found in CN$^-$-bridged Cu(I)–Cu(II) systems[30] and the 1.096–1.152 Å variation in some Cu(I) polymeric compounds.[31] As has been discussed elsewhere,[11,13] the ir spectrum of I shows a weak cyanide stretch at 2130 cm^{-1} which is shifted to higher frequency compared to a terminal cyanide in five-coordinate Cu(II) complexes, a well-known property of bridging cyanide groups. Scarcity of structural data on Cu(II) cyanide-bridged systems prevents comparison with more closely related species.

It has been found[13] from a variable-temperature magnetic study (4.2–283°K) that the copper atoms in compound I are antiferromagnetically coupled through the cyanide bridge ($J = -4.8$ cm^{-1}). This must be an intradimer interaction since the structure consists of isolated dimer units arranged in chains with intervening perchlorate anions. There are two dimer orientations present which are related by a crystallographic twofold axis, but within each dimer the coordination spheres of the copper atoms are aligned due to positioning about a center of inversion. Room-temperature Q-band powder esr spectra of I show three **g** values which could arise from a slight misalignment of the **g** tensors on the two ends of the dimer due to one copper atom having a cyanide carbon atom bonded to it and the other a cyanide nitrogen.[13] Structurally, this misalignment is not observed. Differentiation of this explanation from others such as rhombic symmetry will require comprehensive esr single-crystal or spectral simulation studies.

The structure of $[Cu_2(\text{tet } b)_2Cl](ClO_4)_3$, where tet *b* is a saturated analog of the macrocycle in I, has been recently determined[12] and, while it does not contain cyanide, general similarities of this compound to I can be noted. It is observed that the chloride forms a nearly linear bridge between the two copper atoms but the metal–metal distance is somewhat shorter (5.0 Å instead of the 5.4 Å found in the cyanide dimer) and the exchange interaction is larger ($J = -144$ cm^{-1}). Although these two complexes crystallize in the same space group, the chloride bridge is situated on a twofold axis rather than an inversion center and this results in the coordination spheres of the two copper atoms in each dimer being skewed with respect to each other. The greater length of the cyanide compared to the chloride bridge is certainly one factor which is important in reducing the exchange, and changes in the orientation of the axes of the g tensors with respect to the bridge direction caused by differing amounts of distortion from trigonal-bipyramidal geometry and differing strengths of the Cu–bridge bonds in the two cases are also likely to have an important effect.

Acknowledgment. This research was supported in part by National Science Foundation Grant NSF-GH-33634. We also wish to thank Dr. P. W. Corfield for communication of crystallographic results prior to publication.

Registry No. I, 51922-78-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2404.

---

[30] R. J. Williams, D. T. Cromer, and A. C. Larson, *Acta Crystallogr., Sect. B,* 27, 1701 (1971).

[31] R. J. Williams, D. T. Cromer, and A. C. Larson, *Acta Crystallogr., Sect. B,* 28, 858 (1972).

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta Canada T6G 2G2

Crystal and Molecular Structure of η^5-Cyclopentadienyl(triphenylphosphine)carbonyliridium, $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$

M. J. BENNETT,* J. L. PRATT and R. M. TUGGLE

Received March 4, 1974 AIC401441

The crystal and molecular structure of η^5-cyclopentadienyl(triphenylphosphine)carbonyliridium, $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as discrete molecules in the triclinic space group $P\bar{1}$ with two molecules per reduced cell of dimensions $a = 10.028$ (4) Å, $b = 10.578$ (4) Å, $c = 11.291$ (4) Å, $\alpha = 72.06$ (4)°, $\beta = 81.56$ (4)°, and $\gamma = 62.53$ (4)°. The structure has been refined by full-matrix least-squares methods to a conventional R factor of 0.033 for the 2525 significant intensities. The cyclopentadienyl ring center, triphenylphosphine, and carbonyl groups form a planar, triangular array with the central iridium atom. The iridium–phosphorus distance is 2.237 (2) Å, and the average iridium–carbon(cyclopentadienyl) distance is 2.272 (5) Å.

Introduction

Oxidative addition reactions, of d^8 complexes in particular, have been the subject of much interest.[1,2] One interesting class of d^8 complexes comprises compounds of the type $(C_5H_5)MLL'$, where M = Co, Rh, or Ir and L and L′ may be a combination of tertiary phosphines, carbonyls, and olefins. Until lately work was directed mainly at the cobalt and rhodium members of this group. Recently Oliver and Graham[3] reported a facile synthesis and some interesting reactions of the iridium compound $(C_5H_5)IrP(C_6H_5)_3(CO)$, **1**, and this has been followed by a kinetic study.[4] These studies showed that **1** exhibits substantial nucleophilic character in reactions

---

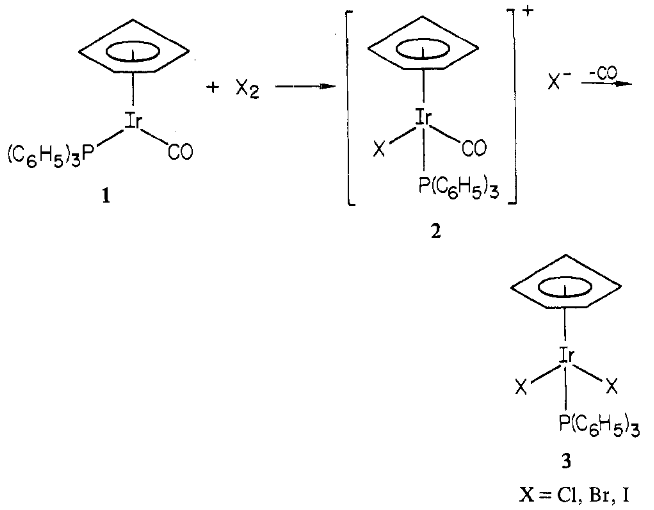
[1] J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.,* 7, 53 (1968).

