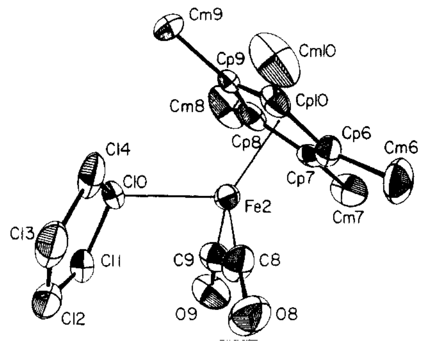

Figure 5. ORTEP drawing of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ (2) molecule 2, with non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 30% of the electron density.

The structure is initially solved by direct methods using MULTAN (1978 version) program. The remaining non-hydrogen atoms were located by standard difference Fourier techniques. The structure is refined by using two molecular fragments due to the large number of parameters during refinement. The resulting structural parameters for 2 have been refined to convergence [$R_1 = 0.063$ and $R_2 = 0.084$ for 2563 reflections having $I > 3\sigma(I)$] using counter-weighted least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. No effort was made to locate the hydrogen atoms in the structure. The largest peak found in the final difference Fourier map was 0.49 e/Å^3.

Acknowledgment. M.E.W. expresses his gratitude for partial funding of this work through a grant from the Graduate Student Development fund administered by the University of Arizona Graduate College. G.O.N. thanks the National Science Foundation (Grant CHE-8102918) for partial support of this work. R.S.G. makes acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Dr. D. C. England of Central Research and Development, E.I. duPont Co. for generously supplying the bis(trifluoromethyl)ketene and Dr. K. Christensen and Mr. J. F. Hoover of the University of Arizona for help in obtaining NMR spectra.

Registry No. 1, 12247-96-0; 2, 92366-04-6; **3a**, 84500-51-6; **3b**, 92366-05-7; 4, 92366-06-8; 5, 92366-07-9; 6, 92366-08-0; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I$, 88363-26-2; dimethyl fumarate, 624-49-7; bis(trifluoromethyl)ketene, 684-22-0.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths and angles, and structure factor amplitudes and a crystallographic report (21 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Fluxional Properties of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$. A Compound with an Ir–W Dative Bond

Frederick W. B. Einstein, Roland K. Pomeroy,* Paul Rushman, and Anthony C. Willis

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

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The compound $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ (1) has been synthesized by the reaction of $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_5(THF)$ in hexane. The structure of 1 has been solved by conventional crystallographic techniques: space group $P\bar{1}$ with $a = 9.057$ (2) Å, $b = 9.560$ (3) Å, $c = 12.695$ (2) Å, $\alpha = 71.83$ (2)°, $\beta = 83.07$ (2)°, $\gamma = 68.62$ (2)°, $Z = 2$; $R_F = 0.027$, $R_{wF} = 0.032$ for 3426 reflections with $I > 3\sigma(I)$ having $2\theta < 55°$. It reveals that the 18-electron complex $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ acts as a donor ligand toward the $W(CO)_5$ fragment via an unbridged Ir–W dative bond of length 3.0539 (11) Å. The ^{13}C NMR spectrum of the compound in CD_2Cl_2/CH_2Cl_2 at −97 °C was that expected from the solid-state structure. However, on warming the solution all the carbonyl resonances coalesced such that a single broad signal was observed at ambient temperature. A mechanism that involves an intermediate with bridging carbonyls is proposed to account for the carbonyl exchange. The donor–acceptor, metal–metal bond in $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ was weak since the compound reacted with the donor ligand L (L = CO, PPh_3, or $Os(CO)_4(PMe_3)$) to yield $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_5L$ (in solution at room temperature over a period of ca. 90 min).

Introduction

We have recently described the synthesis and structure of $(Me_3P)(OC)_4OsW(CO)_5$ in which the 18-electron complex $Os(CO)_4(PMe_3)$ acts as a ligand to the 16-electron fragment $W(CO)_5$.[1] The osmium–tungsten donor–acceptor bond was unbridged which made it the first bond of this type to be structurally characterized where the transition-metal atoms were different. (The compound $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$, also synthesized in this laboratory, contains an unbridged Os–Os dative bond.[2]) In solution $(Me_3P)(OC)_4OsW(CO)_5$ was found to exist in two isomeric forms that were shown to be in dynamic equilibrium by ^1H NMR spin saturation transfer techniques.[1]

The investigation of the ability of 18-electron complexes to act as ligands has been extended to $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$. This complex was chosen because it contained a five-coordinate metal atom that would be expected to readily expand its coordination number to six. Also, it is our experience that with neutral transition-metal donors the third-row metal forms much stronger dative bonds than its lighter congeners.

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(2) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.

