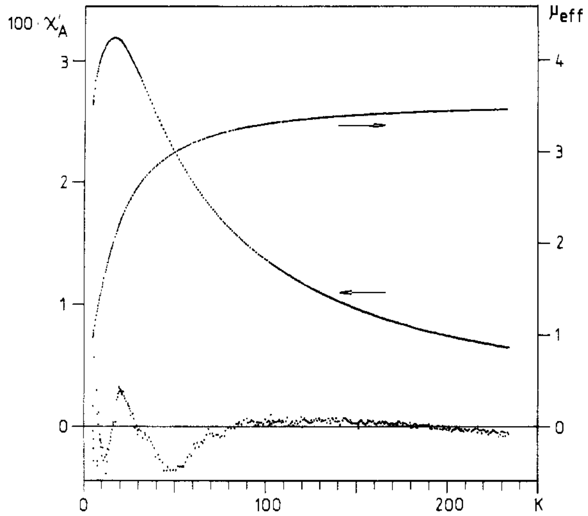

Figure 3. Temperature dependence of the magnetic susceptibility per chromium (left scale, cgs units) and effective magnetic moment (right scale, Bohr magnetons) of $[(tmhd)_2Cr(OCH_3)]_2$. The lower, almost random distribution of dots around the abscissa is $(\chi_{obsd} - \chi_{calcd}) \times 50$, where χ_{calcd} is based on the parameters in the text.

1.945 (4)–1.975 (3) Å with an average value of 1.958 (14) Å; these values are almost identical with those[12] in $[Cr(acac)_2(OCH_3)]_2$. It is noteworthy that the two bonds that are trans to the methoxy bridges [Cr–O(3)A and Cr–O(5)B] are significantly shorter than the other two, with lengths of 1.948 (3) and 1.945 (4) Å as compared to 1.963 (3) and 1.975 (3) Å. This apparent shortening does not occur[12] in $[Cr(acac)_2(OCH_3)]_2$. The chelating O–Cr–O angles of 88.7 (1) and 89.0 (1)° are comparable to the values of 89.4–90.1° found in the acac analogue.[12]

Magnetic Properties

The temperature dependence of the magnetic susceptibility and the effective magnetic moment of a powdered sample of the complex are shown in Figure 3.

The observed susceptibility data were fitted to the simple Van Vleck Hamiltonian

$$\mathcal{H} = JS_1 \cdot S_2$$

by using the fitting procedure described earlier.[5,12] The fit to this model, while generally good, is only approximate, the variance per degree of freedom being 4.07. Inclusion of a second-order term (biquadratic exchange) in the Hamiltonian[10]

$$\mathcal{H} = JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2$$

gave a markedly improved fit, the variance/degree of freedom falling to 1.12. The parameters derived from this model are $g = 1.980$ (1), $J = 8.18$ (2) cm^{-1}, and $j = 0.105$ (8) cm^{-1}. The calculated energies of the triplet, quintet, and septet states relative to the singlet ground state are, therefore, 8.86 (5), 25.96 (9), and 50.0 (2) cm^{-1}, respectively.

Agreement between the observed structural and magnetic properties and those calculated from our empirical model[8] is not entirely satisfying; the value calculated by using the present structural parameters and the values for a, b, and c in the expression[8]

$$J = [\exp(-ar')](bJ_{AF} - cJ_F)$$

where $r' = R - 1.8$ Å, J_{AF} is the antiferromagnetic contribution to J (dependent on θ and ϕ), and J_F is the ferromagnetic contribution (dependent on ϕ), is 18 (8) cm^{-1}. The parameters a, b, and c can be improved only by the advent of additional precise data for θ and ϕ, such as are available from the present experiment and the other studies in alkoxo-bridged systems. Regretably, the five structures of this type are all in the same ϕ and θ range, and consequently while an excellent fit $[|J_{obsd} - J_{calcd}| < 1$ cm$^{-1}]$ to the magnetic properties of these complexes can be obtained by using only these five data, the esd's on the derived parameters are so large as to render the results meaningless. We are, therefore, attempting to design, synthesize, and characterize complexes of this type that will have structural parameters markedly different from those observed here.

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Registry No. $[(tmhd)_2Cr(OCH_3)]_2$, 93383-90-5.