[2] J. Halpern, *Accounts Chem. Res.,* 3, 386 (1970).

[3] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.,* 9, 2653 (1970).

[4] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.,* 9, 2658 (1970).

with halogens and alkyl halides and that these reactions are influenced by a considerable steric factor. For example, primary alkyl iodides up through *n*-hexyl undergo reaction with **1** but apparently isopropyl iodide does not.[3] Reactions of **1** with halogens are interesting in that these yield isolable ionic intermediates; *e.g.*



In view of the varied reactions of **1**, the marked steric factors influencing its reactions with alkyl halides, and the paucity[5,6] of X-ray structural data on cyclopentadienyl iridium compounds, we undertook this structural analysis of (C_5H_5)IrP(C_6H_5)$_3$(CO).

Collection and Reduction of Intensity Data

(C_5H_5)IrP(C_6H_5)$_3$(CO) was prepared by the reported[3] method, and its identity was confirmed by infrared and mass spectral analysis. Recrystallization of the compound from a benzene–hexane mixture gave well-formed yellow crystals suitable for X-ray studies. Precession and Weissenberg photography established that the crystals belonged to the triclinic system. Space group $P\bar{1}$ (C_i^1) was assumed, and subsequent refinement confirmed this choice. Least-squares refinement of the reduced cell parameters on the 2θ values observed for 12 high-order ($80° < 2\theta < 105°$) reflections accurately centered on a Picker four-circle diffractometer gave the following values: a = 10.028 (2) Å, b = 10.578 (4) Å, c = 11.291 (4) Å, α = 72.06 (4)°, β = 81.56 (4)°, and γ = 62.53 (4)°. Cu Kα_1 radiation (λ 1.5405 Å) and a 2° takeoff angle were used. The density, measured by flotation in an aqueous solution of zinc bromide, 1.79 (1) g cm^{-3}, agrees well with 1.797 g cm^{-3} calculated for two molecules in the unit cell. All measurements were made at 25°.

For intensity measurements a crystal of approximate dimensions 0.11 × 0.08 × 0.02 mm along a^*, b^*, and c^* was mounted with its a axis coincident with the ϕ axis of a Picker manual four-circle diffractometer. For absorption correction purposes seven distinct crystal faces, {100}, {01̄0}, {001̄}, and (111), were identified and measured. Intensities were measured by the coupled ω–2θ scan method using Cu Kα radiation filtered through a 0.0005-in. thickness of nickel foil. The X-ray tube was set to a 4° takeoff angle. Symmetric 2° scan ranges an a scan rate of 2° min^{-1} were used. Twenty-second stationary background counts were taken at the lower and upper limits of each scan. Intensities were measured with a scintillation counter with the pulse height analyzer set to accept approximately a 95% window when centered on the Cu Kα peak. Crystal and instrumental stabilities were monitored by a set of four standard reflections measured at regular intervals. These standards remained constant within counting and instrumental error throughout the data collection. A total of 2995 independent intensities in the range $2\theta \leqslant 120°$ ($(\sin\theta)/\lambda \leqslant 0.56$) were measured. Net intensities were calculated assuming a linear background profile between the scan limits of each reflection. The 2525 reflections for which $I > 3.0\sigma(I)$ were used in the solution and refinement of the structure.

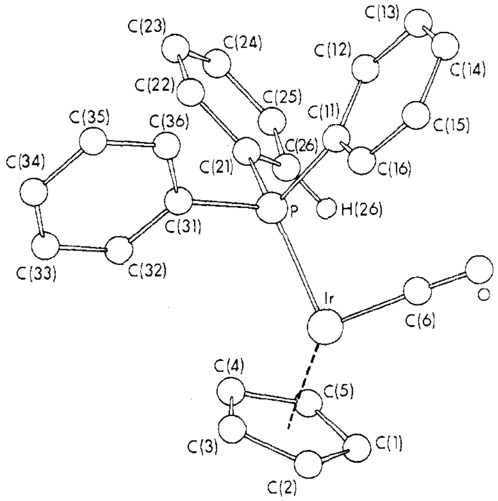


Figure 1. View of a molecule of (η^5-C_5H_5)IrP(C_6H_5)$_3$(CO). All hydrogen atoms (except H(26), see text) have been omitted for clarity.