0276-7333/85/2304-0250$01.50/0

Herein we describe the synthesis and structure of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ in which an 18-electron iridium complex acts as a ligand toward a second transition metal. Furthermore, the molecule has been found to be highly fluxional in solution such that averaging of the ^{13}C NMR resonances of the carbonyl ligands occurred at ambient temperature. We believe this observation has important implications concerning exchange that occurs in some other metal carbonyl derivatives.

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane, tetrahydrofuran (THF), and dichloromethane were distilled under nitrogen from potassium, potassium benzophenone ketyl, and P_2O_5, respectively. The method of Maitlis[3] was used to prepare $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ with the exception that $[(\eta^5\text{-}C_5Me_5)Ir(Cl)_2]_2$ was prepared with use of pentamethylcyclopentadiene.[4] Other chemicals were commercially available.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer, NMR spectra on a Bruker WM400 instrument (operating frequency: 400 MHz for ^1H and 100.6 MHz for ^{13}C), and mass spectra on a Hewlett-Packard 5985 GC–MS spectrometer. The microanalysis was performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$. The tungsten derivative $W(CO)_5(THF)$ was first prepared by the UV irradiation of $W(CO)_6$ (70 mg, 0.20 mmol) in THF (10 mL) contained in an evacuated, sealed quartz tube. An external, medium-pressure mercury discharge lamp (200 W, Hanovia Model 654 A36) contained in a water-cooled quartz jacket was employed for the irradiation. There was 5 cm from the source to the edge of the sample. The progress of the reaction was monitored by infrared spectroscopy, and when complete the THF was removed under reduced pressure and the resultant yellow solid cooled immediately in liquid nitrogen. Hexane (10 mL) and $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ (76 mg, 0.20 mmol) were added to the reaction vessel. The frozen mixture was then allowed to warm (with stirring) to room temperature whereupon a yellow-brown precipitate formed. The hexane supernatant was decanted and discarded. The precipitate was dissolved in CH_2Cl_2/hexane (1:1) and chromatographed on a Florisil column (12 cm) with CH_2Cl_2/hexane (1:1) as the eluant. The yellow fraction was collected and reduced in volume to give bright yellow crystals of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ in good yield. These were filtered and washed with a minimum volume of hexane: IR (CH_2Cl_2) ν(CO) 2063.5 (m), 2022.5 (m), 1985.5 (m), 1915 (s), 1880.5 (m, sh) cm^{-1}; IR (hexane) ν(CO) 2066.5 (m), 2026 (w), 1991.5 (m), 1924 (s), 1919 (s), 1905.5 (m) cm^{-1}, very weak bands attributed to $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ (2020, 1953 cm^{-1}) and $W(CO)_6$ (1983 cm^{-1}) were also detected in the latter spectrum; MS, m/e 707 (M^+); ^1H NMR ($CDCl_3$) δ 2.27 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 1:4; −97 °C) δ 203.1 ($J_{^{183}W-C}$ = 164 Hz, 1 CO), 199.9 ($J_{^{183}W-C}$ = 127 Hz, 4 CO), 171.2 (s, 2 CO), 100.2 (s), 9.7 (s). Anal. Calcd for $C_{17}H_{15}O_7IrW$: C, 28.87; H, 2.14. Found: C, 28.70; H, 2.14.

A sample of $W(CO)_6$ enriched in ^{13}CO was prepared by the UV irradiation of a THF solution of $W(CO)_6$ under ca. 2 atm of ^{13}CO (Mound Laboratories, 90% isotopic enrichment) using the photolysis apparatus described above. The irradiation was stopped after about 90 min and the solution stirred until its yellow color was discharged. This procedure was repeated. The resulting enriched $W(CO)_6$ was used to prepare an enriched sample of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ which was estimated to have 40% ^{13}CO by mass spectroscopy. The ^{13}C NMR spectrum of the sample indicated that all carbonyl sites were equally enriched.

Substitution Reactions of 1. Substitution reactions of 1 with the solid donor ligands PPh_3 and $Os(CO)_4(PMe_3)$ were carried out at room temperature in a stirred CH_2Cl_2 solution that was diluted to a concentration suitable for infrared spectroscopy. An appropriate amount of the ligand was added to the solution and the reaction monitored by infrared spectroscopy (carbonyl region). In each case the reaction was complete after approximately 90 min. The products $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_5L$ were identified by infrared spectroscopy. The reaction with CO was similar with the exception that it was carried out in a closed vessel under ca. 1.5 atm of the gas.

