1.365 (7)
C(31)–C(32)	1.387 (7)	C(34)–C(35)	1.384 (6)
C(32)–C(33)	1.370 (8)	C(35)–C(30)	1.378 (5)

[a] Atom C is a composite C(carbonyl)/C(methyl). These distances must be carefully interpreted—see text.

Results and Discussion

The synthesis of *trans*-$CH_3Ir(CO)(PPh_3)_2$ by nucleophilic attack of CH_3Li on *trans*-$Ir(CO)(PPh_3)_2Cl$ occurs in high yield to a stable product (eq 5). The instability

$$trans\text{-}Ir(CO)(PPh_3)_2Cl \xrightarrow{CH_3Li} \xrightarrow{\text{Florisil}} trans\text{-}CH_3Ir(CO)(PPh_3)_2 \quad (5)$$

previously described[19] for this complex appears to result from a complex of CH_3Li with *trans*-$CH_3Ir(CO)(PPh_3)_2$ or from reactions with OMe^- produced when CH_3Li is decomposed with MeOH. Except for reaction with O_2, *trans*-$CH_3Ir(CO)(PPh_3)_2$ is quite stable. This complex undergoes an array of addition reactions as anticipated for a 16-electron complex. The reactions reported herein are summarized in Figure 1, and the spectroscopic characterizations are given in Table I.

Description of the Molecular Geometry of MeIr(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 molecule lies on a crystallographic inversion center and is therefore disordered. However, this disorder manifests itself only in a scrambling of the mutually trans carbonyl and methyl ligand. The deconvoluted ordered structure is illustrated in Figure 2. Interatomic distances and angles are collected in Tables IV and V.

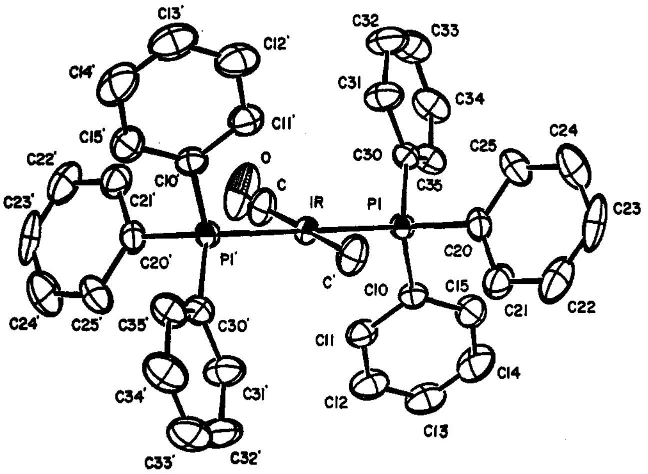

Figure 2. The *trans*-MeIr(CO)$(PPh_3)_2$ molecule. This is actually the disordered ensemble with atom O′ omitted. Atoms C and C′ represent composite C(carbonyl)/C(methyl) positions. [ORTEP-II diagram].