Intensities were reduced to values of F^2 after correction for Lorentz, polarization, and absorption effects. Standard deviations were estimated using the procedure of Doedens and Ibers[7] with a p factor of 0.03. The linear absorption coefficient of this compound for Cu Kα radiation is 133.7 cm^{-1}, and transmission factors ranged from 0.339 to 0.576 for this crystal.

Solution and Refinement of Structure

The iridium and phosphorus atoms were located from a three-dimensional Patterson map. A subsequent difference Fourier map phased on these two atoms gave the positions of the remaining nonhydrogen atoms. Full-matrix least-squares refinement with isotropic temperature factors for all atoms converged at R_1 = 0.072 and R_2 = 0.084. The residuals are defined by $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, where the weights $w = 1/\sigma^2(F_o)$. All least-squares refinements were made on F where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors used were those of Cromer and Mann[8] for nonhydrogen atoms and those of Stewart, *et al.*,[9] for hydrogen atoms. Iridium and phosphorus atom scattering factors included the real and imaginary components of anomalous dispersion for Cu Kα radiation.[10] A difference Fourier map at this stage of the refinement showed considerable anisotropy in the thermal motion of the carbonyl and cyclopentadienyl groups. The iridium, phosphorus, oxygen, and carbonyl carbon atoms were given anisotropic temperature factors. The cyclopentadienyl group was initially treated as a hindered rotor.[11] Refinement lowered R_1 to 0.038 and R_2 to 0.045 at which point a difference Fourier map in which the contributing data were restricted to reflections with $(\sin\theta)/\lambda < 0.35$ showed peaks of intensity 0.4–0.9 e/Å^3 for all hydrogen atoms. Refinement including all hydrogen atoms (cyclopentadienyl hydrogens at fixed idealized positions) was continued with phenyl hydrogen temperature factors fixed. This refinement, for which the cyclopentadienyl ring was treated as a hindered rotor, converged at R_1 = 0.034 and R_2 = 0.039. Since the field imposed by the ligands trans to the cyclopentadienyl group (*i.e.*, C_s) should maximize any deviations of this group from its idealized fivefold symmetry, it was felt that the fivefold symmetry constraint imposed by the hindered-rotor model[11] should be relaxed in the final refinement cycles. This should have little effect on the iridium–carbon distances and should show up any alternations in the cyclopentadienyl carbon–carbon distances.[12] Accordingly, cyclopentadienyl carbon atoms were

---

(5) During the course of this work a structural characterization of cyclopentadienyliridium duroquinone appeared.[6]

(6) G. G. Aleksandrov and Yu. T. Struchkov, *J. Struct. Chem. (USSR)*, 12, 953 (1971).

(7) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6, 204 (1967).

(8) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

(9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(10) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(11) M. J. Bennett, W. L. Brooks, and B. M. Foxman, in preparation.

(12) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature (London)*, 201, 1318 (1964).

Table I

Final Positional and Thermal Parameters[a]

Atom	x	y	z	B, Å^2
Ir	0.22282 (4)	0.22815 (4)	0.01856 (3)	3.10[b]
P	0.1464 (2)	0.1221 (2)	0.2013 (3)	2.88
O	0.2674 (8)	0.4203 (7)	0.1380 (6)	5.82
C(1)	0.2446 (20)	0.3260 (16)	−0.1844 (10)	8.76
C(2)	0.3681 (13)	0.1843 (18)	−0.1522 (10)	7.64
C(3)	0.3134 (14)	0.0837 (11)	−0.1181 (9)	6.14
C(4)	0.1574 (14)	0.1554 (15)	−0.1243 (9)	7.29
C(5)	0.1140 (13)	0.3084 (14)	−0.1712 (9)	6.39
C(6)	0.2497 (9)	0.3429 (9)	0.0927 (8)	3.93
C(11)	0.1714 (8)	0.1736 (8)	0.3343 (6)	2.48 (13)
C(12)	0.0540 (10)	0.2503 (9)	0.4030 (8)	3.54 (16)
C(13)	0.0799 (12)	0.2972 (11)	0.4963 (9)	4.69 (20)
C(14)	0.2205 (11)	0.2681 (10)	0.5203 (9)	4.57 (20)
C(15)	0.3408 (11)	0.1891 (10)	0.4540 (8)	4.06 (18)
C(16)	0.3164 (9)	0.1416 (9)	0.3613 (7)	2.99 (15)
C(21)	−0.0538 (8)	0.1684 (8)	0.2087 (7)	2.58 (13)
C(22)	−0.1126 (10)	0.0782 (10)	0.2902 (8)	3.68 (16)
C(23)	−0.2643 (10)	0.1200 (10)	0.2968 (8)	4.03 (17)
C(24)	−0.3610 (10)	0.2513 (10)	0.2228 (8)	4.21 (18)
C(25)	−0.3062 (11)	0.3428 (11)	0.1422 (9)	4.48 (19)
C(26)	−0.1517 (10)	0.3004 (10)	0.1331 (8)	3.84 (17)
C(31)	0.2300 (8)	−0.0823 (8)	0.2560 (7)	2.98 (14)
C(32)	0.2733 (11)	−0.1587 (10)	0.3761 (9)	4.29 (19)
C(33)	0.3306 (13)	−0.3150 (12)	0.4143 (11)	5.89 (24)
C(34)	0.3350 (13)	−0.3854 (13)	0.3282 (11)	6.19 (25)
C(35)	0.2955 (13)	−0.3131 (13)	0.2114 (11)	6.04 (25)
C(36)	0.2399 (11)	−0.1577 (11)	0.1726 (9)	4.43 (19)
H(12)[c]	−0.039 (9)	0.276 (8)	0.383 (7)	*d*
H(13)	−0.002 (10)	0.331 (10)	0.534 (8)	
H(14)	0.244 (10)	0.285 (9)	0.583 (8)	
H(15)	0.439 (10)	0.165 (9)	0.455 (8)	
H(16)	0.389 (8)	0.096 (8)	0.319 (7)	
H(22)	−0.043 (9)	−0.013 (9)	0.348 (8)	
H(23)	−0.301 (9)	0.046 (9)	0.363 (8)	
H(24)	−0.484 (10)	0.284 (9)	0.231 (8)	
H(25)	−0.369 (10)	0.431 (10)	0.090 (8)	
H(26)	−0.124 (9)	0.368 (9)	0.092 (8)	
H(32)	0.278 (9)	−0.116 (9)	0.430 (8)	
H(33)	0.343 (11)	−0.355 (10)	0.504 (9)	
H(34)	0.371 (11)	−0.523 (11)	0.352 (9)	
H(35)	0.288 (11)	−0.342 (10)	0.144 (9)	
H(36)	0.206 (10)	−0.107 (9)	0.089 (8)	
H(1)[e]	0.251	0.427	−0.217	
H(2)	0.479	0.166	−0.155	
H(3)	0.376	−0.032	−0.087	
H(4)	0.084	0.107	−0.105	
H(5)	0.007	0.391	−0.186	