Table I. Crystal Data, Data Collection, and Refinement of the Structure

Crystal Data

formula	$C_{17}H_{15}IrO_7W$	cryst system	triclinic
a, Å	9.057 (2)	space group	$P\bar{1}$
b, Å	9.560 (3)	fw	707.35
c, Å	12.695 (2)	Z	2
α, deg	71.83 (2)	V, Å^3	972.37
β, deg	83.07 (2)	ρ_{calcd}, g cm^{-3}	2.416
γ, deg	68.62 (2)	μ, cm^{-1}	128.83

Data Collection and Refinement

diffractometer: Enraf-Nonius CAD4F
radiation: Mo Kα, graphite monochromator
λ of radiation: 0.709 30 Å (α_1); 0.713 59 Å (α_2)
scan mode: coupled ω-2θ
scan width: 0.55° in ω; also corrected for $\alpha_1 - \alpha_2$ dispersion.
scan speed: 6.7-1.1° in ω
bkgd: scan extended by 25% on each side
2θ range: 0–55°
size of crystl: 0.16 × 0.24 × 0.12 mm
total no. of reflctns: 4457
reflctns with $I > 3\sigma(I)$: 3426
no. of variables: 236
final $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.027$
final $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{1/2} = 0.032$
GOF = $[\Sigma w(|F_o| - |F_c|)^2$/(no. of observns − no. of variables)$]^{1/2} = 1.57$

X-ray Analysis of 1. A single crystal of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ was selected, sealed in a thin-walled glass capillary and mounted on the diffractometer in a non-specific orientation. Unit cell dimensions and the orientation matrix were determined by least-squares analysis of the setting angles of 23 reflections, widely distributed in reciprocal space (29° < 2θ < 36°), which were accurately centered. Crystal data are given in Table I.

The intensities of a unique data set ($\pm h,k,\pm l$) were measured as outlined in Table I. Two standards, measured at regular intervals, showed small fluctuations in intensity so data were scaled according to a five-point-smoothed curve derived from the standards.

The structure was solved by heavy-atom techniques. Least-squares refinement of all non-hydrogen atoms (isotropic temperature factors) (using only data with $2\theta < 45°$ and $I > 2.3\sigma(I)$ and unit weights) converged to $R_F = 0.099$. An analytical absorption correction[5] (T range 0.298–0.148) was applied to all data. Refinement (with the conditions outlined above) converged to $R_F = 0.055$. In view of the difficulty in defining the crystal faces, an absorption correction[6] using curves derived from azimuthal scans of reflections with χ near 90° was also tried (corrections range 1.00–0.63). Refinement with this data yielded $R_F = 0.048$. The latter data was therefore used in all further calculations.

All non-hydrogen atoms were then refined with anisotropic temperature factors, yielding $R_F = 0.030$. An inner-data difference map ($2\theta < 30°$) revealed all 15 hydrogen atoms. Several showed unreasonably long or short C–H distances or poor C–C–H and H–C–H angles and so were adjusted to give C–H = 0.95 Å and tetrahedral angles. Incorporation of the H atoms (isotropic temperature factor = average U_{eq} of C(51)–C(91), parameters invariant) resulted in $R_F = 0.027$. Addition of an extinction correction parameter[7] and the weighting scheme $w = [(\sigma(F))^2 + pF^2]^{-1}$ ($p = 0.0004$) lead to $R_F = 0.023$.

At this stage, the full data set, excluding reflections with $I < 3.0\sigma(I)$, was introduced. After examination of the average $w(|F_o|$

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[7] Larson, A. C. "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 291.

Table II. Positional and Thermal Parameters of Non-Hydrogen Atoms for $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$

atom	x	y	z	B_{eq},[a] Å^2
Ir	0.22159 (3)	0.33740 (3)	0.22595 (2)	2.694 (12)
W	0.04102 (3)	0.67785 (3)	0.22295 (2)	3.142 (14)
C(11)	0.0152 (8)	0.3394 (8)	0.2609 (6)	3.4 (3)
O(11)	−0.1034 (6)	0.3228 (7)	0.2868 (6)	5.3 (3)
C(12)	0.1820 (8)	0.4432 (9)	0.0759 (6)	3.9 (4)
O(12)	0.1715 (6)	0.4912 (8)	−0.0178 (4)	5.1 (3)
C(5)	0.4868 (7)	0.2626 (7)	0.2276 (5)	3.1 (3)
C(6)	0.4359 (7)	0.2885 (8)	0.3318 (5)	3.2 (3)
C(7)	0.3506 (7)	0.1839 (8)	0.3847 (6)	3.4 (3)
C(8)	0.3620 (7)	0.0855 (7)	0.3153 (6)	3.4 (3)
C(9)	0.4469 (7)	0.1332 (7)	0.2185 (6)	3.4 (3)
C(51)	0.5879 (8)	0.3420 (10)	0.1457 (7)	4.3 (4)
C(61)	0.4829 (9)	0.3855 (9)	0.3837 (7)	4.6 (4)
C(71)	0.2823 (9)	0.1599 (10)	0.5005 (6)	4.5 (4)
C(81)	0.3008 (9)	−0.0469 (9)	0.3442 (7)	4.5 (4)
C(91)	0.4930 (9)	0.0625 (9)	0.1239 (7)	4.5 (4)
C(21)	−0.1759 (10)	0.6591 (9)	0.2678 (8)	4.6 (4)
O(21)	−0.3020 (7)	0.6593 (8)	0.2886 (6)	6.6 (4)
C(22)	−0.0386 (11)	0.7764 (9)	0.0639 (7)	5.0 (4)
O(22)	−0.0850 (10)	0.8404 (8)	−0.0231 (6)	8.0 (5)
C(23)	0.2485 (10)	0.7118 (9)	0.1679 (6)	4.0 (4)
O(23)	0.3641 (7)	0.7352 (8)	0.1356 (6)	6.0 (4)
C(24)	0.1027 (9)	0.6106 (9)	0.3853 (7)	4.2 (4)
O(24)	0.1303 (7)	0.5883 (8)	0.4752 (5)	6.1 (4)
C(25)	−0.0487 (9)	0.8880 (10)	0.2391 (7)	4.5 (4)
O(25)	−0.1015 (8)	1.0102 (7)	0.2523 (6)	6.8 (4)