Table V. Interatomic Angles (deg) for *trans*-MeIr(CO)$(PPh_3)_2$

(A) Angles around the Iridium Atom			
P(1)–Ir–P(1′)	180.00 (–)	C–Ir–C′	180.00 (–)
P(1)–Ir–C	88.05 (12)	P(1)–Ir–C′	91.95 (12)
Ir–C–O	174.3 (6)		
(B) Angles Involving the Phosphorus Atom			
Ir–P(1)–C(10)	114.16 (10)	C(10)–P(1)–C(20)	102.23 (15)
Ir–P(1)–C(20)	117.74 (11)	C(20)–P(1)–C(30)	103.80 (15)
Ir–P(1)–C(30)	112.58 (11)	C(30)–P(1)–C(10)	104.86 (15)
P(1)–C(10)–C(11)	118.7 (3)	P(1)–C(20)–C(21)	118.9 (3)
P(1)–C(10)–C(15)	123.3 (3)	P(1)–C(20)–C(25)	122.6 (3)
P(1)–C(30)–C(31)	117.5 (3)	P(1)–C(30)–C(35)	123.6 (3)
(C) Angles within the Phenyl Rings			
C(15)–C(10)–C(11)	118.0 (3)	C(12)–C(13)–C(14)	119.5 (5)
C(10)–C(11)–C(12)	120.9 (4)	C(13)–C(14)–C(15)	120.7 (5)
C(11)–C(12)–C(13)	120.7 (5)	C(14)–C(15)–C(10)	120.1 (4)
C(25)–C(20)–C(21)	118.3 (4)	C(22)–C(23)–C(24)	119.5 (6)
C(20)–C(21)–C(22)	120.2 (4)	C(23)–C(24)–C(25)	120.9 (6)
C(21)–C(22)–C(23)	121.1 (5)	C(24)–C(25)–C(20)	120.0 (5)
C(35)–C(30)–C(31)	119.0 (3)	C(32)–C(33)–C(34)	120.2 (5)
C(30)–C(31)–C(32)	120.3 (4)	C(33)–C(34)–C(35)	120.2 (5)
C(31)–C(32)–C(33)	119.9 (5)	C(34)–C(35)–C(30)	120.4 (4)

The iridium(I) atom is in a rigorously planar, four-coordinate coordination environment. The iridium–phosphorus distances are equivalent, with Ir–P(1) = Ir–P(1′) = 2.300 (1) Å and ∠P(1)–Ir–P(1′) = 180.00° (exactly). Atom "C" is a composite atom representing the disordered C(carbonyl) and C(methyl) atoms. One can estimate the individual Ir–CO and Ir–Me bond lengths on the basis of the following additional assumptions: (i) the Ir–C–O system is essentially linear and is colinear with the Ir–C(methyl) vector; (ii) the true carbon–oxygen bond length in the Ir–C–O system is 1.14 Å. On the basis of these assumptions and the determined Ir···O distance of 2.975 (8) Å, the estimated Ir–CO distance is 1.835 Å (i.e., 2.975 – 1.14). Now assuming that the composite atom "C" represents the strict average position between the C(carbonyl) and C(methyl) atoms, one can estimate the Ir–Me distance as 2.17 Å (i.e., 2 × 2.003 – 1.835). These estimates are both in excellent agreement with known Ir–CO and Ir–Me distances.[35,36]

Distances and angles within the PPh_3 ligands are normal, with P–C = 1.825 (3)–1.834 (3) Å, ∠Ir–P–C = 112.58 (11)–117.58 (11)°, and ∠C–P–C = 102.23 (15)–104.86 (15)°. The carbon atom skeletons of the phenyl groups show the usual slight distortions from D_{6h} toward C_{2v} symmetry (cf. ref 37 and 38).

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(35) (a) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91–164; see, especially, pp 145–147. (b) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1972**, *11*, 2243; Ir–Me = 2.202 (22) Å in $(C_8H_{12})(PPhMe_2)_2IrMe$. (c) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1973**, *12*, 260; Ir–Me = 2.133 (16) Å in $(C_8H_{12})(Ph_2P(CH_2)_2PPh_2)IrMe$. (d) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1973**, *12*, 531; Ir–Me = 2.153 (18) Å in $(C_8H_{12})(Ph_2P(CH_2)_3PPh_2)IrMe$.

(36) (a) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528. (b) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1979**, *18*, 2451. (c) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1980**, *19*, 2765.

(37) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1975**, *14*, 2630.

Table VI. Comparison of Infrared Frequencies for $XIr(CO)_2(PPh_3)_2$

X	ν_{CO}, cm^{-1}	X	ν_{CO}, cm^{-1}
CH_3	1961 (s), 1904 (vs)	I[a]	1955 (s), 1935 (vs)
$CH_3C(O)$	1975 (s), 1916 (vs), 1612 (m)	$CH_3C(O)$[a]	1975 (s), 1925 (vs), 1615
Cl[a]	1976 (vs), 1923 (s)	H[a]	1960 (s), 1915 (s)

[a] Reference 19.