Anisotropic Temperature Factors[f] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	85.9 (5)	100.8 (5)	51.1 (3)	−46.6 (4)	5.8 (3)	27.6 (3)
P	79 (3)	81 (3)	57 (2)	−38 (2)	4 (2)	−26 (2)
O	228 (13)	126 (9)	101 (7)	−110 (9)	−42 (8)	−6 (7)
C(1)	400 (35)	251 (24)	78 (11)	−238 (26)	4 (16)	−28 (13)
C(2)	183 (20)	344 (29)	80 (10)	−144 (22)	48 (12)	−95 (15)
C(3)	222 (22)	154 (16)	82 (10)	−27 (16)	−10 (12)	−63 (11)
C(4)	222 (21)	314 (26)	69 (9)	−184 (21)	29 (11)	−82 (13)
C(5)	171 (18)	233 (22)	55 (9)	2 (17)	−48 (10)	−46 (11)
C(6)	111 (12)	120 (12)	72 (8)	−64 (11)	−10 (8)	−26 (8)

[a] Numbers in parentheses are estimated standard deviations in the last figure quoted. [b] Equivalent isotropic B's. Anisotropic temperature factors listed separately. [c] Hydrogen atoms have the same numbers as the carbon atoms to which they are bonded. [d] Hydrogen atom temperature factors fixed at one unit in B greater than the carbon atoms to which they are bonded. [e] Cyclopentadienyl hydrogen atom positional parameters were derived from hindered-rotor parameters and were not varied in the refinement. [f] Anisotropic temperature factors are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

treated as individual anisotropic atoms. This refinement converged at the lower residual factors $R_1 = 0.033$ and $R_2 = 0.036$. Although this lowering is significant by the R factor ratio test,[13] it is felt that it *cannot* be construed as evidence against the fivefold symmetry of the cyclopentadienyl ring. In the final refinement cycle the maximum change in a nonhydrogen parameter was 0.21σ. The final value of $[\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$ was 1.35. The largest peak in a final difference Fourier map ($\sigma(\Delta\rho)$ [14] $= 0.08$ e$^-$/Å^3) was 1.03 e/Å^3 and lay along the iridium–phosphorus bond. Other peaks greater than 0.5 e/Å^3 lay near phenyl ring carbon atoms and presumably reflected the anisotropic nature of their thermal motion. Structure factors were calculated for the 470 unobserved reflections and none had F_c greater than 1.5 times the minimum observable value.

---

(13) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(14) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, Ltd., London, 1953, p 308.

Table II. Root-Mean-Square Amplitudes of Vibration and Their Direction Cosines[a]