Supplementary Material Available: Tables of hydrogen atom positional and thermal parameters, anisotropic thermal parameters, bond lengths and angles in the tmhd ligands, and observed and calculated structure amplitudes (19 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University
of Southern California, Los Angeles, California 90089,
Dipartimento di Chimica Generale, Università di Milano,
Milano 20133, Italy, Centro di studio sulla sintesi e la
struttura dei composti dei metalli di transizione nei bassi
stati di ossidazione, Milano 20133, Italy,
and Chemistry Department, Brookhaven National Laboratory,
Upton, New York 11973

X-ray and Neutron Diffraction Study of $[P(CH_2C_6H_5)(C_6H_5)_3]^+[HIr_4(CO)_{11}]^-$

Robert Bau,*[†] Michael Y. Chiang,[†] Chiau-Yu Wei,[†]
Luigi Garlaschelli,*[‡] Secondo Martinengo,[§]
and Thomas F. Koetzle*[⊥]

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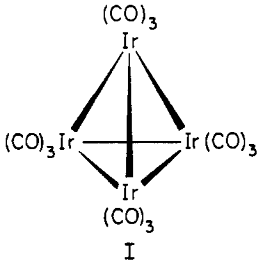
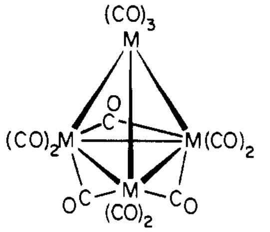
The monohydride anion $[HIr_4(CO)_{11}]^-$ was first prepared by Malatesta and co-workers in 1967 by treatment of $Ir_4(CO)_{12}$ with base.[1] It was subsequently shown that the compound can also be be made via the hydrolysis of $[Ir_4(CO)_{11}(COOR)]^-$ (R = Me, Et).[2a] There has been no report in the literature of the crystal structure of $[HIr_4(CO)_{11}]^-$ in spite of intensive structural interest in the parent compound $Ir_4(CO)_{12}$ (I)[3,4] and its derivatives. As opposed to configuration II of



I



II

M = Co, Rh

[†] University of Southern California.

[‡] Università di Milano.

[§] Centro di studio sulla sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione.

[⊥] Brookhaven National Laboratory.

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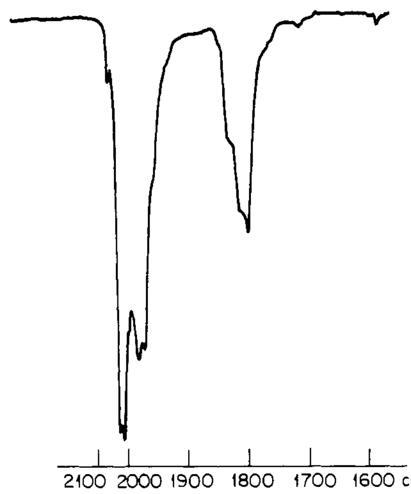
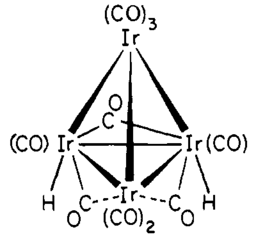


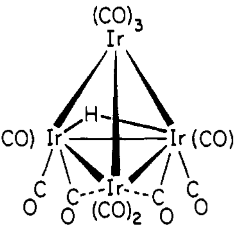
Figure 1. Infrared spectrum of $[P(CH_2C_6H_5)(C_6H_5)_3]^+[HIr_4(CO)_{11}]^-$ (THF solution).

$Co_4(CO)_{12}$[5,6] and $Rh_4(CO)_{12}$,[5] with three bridging carbonyl ligands around one triangular face of the tetrahedral cluster, $Ir_4(CO)_{12}$ possesses only terminal carbonyl ligands (I). However, this nonbridged configuration of $Ir_4(CO)_{12}$ is no longer retained in its derivatives: $Ir_4(\mu\text{-}CO)_3(CO)_7(PPh_3)_2$ and $Ir_4(\mu\text{-}CO)_3(CO)_6(PPh_3)_3$,[7] $Ir_4(\mu\text{-}CO)_3(CO)_7(diars)$,[8] $[Ir_4(\mu\text{-}CO)_3(CO)_8Br]^-$,[9] $[Ir_4(\mu\text{-}CO)_3(CO)_8(COOMe)]^-$,[2] and $[H_2Ir_4(\mu\text{-}CO)_3(CO)_7]^{2-}$.[10] The only exception is $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$.[11] This latter monosubstituted species and $Ir_4(CO)_{12}$ itself are, to our knowledge, the only two nonbridged examples of tetrahedral Ir_4 carbonyl cluster complexes studied to date.