Reactions. The compound *trans*-$CH_3Ir(CO)(PPh_3)_2$ reacts readily with CO to produce first the 18-electron alkyl complex $CH_3Ir(CO)_2(PPh_3)_2$ and subsequently the 18-electron acyl complex $CH_3C(O)Ir(CO)_2(PPh_3)_2$ (eq 6). Both reactions are readily reversed in solution at room temperature.

$$trans\text{-}CH_3Ir(CO)(PPh_3)_2 \xrightarrow[CO]{-78\ °C} CH_3Ir(CO)_2(PPh_3)_2 \xrightarrow{\text{room temp, CO}} CH_3C(O)Ir(CO)_2(PPh_3)_2 \tag{6}$$

The infrared spectra of $XIr(CO)_2(PPh_3)_2$ complexes (X = CH_3, $CH_3C(O)$, Cl, I, H) are quite similar (Table VI), suggesting similar structures for these complexes.[19] The energetics for CO loss from $XIr(CO)_2(PPh_3)_2$ are rather interesting; for X = CH_3, $CH_3C(O)$, and Cl, CO dissociation from solutions is quite rapid leading to stable products. Dissociation of CO from $IIr(CO)_2(PPh_3)_2$ requires higher temperatures but still leads to the stable *trans*-$IIr(CO)(PPh_3)_2$. Dissociation of CO from the hydride $HIr(CO)_2(PPh_3)_2$ leads to an unstable product. The donor character of the ligands (as measured by infrared stretching frequencies) does not appear to be important; perhaps the instability of the hydride $HIr(CO)(PPh_3)_2$ arises from the small size of the hydride, thus favoring the five-coordinate 18-electron complex over the four-coordinate 16-electron complex.

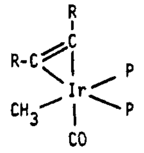
The oxidative addition of H_2 occurs at −78 °C. As the compound $CH_3Ir(H)_2(CO)(PPh_3)_2$ is warmed to −40 °C, reductive elimination of CH_4 occurs and the known $H_3Ir(CO)(PPh_3)_2$ is formed as a mixture of *mer* and *fac* isomers (eq 7).[39] The methane was determined by gas chromatographic analysis on a Poropak Q column. The reductive elimination of CH_4 is facile and may be contrasted to the failure of $(CH_3)_2Ir(CO)(PPh_3)_2I$ to eliminate two CH_3 groups as C_2H_6. That reductive elimination of R and H is more facile than R and R has been previously noted.[40]

$$trans\text{-}CH_3Ir(CO)(PPh_3)_2 + H_2 \xrightarrow{H_2,\ -78\ °C} CH_3Ir(H)_2(CO)(PPh_3)_2 \xrightarrow{-40\ °C,\ H_2} H_3Ir(CO)(PPh_3)_2 + CH_4 \tag{7}$$

Table VII. Oxygen-Oxygen Stretching Frequencies of Ir(III) Complexes $Ir(CO)(PPh_3)_2(O_2)X$

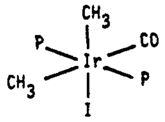
X	ν_{O-O}, cm^{-1}	ref
CH_3	827	*a*
Cl	858	41
Br	862	41
I	862	41
N_3	855	41
$C{\equiv}CR$	832	41
C_6H_5	825	23

[a] This work.



R = CO_2Me, P = PPh_3

Figure 3. Proposed structure of the acetylene adduct $CH_3Ir(MeO_2CC{\equiv}CCO_2Me)(CO)(PPh_3)_2$.



P = PPh_3

Figure 4. Proposed structure of $(CH_3)_2Ir(CO)(PPh_3)_2I$.