Atom	Rms displacement, Å	*l*	*m*	*n*
Ir	Max: 0.205	-0.100	0.903	-0.418
	Med: 0.179	0.995	0.094	-0.036
	Min: 0.165	-0.007	0.419	0.908
P	Max: 0.191	0.176	-0.608	0.774
	Med: 0.175	0.895	-0.228	-0.383
	Min: 0.169	0.409	0.760	0.505
O	Max: 0.322	-0.697	0.579	0.424
	Med: 0.223	0.372	-0.214	0.903
	Min: 0.190	0.613	0.787	-0.006
C(1)	Max: 0.411	-0.732	0.681	-0.017
	Med: 0.234	-0.681	-0.732	-0.033
	Min: 0.214	0.035	0.012	-0.999
C(2)	Max: 0.378	-0.035	-0.939	0.341
	Med: 0.260	-0.958	-0.065	-0.278
	Min: 0.176	0.283	-0.337	-0.898
C(3)	Max: 0.347	-0.930	-0.261	0.257
	Med: 0.249	0.365	-0.731	0.577
	Min: 0.180	-0.038	-0.631	-0.775
C(4)	Max: 0.368	-0.259	0.920	-0.293
	Med: 0.234	0.933	0.160	-0.323
	Min: 0.168	0.250	0.357	0.900
C(5)	Max: 0.389	-0.746	-0.603	0.282
	Med: 0.245	-0.547	0.797	0.256
	Min: 0.138	-0.379	0.037	-0.925
C(6)	Max: 0.228	0.421	-0.900	-0.117
	Med: 0.212	0.383	0.293	-0.876
	Min: 0.175	-0.822	-0.324	-0.468

[a] Direction cosines are referred to a right-handed orthogonal axis system with *X* and *Z* along *a* and *c**, respectively.

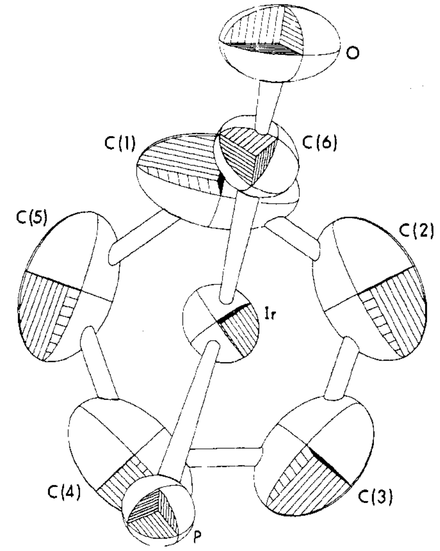


Figure 2. View of the inner coordination sphere around the iridium atom. The 50% probability ellipsoids of anisotropic thermal vibration are shown.

The final refined positional parameters and temperature factors are given in Table I. The rms amplitudes of thermal vibration and direction cosines for the atoms refined anisotropically are given in Table II.

Major programs used in the solution and refinement of this structure were local modifications of SFLS5 by C. T. Prewitt, FORDAP by A. Zalkin, GONO9 by W. C. Hamilton, ORFFE by W. R. Busing and H. A. Levy, and ORTEP by C. K. Johnson.

Results and Discussion

Table III. Selected Interatomic Distances and Angles[a]

Bond Distances, Å			
Ir-P	2.237 (2)	Ir-C(6)	1.800 (8)
Ir-RC[b]	1.941 (4)	C(6)-O	1.176 (9)
Ir-C(1)	2.229 (10)	C(1)-C(2)	1.413 (17)
Ir-C(2)	2.271 (10)	C(2)-C(3)	1.345 (15)
Ir-C(3)	2.303 (9)	C(3)-C(4)	1.390 (15)
Ir-C(4)	2.273 (9)	C(4)-C(5)	1.406 (16)
Ir-C(5)	2.283 (9)	C(5)-C(1)	1.387 (16)
Av of 5 Ir-C-(Cp)	2.272 (4)	Av of 5 C-C in Cp ring	1.388 (7)
P-C(11)	1.832 (7)	P-C(31)	1.847 (8)
P-C(21)	1.829 (7)		
C(11)-C(12)	1.373 (11)	C(25)-C(26)	1.397 (12)
C(12)-C(13)	1.393 (13)	C(26)-C(21)	1.374 (11)
C(13)-C(14)	1.348 (13)	C(31)-C(32)	1.362 (11)
C(14)-C(15)	1.380 (13)	C(32)-C(33)	1.416 (13)
C(15)-C(16)	1.386 (12)	C(33)-C(34)	1.381 (15)
C(16)-C(11)	1.391 (10)	C(34)-C(35)	1.316 (15)
C(21)-C(22)	1.387 (10)	C(35)-C(36)	1.409 (14)
C(22)-C(23)	1.372 (12)	C(36)-C(31)	1.377 (12)
C(23)-C(24)	1.359 (12)	Av of 18 phenyl C-C	1.377 (3)
C(24)-C(25)	1.366 (12)		
Distances from Hindered-Rotor Refinement, Å			
Ir-C(1)	2.262 (7)	C(1)-C(2)	1.425 (5)
Ir-C(2)	2.286 (7)	C(2)-C(3)	1.425 (5)
Ir-C(3)	2.316 (7)	C(3)-C(4)	1.425 (5)
Ir-C(4)	2.311 (7)	C(4)-C(5)	1.425 (5)
Ir-C(5)	2.278 (7)	C(5)-C(1)	1.425 (5)
Av of 5 Ir-C(Cp)	2.291 (3)	Av of 5 C-C in Cp ring	1.425 (5) 1.425 (5)
Nonbonded Intramolecular Distances, Å			
Ir···H(16)	3.58 (8)	Ir···H(36)	3.47 (8)
Ir···H(26)	3.18 (8)		
Angles, Deg			
RC[b]-Ir-P	135.0 (2)	P-C(31)-C(36)	117.8 (6)
RC-Ir-C(6)	135.7 (3)	C(16)-C(11)-C(12)	118.6 (7)
P-Ir-C(6)	89.2 (3)	C(11)-C(12)-C(13)	120.5 (8)
Ir-C(6)-O	178.2 (7)	C(12)-C(13)-C(14)	120.6 (9)
C(5)-C(1)-C(2)	108.5 (9)	C(13)-C(14)-C(15)	120.1 (9)
C(1)-C(2)-C(3)	107.5 (10)	C(14)-C(15)-C(16)	119.9 (8)
C(2)-C(3)-C(4)	109.7 (10)	C(15)-C(16)-C(11)	120.4 (7)
C(3)-C(4)-C(5)	107.7 (11)	C(26)-C(21)-C(22)	118.1 (7)
C(4)-C(5)-C(1)	106.5 (12)	C(21)-C(22)-C(23)	121.1 (8)
Ir-P-C(11)	114.6 (2)	C(22)-C(23)-C(24)	120.6 (8)
Ir-P-C(21)	114.4 (2)	C(23)-C(24)-C(25)	119.5 (9)
Ir-P-C(31)	118.7 (2)	C(24)-C(25)-C(26)	120.5 (9)
C(11)-P-C(21)	103.1 (3)	C(25)-C(26)-C(21)	120.2 (8)
C(21)-P-C(31)	100.8 (3)	C(36)-C(31)-C(32)	119.5 (8)
C(31)-P-C(11)	103.1 (3)	C(31)-C(32)-C(33)	120.2 (9)
P-C(11)-C(12)	123.4 (6)	C(32)-C(33)-C(34)	118.1 (10)
P-C(11)-C(16)	117.8 (5)	C(33)-C(34)-C(35)	122.2 (11)
P-C(21)-C(22)	122.9 (6)	C(34)-C(35)-C(36)	119.8 (11)
P-C(21)-C(26)	119.0 (6)	C(35)-C(36)-C(31)	120.1 (9)
P-C(31)-C(32)	122.6 (6)		