[a] $B_{eq} = 8\pi^2(^1/_3 \text{ trace } (U))$.

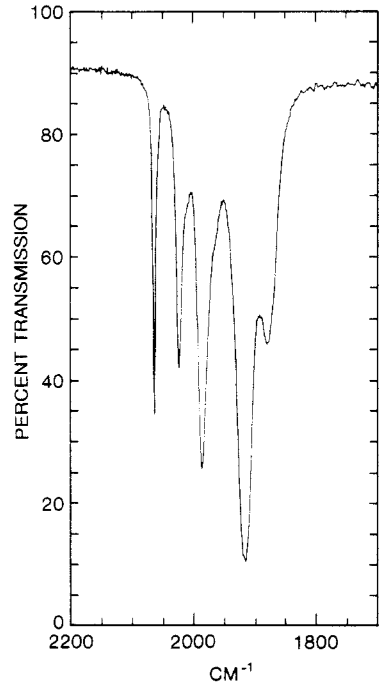

Figure 1. Carbonyl stretching region of the infrared spectrum of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ in CH_2Cl_2 solution.

$- F_c|)^2$ as a function of $|F_o|$ and $(\sin \theta)/\lambda$ the value of p in the weighting scheme was changed to 0.0002. The hydrogen atom coordinates were redetermined from the inner data. The hydrogen atoms refined to unreasonable locations if allowed to vary in further least squares and so were held invariant. The structure was refined to completeness (all shift-to-error ratios < 0.01). Final $R_F = 0.027$. The biggest features in a final difference map were near the W and Ir atoms; all others were <0.90 (15) e Å^{-3}.

Refinement throughout was by full-matrix least-squares analysis minimizing the function $\sum w(|F_o| - |F_c|)^2$. Neutral atom scattering factors with anomalous dispersion corrections were used.[8] Computer program[9] were run on a VAX11/750 computer.

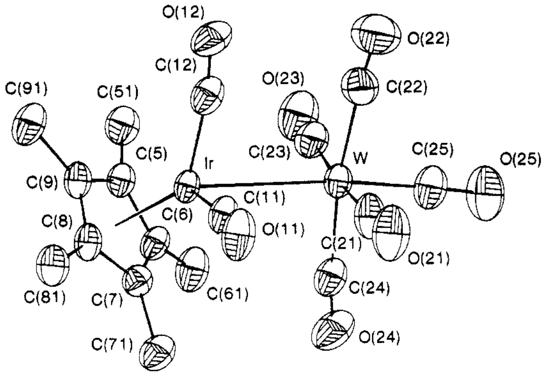

Figure 2. An ORTEP diagram of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ with the labeling scheme. Hydrogen atoms have been deleted.

Thermal motion corrections were calculated for the bond lengths in Table III; rigid-body[9b] and riding-motion[9c] models were used as appropriate. Corrections to angles were small (typically ≤ esd) and are not reported.

Results and Discussion

Warming a cold hexane solution of $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_5(THF)$ to room temperature gave a precipitate of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$, **1** (eq 1), which was purified

$$(\eta^5\text{-}C_5Me_5)Ir(CO)_2 + W(CO)_5(THF) \rightarrow (\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5 + THF \quad (1)$$

by chromatography. The compound was a moderately air-stable, pale yellow, crystalline solid; it did, however, decompose in solution over a period of several hours to give $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_6$ among other products. It was slightly soluble in hexane; this is unlike the osmium compounds we have prepared with donor–acceptor met-

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Table III. Interatomic Distances (Å) in $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$[a]