In this paper we describe the structure of the benzyltriphenylphosphonium salt of $[HIr_4(CO)_{11}]^-$, as solved by X-ray and neutron diffraction techniques. In contrast to $[H_2Ir_4(CO)_{10}]^{2-}$, in which the two hydride ligands are believed to be in terminal positions (III),[10] the H atom in $[HIr_4(CO)_{11}]^-$ is found to be edge bridging (IV).



III



IV

Table I. Crystal Data for $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$

space group $P2_1/c$ fw = 1431.3

$Z = 4$ $\rho(\text{obsd})^a = 2.37$ g/cm³

params	X-ray (298 K)	neutron (80 K)
a, Å	9.330 (3)	9.243 (4)
b, Å	21.971 (5)	21.731 (3)
c, Å	19.190 (17)	18.997 (6)
β, deg	96.86 (6)	97.12 (2)
V, Å³	3905 (4)	3786 (4)
ρ(calcd), g/cm³	2.36	2.43
μ, cm⁻¹	141.3[b]	2.176[c]

[a] Obtained via flotation in a mixture of bromoform and carbon tetrachloride at room temperature. [b] For Mo Kα radiation, λ = 0.710 69 Å. [c] For λ = 1.161 73 Å neutrons.

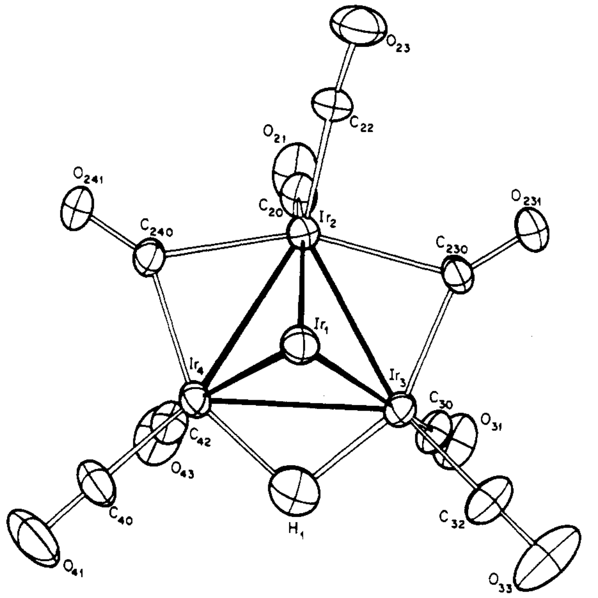


Figure 2. Molecular structure[24] of the $[HIr_4(CO)_{11}]^-$ anion. The three terminal carbonyl groups [C(10), O(11), C(12), O(13), C(14), O(15)] on atom Ir(1) have been removed for clarity. Atoms are plotted as 80% probability ellipsoids.

Experimental Section

Preparation of $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$ (Bz = CH_2Ph). The title compound was prepared according to the method published by Malatesta and co-workers.[1] In a typical experiment, a suspension of $Ir_4(CO)_{12}$ (0.645 g, 0.58 mmol) in methanol (20 mL) was stirred at room temperature with K_2CO_3 (0.285 g) under a carbon monoxide atmosphere until all the iridium carbonyl had reacted (ca. 15 h). The resulting yellow solution was dropped into a stirred solution of $[BzPh_3P]Cl$ (Bz = CH_2Ph) (0.5 g) and KCl (2 g) in water (75 mL). The yellow precipitate that was obtained was collected by filtration, washed with water (30 mL), and vacuum dried; yield 90%. Crystals were obtained by layering heptane over a dichloromethane solution of the compound under a carbon monoxide atmosphere. The compound was identified by IR spectroscopy [see Figure 1: bands at 2015 (vs), 2005 (vs), 1985 (s), 1970 (s), 1800 (m) cm⁻¹ in THF solution] and ¹H NMR spectroscopy [$\delta = -15.2$ ppm in dichloromethane solution; with the correct intensity ratio (1:2) relative to the cation benzyl hydrogens at $\delta = 4.65$]. The IR and NMR spectra were recorded on Perkin-Elmer 457 and Varian NV-14 spectrometers, respectively. Incidentally, the IR spectrum of $[HIr_4(CO)_{11}]^-$ in Nujol mull has been reported previously.[1b]