[a] Numbers in parentheses are estimated standard deviations in the last figure quoted. [b] RC is the point at the center of the cyclopentadienyl ring.

The crystal structure consists of discrete molecules of $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$. The molecule is shown in Figure 1. Selected interatomic distances and angles are given in Table III. The cyclopentadienyl ring center (RC), triphenylphosphine, and carbonyl groups are disposed about the central iridium atom in a planar triangular arrangement. A view of the inner coordination sphere around the iridium atom is given in Figure 2. The phosphine and carbonyl groups are each bent away from the Ir-RC vector by about 135°. A similar coordination geometry was observed[15] for $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(C_2F_4)$.

The carbonyl group shows distances comparable to carbonyls in other iridium compounds. The present iridium-carbon distance 1.800 (8) Å is at the lower end of the range of 1.82 (2) Å in $[Ir(CO)(Ph_2PCH_2CH_2PPh_2)_2]Cl$[16], 1.828 (9)

---

(15) L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, **94**, 3779 (1972).

Table IV

Weighted[a] Least-Squares Planes of the Form $Ax + By + Cz + D = 0$[b]

Plane no.	Atoms	*A*	*B*	*C*	*D*
1	Ir, P, O, C(6), RC[c]	0.9442	−0.2515	0.2126	−1.0313
2	C(1), C(2), C(3), C(4), C(5)	−0.0663	0.3269	0.9427	0.7367
3	C(11), C(12), C(13), C(14), C(15), C(16)	0.1028	−0.7377	0.6673	0.2357
4	C(21), C(22), C(23), C(24), C(25), C(26)	−0.0860	0.7058	0.7032	−3.2055
5	C(31), C(32), C(33), C(34), C(35), C(36)	−0.9277	−0.2826	0.2440	1.5482
6	Ir, RC	−0.0714	0.3528	0.9330	*d*
7	Ir, P	0.2989	0.3754	−0.8773	*d*

Distances of Atoms from Planes, Å

1: Ir, 0.002; P, −0.001; O, −0.012; C(6), −0.001; RC, −0.080
2: C(1), 0.013; C(2), 0.000; C(3), −0.014; C(4), 0.020; C(5), −0.019; Ir, 1.940
3: C(11), −0.007; C(12), 0.005; C(13), 0.004; C(14), −0.009; C(15), 0.001; C(16), 0.005
4: C(21), 0.044; C(22), −0.001; C(23), −0.001; C(24), −0.003; C(25), 0.011; C(26), −0.011
5: C(31), 0.000; C(32), 0.005; C(33), −0.015; C(34), 0.017; C(35), −0.007; C(36), −0.001

Dihedral Angles

Planes	Angle, deg	Planes	Angle, deg
1,2	86.8	3,7	33.7
1,6	87.6	4,7	67.8
2,6	1.6	5,7	53.3

[a] Atoms are weighted by the reciprocals of their variances. [b] Coordinates are referred to a right-handed angstrom-orthogonal system with *y* and *z* directed along *b* and *c**, respectively. [c] RC is the point at the center of the cyclopentadienyl ring. [d] *Vectors*—only direction cosines are given.

and 1.863 (9) Å in $IrH(CO)_2(PPh_3)_2$,[17] and 1.873 (11) Å in $Ir(CO)(NO)(PPh_3)_2$.[18] The carbonyl carbon-oxygen distance 1.176 (9) Å is within the observed range of such distances.