Ir-W	3.0539 (11)	3.0568[b]			
Ir-C(11)	1.863 (7)	1.869[b]	C(11)-O(11)	1.138 (8)	1.147[e]
Ir-C(12)	1.865 (8)	1.875[b]	C(12)-O(12)	1.136 (9)	1.141[e]
W-C(21)	2.034 (9)	2.044[b]	C(21)-O(21)	1.140 (11)	1.150[e]
W-C(22)	2.038 (8)	2.053[b]	C(22)-O(22)	1.129 (10)	1.142[e]
W-C(23)	2.027 (8)	2.032[b]	C(23)-O(23)	1.151 (10)	1.163[e]
W-C(24)	2.040 (8)	2.047[b]	C(24)-O(24)	1.136 (10)	1.146[e]
W-C(25)	1.940 (8)	1.950[b]	C(25)-O(25)	1.147 (10)	1.161[e]
Ir-C(5)	2.243 (6)	2.247[c]	C(5)-C(51)	1.510 (10)	1.515[d]
Ir-C(6)	2.317 (6)	2.321[c]	C(6)-C(61)	1.487 (10)	1.493[d]
Ir-C(7)	2.248 (6)	2.251[c]	C(7)-C(71)	1.506 (10)	1.512[d]
Ir-C(8)	2.262 (6)	2.264[c]	C(8)-C(81)	1.488 (10)	1.494[d]
Ir-C(9)	2.269 (6)	2.273[c]	C(9)-C(91)	1.500 (10)	1.506[d]
C(5)-C(6)	1.413 (9)	1.419[d]	C(8)-C(9)	1.410 (10)	1.415[d]
C(6)-C(7)	1.438 (10)	1.443[d]	C(9)-C(5)	1.450 (9)	1.455[d]
C(7)-C(8)	1.448 (10)	1.454[d]			
W···C(11)	3.210 (7)		Ir···C(23)	3.516 (7)	
W···C(12)	3.177 (8)		Ir···C(24)	3.576 (8)	

[a] The first value was derived directly from the atomic coordinates; the second has been corrected for thermal motion. [b] Corrected for riding motion, the second mentioned atom riding on the first. [c] Corrected for rigid-body motion (Ir and C(5)-C(9)). [d] Corrected for rigid-body motion (C(5)-C(9) and C(51)-C(91)). [e] Corrected for riding motion, both C and O riding on corresponding metal atom.

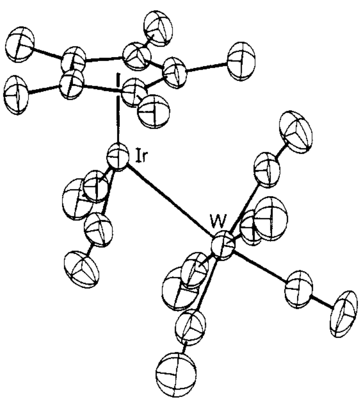

Figure 3. A second view $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$.

al–metal bonds that were completely insoluble in this solvent. The infrared spectrum of 1 in CH_2Cl_2 (Figure 1) showed only terminal carbonyl stretches which indicated that the Ir–W bond was unbridged. This was confirmed by the single-crystal X-ray diffraction study.

Molecular Geometry of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$. The experimental data for the X-ray study can be found in Table I, final positional and isotropic thermal parameters in Table II, and selected distances and angles in Tables III and IV, respectively. Two ORTEP views of the molecule are given in Figures 2 and 3. As can be seen, the 18-electron complex $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ acts as a donor ligand toward the tungsten atom of the $W(CO)_5$ unit via an unsupported iridium–tungsten bond of length 3.054 (1) Å. In the cluster compounds $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ and $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ the Ir–W distances were in the range 2.792 (1)–2.865 (1) Å;[10a] the phosphido-bridged Ir–W separations in $WIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)$ and $WIrH(\mu\text{-}PPh_2)_2\{C(OMe)Ph\}(CO)_4(PPh_3)$ were 2.876 (1) and 2.858 (1) Å, respectively.[10b] Also, an $Ir(\mu\text{-}H)W$ bond length of 3.0771 (7) Å was found in $[(Ph_2P)(Ph_2PCH_2CH_2PPh_2)(H)Ir(\mu\text{-}H)(\mu\text{-}\sigma,1\text{-}5\text{-}\eta\text{-}C_5H_4)W(H)(\eta^5\text{-}C_5H_5)][PF_6]$.[11] Since the presence of a bridging hydride ligand generally causes a significant lengthening of a metal–metal bond,[12] the Ir–W distance in 1 must be considered long and, by inference, weak. Consistent with the latter view is the facile cleavage of the bond by CO and PPh_3 reported in more detail in a subsequent section of this discussion.