Reactivity of $[HIr_4(CO)_{11}]^-$. The hydride derivative is stable for prolonged periods, under a nitrogen atmosphere, in pyridine solution or in methanol solution containing KOH (molar ratio $[HIr_4(CO)_{11}]^-$:KOH = 1:8). A partial deprotonation is observed when $[HIr_4(CO)_{11}]^-$ is dissolved in isopropylamine. A complete deprotonation is observed when $[HIr_4(CO)_{11}]^-$ is reacted with potassium *tert*-butoxide (*t*-BuOK) in dimethyl sulfoxide (Me_2SO). The reaction is complete with a molar ratio $[HIr_4(CO)_{11}]^-$:*t*-BuOK = 1.0:1.2. The IR spectrum of the solution features bands at 1960 (s), 1927 (ms), and 1760 (m) cm⁻¹, consistent with a compound with formula $[Ir_4(CO)_{11}]^{2-}$.[2b] Further support of this formulation comes from the reaction of $[Ir_4(CO)_{11}]^{2-}$ with acids. Thus, when $[Ir_4(CO)_{11}]^{2-}$ reacts with a slight excess of acids such as acetic or *p*-toluenesulfonic acid, $[HIr_4(CO)_{11}]^-$ is obtained. $[Ir_4(CO)_{11}]^{2-}$ also reacts with gaseous