The iridium-phosphorus distance in this complex, 2.237 (2) Å, is one of the shortest observed in any iridium complex. This distance may be contrasted with 2.316 (5) and 2.329 (5) Å found[19] in $Ir(CH_3(C_8H_{12})(PPh(CH_3)_2)_2$ and with 2.317 (3) Å observed[20] in $IrH(CO)(C_2H_2(CN)_2)(PPh_3)_2$. Iridium-phosphorus multiple bonding cannot be completely discounted although several factors argue against this possibility. Back-donation from iridium to phosphorus is not consistent with the nucleophilic character observed for this complex. The carbonyl stretching frequency[3] 1944 cm^{-1} is more consistent with an Ir(I) complex than with one with iridium in a higher oxidation state. The overall geometry of the triphenylphosphine group, $P\text{-}C_{av} = 1.836$ (4) Å, $\angle C\text{-}P\text{-}C_{av} = 102.3$ (2)°, is essentially the same as that found[21] in the free ligand. The average C-C distance in the phenyl rings is 1.377 (3) Å, and the average C-H distance is 0.95 (2) Å.

The average iridium-carbon (cyclopentadienyl) distance is 2.272 (4) Å. (Hindered rotor refinement gave 2.291 (3) Å.) In the duroquinone complex[6] $(\eta^5\text{-}C_5H_5)Ir(\eta\text{-}C_6(CH_3)_4O_2)$ this average is 2.16 (2) Å, or 0.11 Å shorter. The present average is intermediate to metal-carbon(cyclopentadienyl) distances found in $(\eta^5\text{-}C_5H_5)_2Os$,[22] 2.22 Å, and in $(\eta^5\text{-}C_5H_5)Pt(CH_3)_3$,[23] 2.32 Å. Assumption of a covalent radius of 0.77 Å[24] for cyclopentadienyl carbon atoms leads to an iridium covalent radius of 1.50 Å which agrees with the 1.47 Å value predicted[25] by similar arguments. But an estimate of the iridium covalent radius from the iridium phosphorus bond ($r_p = 1.10$ Å[26]) is 1.13 Å. This result serves well to illustrate the anisotropy[27] that can occur in the covalent radii of transition metals, in particular, those with π-complexed cyclopentadienyl groups. It is perhaps appropriate here to reemphasize the conclusions drawn in other investigations:[24,25] estimates of transition metal covalent radii from π-cyclopentadienyl complexes have their greatest utility in elucidating *trends* in series of structurally related complexes but *not* in the determination of absolute metal covalent radii.

The plane of the cyclopentadienyl ring deviates only slightly (3.2°) from perpendicularity with the molecular plane about the iridium atom. Some pertinent least squares-planes are given in Table IV. The average carbon-carbon distance in the cyclopentadienyl ring, 1.388 (7) Å, is somewhat shorter than the average,[28] 1.419 Å, found in 23 structures containing this ring. The C-C (Cp) distance derived from the hindered-rotor[11] refinement, 1.425 (5) Å, agrees quite well with this latter average. Analysis of both the hindered-rotor model and the individual ellipsoids of thermal vibration of the cyclopentadienyl carbon atoms indicates that this group undergoes an rms libration of approximately 15° about its principal axis. Since the standard deviations associated with carbon-carbon distances in this ring are relatively large, no deviation from fivefold symmetry is detected.

The difference in the reactivity of $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$ toward primary and secondary alkyl halides is somewhat curious. For example, benzyl iodide reacts with the iridium compound whereas isopropyl iodide does not.[3] The structural aspects of this behavior were looked at further. Models, based on idealized geometries, for benzyl and isopropyl iodide show (qualitatively, at least) that the approach of isopropyl iodide to the iridium complex *is* in fact

---

(16) J. A. Jarvis, R. H. B. Mais, P. G. Owston, and K. A. Taylor, *Chem. Commun.*, 906 (1966).

(17) M. Ciechanowicz, A. C. Skapski, and P. G. H. Troughton, *Acta Crystallogr., Sect. A*, **25**, s172 (1969).

(18) C. P. Brock and J. A. Ibers, *Inorg. Chem.*, **11**, 2812 (1972).

(19) M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, **11**, 2243 (1972).

(20) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **47**, 84 (1969).

(21) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

(22) F. Jellinek, *Z. Naturforsch. B*, **14**, 737 (1959).

(23) G. W. Adamson, J. C. J. Bart, and J. J. Daly, *J. Chem. Soc. A*, 2616 (1971).

(24) M. J. Bennett and R. Mason, *Nature (London)*, **205**, 760 (1965).

(25) V. G. Andrianov, B. P. Biryukov, and Yu. T. Struchkov, *J. Struct. Chem. (USSR)*, **10**, 1014 (1970).

(26) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(27) R. Mason and L. Randaccio, *J. Chem. Soc. A*, 1150 (1971).