The reaction of O_2 with iridium(I) complexes is well-known.[18,23,41,42] The reaction of O_2 with *trans*-$CH_3Ir(CO)(PPh_3)_2$ occurs irreversibly in solution or the solid state (eq 8). Oxygen uptake was 0.85 mol in a solid-state

$$trans\text{-}CH_3Ir(CO)(PPh_3)_2 + O_2 \xrightarrow{\text{toluene,room temp}} CH_3Ir(O_2)(CO)(PPh_3)_2 \tag{8}$$

reaction at room temperature. The O_2 stretch at 827 cm^{-1} is quite low in frequency and consistent with side bonding typical for Ir(III) dioxygen complexes.[41] The comparison of several complexes is shown in Table VII. The O_2 could not be removed under high vacuum over several days at room temperature; similarly the dioxygen complex could be recovered after 24 h refluxing under N_2 in pentane. The presence of an alkyl and a dioxygen on the same metal center suggested possible oxidation chemistry. However no reaction occurs before the decomposition point of 90 °C; at this temperature no combination of O_2 and CH_3 could be found. Only CH_4, traces of C_2H_4 and C_2H_6, and $OPPh_3$ were found (eq 9). The dioxygen can be smoothly

$$CH_3Ir(O_2)(CO)(PPh_3)_2 \xrightarrow{90\ °C} CH_4 + C_2H_6 + C_2H_4 + OPPh_3 + ? \tag{9}$$

removed by excess PPh_3 at room temperature (eq 10) providing a catalytic cycle for the oxidation of PPh_3. Other oxidation chemistry is under investigation.

$$CH_3Ir(O_2)(CO)(PPh_3)_2 + 2PPh_3 \rightarrow trans\text{-}CH_3Ir(CO)(PPh_3)_2 + 2OPPh_3 \tag{10}$$

Alkenes can be added to *trans*-$CH_3Ir(CO)(PPh_3)_2$ with no evidence for insertion of the alkene into the CH_3–Ir bond.[43-47] For nonactivated alkenes this reaction is readily reversible at ambient conditions (eq 11).

$$trans\text{-}CH_3Ir(CO)(PPh_3)_2 + \text{alkene} \rightleftarrows CH_3Ir(\text{alkene})(CO)(PPh_3)_2 \tag{11}$$

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Table VIII. Comparison of Carbonyl Stretching Frequencies (in cm^{-1}) for *trans*-$Ir(CO)(PPh_3)_2Cl$ and *trans*-$CH_3Ir(CO)(PPh_3)_2$ and Their Adducts

L	$Ir(CO)(PPh_3)_2Cl{\cdot}L$	$CH_3Ir(CO)(PPh_3)_2{\cdot}L$
nothing	1955	1937
H_2	1975	
alkene[a]	2040	1993
CO	1923 (s), 1976 (vs)	1904 (vs), 1961 (s)
$CH_3CO_2C{\equiv}CCO_2CH_3$	1980	1943
O_2	2000	1967
CH_3I	2048	1993

[a] Alkene = C_2F_4 for chloro and $MeO_2CCH{=}CHCO_2Me$ for methyl.

Reaction of a 1:1 ratio of *trans*-$CH_3Ir(CO)(PPh_3)_2$ and dimethyl acetylenedicarboxylate leads to a stable adduct in good yield (eq 12). That this compound has a rigid

$$trans\text{-}CH_3Ir(CO)(PPh_3)_2 + CH_3O_2CC{\equiv}CCO_2CH_3 \rightarrow CH_3Ir(CO)(CH_3O_2CC{\equiv}CCO_2CH_3)(PPh_3)_2 \quad (12)$$

structure with inequivalent PPh_3 ligands is shown by the ^1H NMR spectrum which shows the Ir–CH_3 as a doublet of doublets, indicating inequivalent methyl carboxylate groups. Tentatively, we assign the alkyne adduct the structure shown in Figure 3.