Table IV. Angles (deg) in $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$[a]

W-Ir-C(11)	77.4 (2)	C(11)-Ir-C(12)	95.1 (3)
W-Ir-C(12)	76.2 (2)	C(11)-Ir-Cp	129.3
W-Ir-Cp	130.9	C(12)-Ir-Cp	128.7
Ir-W-C(21)	98.0 (2)	C(21)-W-C(25)	87.0 (3)
Ir-W-C(22)	101.5 (2)	C(22)-W-C(23)	88.4 (3)
Ir-W-C(23)	85.0 (2)	C(22)-W-C(24)	171.7 (3)
Ir-W-C(24)	86.8 (2)	C(22)-W-C(25)	86.6 (3)
Ir-W-C(25)	170.6 (2)	C(23)-W-C(24)	92.8 (3)
C(21)-W-C(22)	87.5 (4)	C(23)-W-C(25)	90.6 (3)
C(21)-W-C(23)	175.4 (3)	C(24)-W-C(25)	85.1 (3)
C(21)-W-C(24)	90.9 (3)		
Ir-C(11)-O(11)	172.3 (6)	Ir-C(12)-O(12)	171.4 (7)
W-C(21)-O(21)	175.1 (7)	W-C(24)-O(24)	173.2 (7)
W-C(22)-O(22)	175.4 (8)	W-C(25)-O(25)	177.8 (8)
W-C(23)-O(23)	178.2 (7)		
C(9)-C(5)-C(6)	109.7 (6)	C(7)-C(8)-C(9)	107.8 (6)
C(5)-C(6)-C(7)	106.4 (6)	C(8)-C(9)-C(5)	107.2 (6)
C(6)-C(7)-C(8)	108.6 (6)		
C(51)-C(5)-C(6)	124.8 (6)	C(51)-C(5)-C(9)	125.0 (6)
C(61)-C(6)-C(7)	126.4 (6)	C(61)-C(6)-C(5)	126.6 (7)
C(71)-C(7)-C(8)	124.1 (7)	C(71)-C(7)-C(6)	126.6 (4)
C(81)-C(8)-C(9)	126.5 (6)	C(81)-C(8)-C(7)	125.6 (7)
C(91)-C(9)-C(5)	125.4 (7)	C(91)-C(9)-C(8)	127.4 (6)

[a] Cp is the centroid of atoms C(5)-C(9): (0.4164, 0.1907, 0.2956).

The W–C distance trans to the iridium ligand (1.940 (8) Å) is significantly shorter than the corresponding lengths of the radial carbonyls (range 2.027 (8)–2.040 (8) Å). In molecules of the type $M(CO)_5(L)$ (M = Cr, Mo, W) the trans influence of L is usually attributed to π-bonding effects: L is usually a weaker π-bonding ligand that causes increased back-donation of the trans carbonyl and consequently a shorter metal–carbon bond length.[13] However, in $W(CO)_5(PMe_3)$ the W–C distance trans to the poor π-acceptor ligand PMe_3 is identical within experimental error to the other W–C distances.[14] This suggests that

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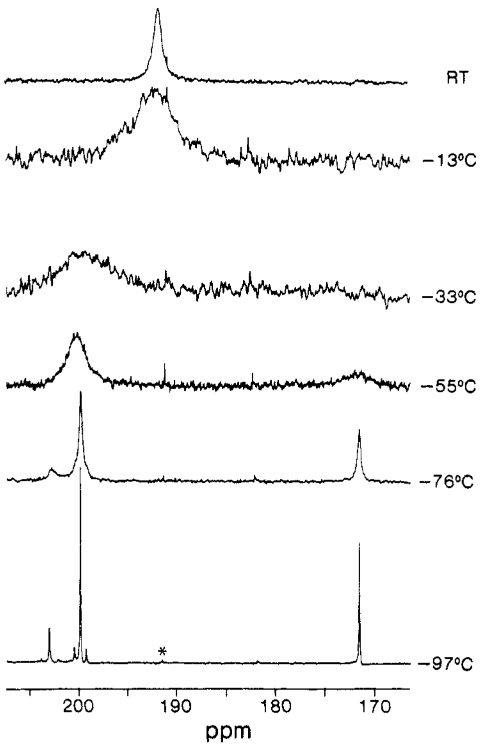


Figure 4. The carbonyl region of the 100.6-MHz $^{13}C\{^1H\}$ NMR spectrum of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ (enriched in ^{13}CO) in CD_2Cl_2/CH_2Cl_2 at different temperatures. The signal marked with an asterisk is due to $W(CO)_6$.

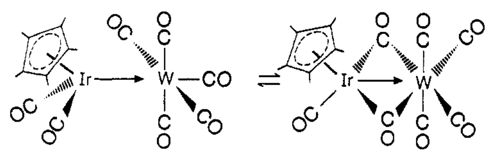
σ-effects are also important; i.e., the PMe_3 group that has strong donor properties weakens the trans W–C bond by a mechanism similar to that found for strong donor ligands in square-planar complexes.[15] Certainly, the short trans W–C distance in 1 implies that the $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ is a weak ligand. The iridium complex may act as a π-donor to the tungsten atom that would be expected to further shorten the trans W–C bond.