(28) P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 1 (1967).

much more hindered. It is assumed here that a bimolecular nucleophilic displacement mechanism applies[4] and that the path of approach lies along a line approximately normal to the iridium complex molecular plane. Another feature which may be operative in the present case is partial steric blockage by the ortho hydrogens on the phenyl rings. This effect is known to occur in a number of other complexes and in several cases[29-31] has been used as a rationalization for the lowered reactivity observed for those complexes. For $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$ there appears to be some blocking by H(26) (Ir-H(26) = 3.2 (1) Å) and a possibility of interference form H(16) (Ir-H(16) = 3.6 (1) Å). H(26) is illustrated in Figure 1. It should also be noted here that the observed reactivities of $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$ toward various alkyl halides[3,4] do not preclude the inductive electronic properties of the alkyl substituents from being an important factor in these reactions. Although both electronic and steric factors seem to be operative in the reactions of this complex, further studies are required to assess the relative importance of these.

An inspection of the closest intermolecular contacts shows that none of these is significantly less than the distance predicted from the sum of van der Waals radii.

Acknowledgment. We thank the National Research Council of Canada for financial support.

Registry No. $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$, 32612-68-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2408.

(29) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 4, 778 (1965).
(30) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 9, 440 (1970).
(31) (a) M. L. Schneider, W. H. De Camp, J. D. Scott, J. M. Stewart, and L. Vaska, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, No. INOR 98; (b) L. Vaska and L. S. Chen, *Chem. Commun.*, 1080 (1971).

Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

X-Ray Crystallographic Determination of the Molecular Structure of Bis(tetraethylammonium) Di-μ-hydrido-octacarbonylditungstate(2−), $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$. A Unique Example of the Successful Location and Refinement of Hydride Ligands in Positions Bridging Third-Row Transition Metal Atoms

MELVYN ROWEN CHURCHILL* and SHIRLEY W.-Y. CHANG

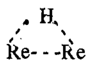
Received February 22, 1974 AIC40121M

The species bis(tetraethylammonium) di-μ-hydrido-octacarbonylditungstate(2−), $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$, crystallizes in the centrosymmetric monoclinic space group $C2/m$ [$C_{2h}{}^3$; No. 12] with $a = 15.863$ (4) Å, $b = 12.129$ (3) Å, $c = 8.145$ (2) Å, $\beta = 105.28$ (2)°, $V = 1511.7$ Å^3, and $Z = 2$. Observed and calculated densities are 1.86 (1) and 1.877 g cm^{-3}, respectively. All atoms, including hydrogen atoms, have been located from a single-crystal X-ray structural analysis based on counter data collected with a Picker FACS-1 automated diffractometer. Final discrepancy indices are $R_F = 3.34\%$ and $R_{wF} = 3.18\%$ for 1051 independent reflections representing data complete to $2\theta = 45°$ (Mo Kα radiation). The $[H_2W_2(CO)_8{}^{2-}]$ dianion has crystallographically dictated C_{2h} symmetry with a planar $W(\mu\text{-}H)_2W$ bridge in which W–H = 1.857 (60) Å, W–H–W′ = 108.6 (52)°, and H–W–H′ = 71.4 (52)°. The tungsten–tungsten distance of 3.0162 (11) Å is shorter than the W–W single-bond distance of 3.222 (1) Å in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ and is described (using the Mason–Mingos formalism) as approaching a W=W double bond. The $[Et_4N^+]$ cation is disordered about a crystallographic mirror plane; however its hydrogen atoms (each of occupancy $^1/_2$) have been located unambiguously and their parameters refined (with limited success).

Introduction

For some years we have been interested in the structural characterization of polynuclear transition metal complexes containing bridging hydride ligands. A series of X-ray crystallographic investigations on the hydridorhenium species $HRe_2Mn(CO)_{14}$,[1] $[H_2Re_3(CO)_{12}{}^-]$,[2] $[HRe_3(CO)_{12}{}^{2-}]$,[3] and $[H_6Re_4(CO)_{12}{}^{2-}]$[4] failed to reveal directly the positions of the μ_2-bridging hydride ligand(s) but did show a pattern of molecular distortions indicating that these positions could be determined *indirectly* by considering (i) metal-metal distances and (ii) "holes" in the distribution of ligands around the metal atom cluster, as indicated (for example) by abnormally large M–M–(CO) angles. The net result of these studies was some quantitative information on rhenium–rhenium distances: (1) a normal rhenium–rhenium single bond (in rhenium carbonyl species) is ~3.0 Å; (2) a singly (μ_2-) hydrido bridged rhenium–rhenium distance in a triangulated rhenium-carbonyl species is ~3.16 Å; (3) a linear Re–H–Re system has a rhenium· · ·rhenium distance ⩾3.40 Å.

We note at this time that cases (2) and (3), which may be represented formally by I and II (respectively), are examples



I

Re- - -H- - -Re

II

(1) M. R. Churchill and R. Bau, *Inorg. Chem.*, 6, 2086 (1967).
(2) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, 90, 7135 (1968).
(3) S. W. Kirtley, H. D. Kaesz, M. R. Churchill, and C. Knobler, in preparation.
(4) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Amer. Chem. Soc.*, 91, 1021 (1969).