Very rapid addition of CH_3I to *trans*-$CH_3Ir(CO)(PPh_3)_2$ occurs (eq 13). The ^1H NMR spectrum shows the methyl

$$trans\text{-}CH_3Ir(CO)(PPh_3)_2 + CH_3I \rightarrow (CH_3)_2Ir(CO)(PPh_3)_2I \quad (13)$$

groups to be inequivalent and the two PPh_3 ligands to be equivalent. This structure shown in Figure 4 is required. This compound is thermally stable below 80 °C. Slow decomposition occurs at 90 °C and is more rapid at 110 °C. In either case the product distribution is similar with predominant formation of CH_4 and small amounts of C_2H_4 and C_2H_6. Apparently the reductive elimination of C_2H_6 from the two *cis*-CH_3 groups does not occur and the decomposition is by cleavage of an Ir–CH_3 bond or α-H abstraction. Certainly the product distribution is similar to decomposition of monomethyl compounds. The reason for the facile elimination of CH_4 from $CH_3Ir(H)_2(CO)(PPh_3)_2$ and the failure to eliminate C_2H_6 from $(CH_3)_2Ir(CO)(PPh_3)_2I$ is not obvious.

The reaction of *trans*-$CH_3Ir(CO)(PPh_3)_2$ with excess paraformaldehyde ($(CH_2O)_x$) results in quantitative formation of $HIr(CO)_2(PPh_3)_2$ (eq 14).[29] This product could

$$trans\text{-}CH_3Ir(CO)(PPh_3)_2 + {}^1/_x(CH_2O)_x \rightarrow HIr(CO)_2(PPh_3)_2 + CH_4 \quad (14)$$

be formed by oxidative addition of $H_2C(O)$ giving $(CH_3)(H)Ir(CH(O))(CO)(PPh_3)_2$, reductive elimination of CH_4, and hydride migration from the 16-electron formyl complex.

Preparation of such a wide range of adducts (as shown in Figure 1) for *trans*-$CH_3Ir(CO)(PPh_3)_2$ invites comparison to *trans*-$Ir(CO)(PPh_3)_2Cl$. One would anticipate that the CH_3 group would place more electron density on the iridium than the Cl. That this is true is shown in the comparison of ν_{CO} stretches in Table VIII. In each case the carbonyl stretch of the analogous methyl complex is lower, indicating more electron density on the iridium. This increased electron density manifests itself in higher reactivity. In each case the methyl complex reacts more rapidly, often forming adducts at −78 °C. This higher electron density may also be important in the irreversibility of the O_2 addition. The structures of the chloro and methyl analogues appear to be similar in each case.

The most significant features of the reactions of *trans*-$CH_3Ir(CO)(PPh_3)_2$ are the differences from the chloro analogue: (1) enhanced reactivity due to the increased electron density on iridium; (2) the subsequent reactions of the added molecule with the CH_3 group; (3) the possibility of a CH_3 migration to a cis CO to open an extra coordination site.

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Registry No. *trans*-$CH_3Ir(CO)(PPh_3)_2$, 82190-06-5; $CH_3Ir(CO)_2(PPh_3)_2$, 96164-72-6; $CH_3C(O)Ir(CO)_2(PPh_3)_2$, 20249-86-9; $H_3Ir(CO)(PPh_3)_2$, 17176-29-3; $D_3Ir(CO)(PPh_3)_2$, 96164-73-7; $CH_3Ir(O_2)(CO)(PPh_3)_2$, 96193-90-7; CH_3Ir(dimethyl maleate)$(CO)(PPh_3)_2$, 96164-74-8; $CH_3Ir(CH_3CO_2C{\equiv}CCO_2CH_3)(CO)(PPh_3)_2$, 96164-75-9; $(CH_3)_2Ir(CO)(PPh_3)_2I$, 96164-76-0; $HIr(CO)_2(PPh_3)_2$, 17250-59-8; *trans*-$Ir(CO)(PPh_3)_2Cl$, 15318-31-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.