The carbonyl ligands on the donor half of the molecule lean toward the acceptor half. This was also observed for $(Me_3P)(OC)_4OsW(CO)_5$.[1] However, the W–C distances to the carbonyls in question preclude a bonding interaction in the ground state for either molecule. (These lengths are 3.177 (8) and 3.210 (7) Å in 1.)

Another structural feature of interest in 1 is that one of the methyl groups (C(61)) of the C_5Me_5 ligand makes close approach to two of the carbonyls on the tungsten atom. This interaction causes it to be raised from the C_5 plane of the cyclopentadienyl ring by 0.304 (14) Å; the other methyl groups are between 0.070 (14) and 0.097 (15) Å above this plane. In spite of this interaction the rotation of the C_5Me_5 ligand about the iridium atom was uninhibited in solution as evidenced by the sharp singlet given by the methyl protons in the ^1H NMR spectrum of 1 at -125 °C ($CD_2Cl_2/CHFCl_2$ solution). There is probably synchronous motion of the methyl and radial carbonyl groups (on tungsten) in order that this unrestricted rotation can occur. The iridium–carbon distances in 1 are not significantly different to the corresponding distances found for the uncomplexed molecule $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.[16]

Fluxionality of 1. In CD_2Cl_2/CH_2Cl_2 (1:4) solution at -97 °C the compound (enriched in ^{13}CO) exhibited a ^{13}C NMR spectrum consistent with the solid-state structure.

Scheme I



However, on warming, all three carbonyl resonances broadened and collapsed such that a single broad signal at the weighted average of the original peaks was observed at ambient temperature (Figure 4). These results are indicative of rapid exchange of the carbonyl ligands. The exchange is much more rapid than the isomerization found for $(Me_3P)(OC)_4OsW(CO)_5$ that was only detected by spin saturation transfer techniques.[1] The ^{13}C NMR spectrum of a solution of 1 at ambient temperature with added $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ showed a sharp carbonyl resonance due to the second component. Also, when 1 was stirred in solution under an atmosphere of ^{13}CO, there was no immediate exchange of the coordinated carbonyls with this reagent. These results indicated that the fluxional process did not involve fragmentation of 1 into $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_5$, and nor did it involve dissociation of CO.

The mechanism proposed for the isomerization in $(Me_3P)(OC)_4OsW(CO)_5$, bridge–terminal carbonyl exchange, successfully accounts for the available evidence concerning the type of exchange operative in 1. Such a mechanism (Scheme I) accounts for the simultaneous broadening of all three carbonyl resonances (the axial carbonyl on tungsten moves to a radial position upon an exchange) and also that preparation of 1 with ^{13}CO-enriched $W(CO)_5(THF)$ and unenriched $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ resulted in the ^{13}C label distributed over all the carbonyl sites.

It is interesting to compare the fluxionality in 1 to that observed for $(\eta^5\text{-}C_5H_5)_2Re_2(CO)_5$. The dirhenium derivative contains a single bridging carbonyl and undergoes dynamic carbonyl exchange that was rapid on the ^{13}C NMR time scale even at -83 °C.[17] A mechanism that involved an intermediate with a Re–Re donor–acceptor bond was proposed to account for the exchange. An intermediate with no bridging carbonyls was preferred to one with two on the basis of the long Re–Re bond length found for the molecule in the ground state (2.957 Å). In 1 the metal–metal bond is longer and yet the carbonyl scrambling is consistent with an intermediate with two bridging CO ligands. On the other hand, the radial carbonyls on the tungsten atom of 1 are all equivalent from the ^{13}C NMR spectrum at -97 °C; this indicates there is rapid rotation about the donor–acceptor bond at this temperature. Our results, therefore, do not favor either intermediate proposed for the fluxional process of $(\eta^5\text{-}C_5H_5)_2Re_2(CO)_5$.

An intermediate with an unbridged dative metal–metal bond was not favored in the carbonyl exchange process of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2[P(OPh)_3]$ but rather one in which synchronous bond making and breaking of bridging carbonyls occurred.[18] The present results suggest that the intermediate with the unbridged donor–acceptor metal bond should not be ruled out when there is no experimental evidence to the contrary.

Reaction of 1 with Donor Ligands. As mentioned above there was no immediate reaction of 1 in solution with ^{13}CO. However, 1 did react in solution with CO (ca. 1.5 atm) over a period of approximately 90 min to give (η^5-

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$C_5Me_5)Ir(CO)_2$ and $W(CO)_6$. Likewise with PPh_3, 1 gave $W(CO)_5(PPh_3)$. (The products in each case were identified by infrared spectroscopy.) These reactions are consistent with the slow dissociation of 1 into $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_5$, in solution at room temperature. The decomposition of 1, mentioned earlier, is also typical of labile $LW(CO)_5$ complexes.[19] The dissociation of 1 (and reaction with PPh_3) may be compared to that of the recently reported species $(\mu\text{-}H)[Fe(CO)_4W(CO)_5]^-$ [20] and $(OC)_5Os\text{-}Ru(CO)_3(SiCl_3)(Br)$.[21] The latter molecule, which contains an Os–Ru dative bond, rapidly dissociates in solution to give an equilibrium mixture with significant concentrations of $Os(CO)_5$ and $[Ru(CO)_3(SiCl_3)(Br)]_2$.

When 1 was stirred in solution with $Os(CO)_4(PMe_3)$, $(Me_3P)(OC)_4OsW(CO)_5$[1] was formed in about the same time period as that required to effect the substitutions described above. In contrast there was no reaction of $(Me_3P)(OC)_4OsW(CO)_5$ with $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ under the same conditions. From these experiments it may be concluded that $Os(CO)_4(PMe_3)$ is a stronger donor ligand than $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.[22]

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Registry No. $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$, 92543-25-4; $W(CO)_5(THF)$, 36477-75-5; $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, 32660-96-1; Ir, 7439-88-5; W, 7440-33-7.

Supplementary Material Available: Tables of atomic coordinates for hydrogen atoms, bond lengths and angles involving hydrogen atoms, least-squares planes, and final temperature factors, and a structure factor listing for $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ (35 pages). Ordering information is given on any current masthead page.

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(22) The W–C bond length trans to osmium in $(Me_3P)(OC)_4OsW(CO)_5$ (1.964 (8) Å)[1] is longer than the corresponding distance in 1 (1.940 (8) Å). Although this is consistent with the view that $Os(CO)_4(PMe_3)$ is a better donor ligand than $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, the difference in the two lengths is not statistically significant.

X-ray Crystal and Molecular Structure of Bis(biphenylyl-2)tin(IV) Dichloride, a Discrete, Molecular, Organotin Chloride

J. L. Baxter,[†] E. M. Holt,*[‡] and J. J. Zuckerman*[†]

Departments of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, and Oklahoma State University, Stillwater, Oklahoma 74078

Received May 14, 1984

Bis(biphenylyl-2)tin(IV) dichloride forms clear, diamond-shaped, monoclinic crystals, mp 165–166 °C, in the space group $P2_1/n$ with a = 13.039 (5) Å, b = 14.173 (4) Å, c = 11.478 (4) Å, β = 90.83 (3)°, V = 2120.8 (12) Å^3, Z = 4, and ρ_{calcd} = 1.553 g cm^{-3}. The structure was determined from 4503 reflections collected on a Syntex P3 automated diffractometer with monochromatic Mo Kα radiation (λ_α = 0.71069 Å) and refined to a final R value of 5.0% for the 2754 reflections included in the least-squares sums. The monomeric molecules are well separated in space with the nearest Cl···Sn contacts at 6.189 (3) Å. The title compound is thus the first tin dihalide to form a monomeric solid. The angles at the badly distorted tetrahedral tin(IV) atom are in the expected order Cl(1)–Sn–Cl(2) [99.71 (9)°] < Cl(1)–Sn–C(13) = Cl(2)–Sn–(1) [104.0 (2)°] < Cl(2)–Sn–C(13) [106.5 (2)°] ≈ Cl(1)–Sn–C(1) [107.8 (2)°] < C(1)–Sn–C(13) [130.8 (3)°], but the compression of the first and the widening of the last, which are more typical of a higher coordinated, chloride-bridged structure, are in this case produced by the steric requirements of the bulky organic ligand.

Organotin chlorides are crossroads materials, centrally poised among trends to higher coordinated, bridged structures: descending the fourth group, carbon to lead; ascending the seventh group, iodine to fluorine; increasing the number of halide substituents, zero to four; or reducing the steric demand of the organic ligands. Among the diorganotin dichlorides themselves there are discrete monomers (gas-phase and solution) and chlorine-bridged solids,[1,2] the latter employing single chlorine atoms linking five-coordinated tins or two chlorine atoms linking six-coordinated tins by chelation of one molecule by its neighbor or employing a more symmetrical mode in which trans octahedral chlorines on each molecule bridge. Validation of higher coordination at the central tin atom or bridging by attached chlorines demands analysis of often ambiguous solid-state structural data in terms of potentially coordinating halogen atoms lying in stereochemically significant positions[3] at short intermolecular contact distances. For the evidence to be truly compelling, angle distortions and bond length increases must be significantly greater than those produced by packing forces or the operation of steric or bonding (isovalent rehybridization) effects in the monomers themselves. Benchmark data are

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[†] University of Oklahoma.

[‡] Oklahoma State University.

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