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Table II. Atomic Coordinates[a,b] for $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H(1)	0.53526 (31)	0.16253 (12)	−0.05397 (13)	C(55)	0.35965 (15)	0.48013 (6)	0.26813 (6)
Ir(1)	0.24315 (8)	0.21098 (3)	−0.02772 (3)		0.3631 (41)	0.4805 (17)	0.2708 (21)
	0.24890 (13)	0.21197 (5)	−0.02718 (7)	C(56)	0.46710 (14)	0.52335 (5)	0.25841 (6)
Ir(2)	0.42855 (8)	0.25806 (3)	0.08103 (3)		0.4774 (33)	0.5224 (14)	0.2618 (17)
	0.43174 (14)	0.24780 (5)	0.07993 (7)	C(57)	0.96083 (14)	0.59552 (5)	0.20755 (6)
Ir(3)	0.47190 (8)	0.14183 (3)	0.02989 (4)		0.9558 (32)	0.5962 (13)	0.2094 (17)
	0.47393 (13)	0.14342 (5)	0.02927 (7)	C(58)	0.93597 (16)	0.65257 (6)	0.23824 (7)
Ir(4)	0.51484 (8)	0.24697 (3)	−0.05011 (3)		0.9300 (39)	0.6486 (16)	0.2427 (20)
	0.51796 (14)	0.24719 (5)	−0.04966 (7)	C(59)	1.04244 (17)	0.69827 (7)	0.24047 (8)
C(10)	0.10683 (13)	0.17792 (6)	0.03068 (6)		1.0365 (46)	0.6968 (19)	0.2425 (22)
	0.1139 (40)	0.1792 (17)	0.0280 (21)	C(60)	1.17223 (16)	0.68719 (6)	0.21266 (7)
O(11)	0.02789 (17)	0.15882 (8)	0.06659 (8)		1.1625 (44)	0.6816 (19)	0.2191 (22)
	0.0448 (33)	0.1573 (13)	0.0661 (16)	C(61)	1.19761 (14)	0.63021 (6)	0.18290 (7)
C(12)	0.20353 (14)	0.16536 (6)	−0.11431 (6)		1.1880 (36)	0.6286 (15)	0.1854 (19)
	0.2217 (36)	0.1694 (15)	−0.1051 (20)	C(62)	1.09212 (14)	0.58411 (5)	0.18035 (6)
O(13)	0.17637 (20)	0.13912 (8)	−0.16625 (8)		1.0826 (35)	0.5831 (14)	0.1794 (18)
	0.1841 (31)	0.1449 (13)	−0.1639 (17)	C(63)	0.84680 (13)	0.48601 (5)	0.12975 (5)
C(14)	0.15942 (13)	0.28961 (5)	−0.05165 (6)		0.8499 (28)	0.4875 (11)	0.1328 (15)
	0.1647 (33)	0.2870 (14)	−0.0489 (17)	C(64)	0.90019 (14)	0.42606 (5)	0.14052 (6)
O(15)	0.11547 (17)	0.33800 (7)	−0.06348 (8)		0.9072 (32)	0.4285 (13)	0.1401 (17)
	0.1214 (26)	0.3339 (11)	−0.0608 (13)	C(65)	0.91251 (15)	0.38817 (6)	0.08243 (6)
C(20)	0.59180 (14)	0.28345 (6)	0.14439 (6)		0.9153 (40)	0.3925 (17)	0.0785 (22)
	0.5939 (39)	0.2833 (16)	0.1461 (19)	C(66)	0.87186 (14)	0.40989 (6)	0.01395 (6)
O(21)	0.68920 (19)	0.30038 (7)	0.18240 (8)		0.8726 (35)	0.4107 (15)	0.0163 (20)
	0.6828 (32)	0.2990 (13)	0.1784 (16)	C(67)	0.82037 (14)	0.46981 (6)	0.00319 (6)
C(22)	0.28234 (13)	0.28794 (5)	0.13282 (6)		0.8164 (40)	0.4705 (16)	0.0033 (20)
	0.2800 (33)	0.2875 (13)	0.1292 (17)	C(68)	0.80746 (14)	0.50797 (5)	0.06073 (6)
O(23)	0.18929 (17)	0.30100 (7)	0.16439 (8)		0.8122 (34)	0.5088 (14)	0.0657 (18)
	0.1951 (26)	0.3009 (10)	0.1599 (13)	C(69)	0.84223 (13)	0.49285 (6)	0.28306 (6)
C(30)	0.65453 (13)	0.11162 (5)	0.07318 (6)		0.8439 (30)	0.4918 (12)	0.2836 (16)
	0.6499 (40)	0.1148 (16)	0.0688 (20)	C(70)	0.75486 (15)	0.44079 (6)	0.28955 (6)
O(31)	0.76178 (17)	0.09350 (7)	0.10147 (9)		0.7514 (36)	0.4397 (15)	0.2861 (19)
	0.7591 (29)	0.0941 (11)	0.0957 (14)	C(71)	0.76734 (16)	0.40871 (7)	0.35311 (7)
C(32)	0.38721 (14)	0.06678 (5)	−0.00035 (7)		0.7624 (42)	0.4055 (17)	0.3569 (22)
	0.3967 (33)	0.0720 (14)	0.0012 (17)	C(72)	0.86798 (17)	0.42745 (7)	0.40987 (7)
O(33)	0.33046 (19)	0.02189 (7)	−0.01924 (10)		0.8737 (50)	0.4243 (21)	0.4086 (25)
	0.3406 (30)	0.0274 (13)	−0.0191 (15)	C(73)	0.95709 (16)	0.47820 (7)	0.40288 (6)
C(40)	0.47359 (14)	0.26015 (6)	−0.14801 (6)		0.9577 (51)	0.4794 (21)	0.4020 (26)
	0.4826 (33)	0.2644 (13)	−0.1396 (18)	C(74)	0.94378 (15)	0.51134 (7)	0.33984 (6)
O(41)	0.44639 (19)	0.26755 (8)	−0.20777 (7)		0.9414 (49)	0.5123 (20)	0.3377 (26)
	0.4529 (35)	0.2701 (14)	−0.2042 (18)	H(50)A	0.64487 (30)	0.61009 (12)	0.22300 (13)
C(42)	0.71926 (13)	0.25754 (6)	−0.04021 (6)	H(50)B	0.63707 (30)	0.59108 (12)	0.13169 (12)
	0.7206 (49)	0.2544 (18)	−0.0377 (22)	H(52)	0.51591 (30)	0.48945 (13)	0.08814 (12)
O(43)	0.84299 (17)	0.26211 (8)	−0.03306 (10)	H(53)	0.32799 (33)	0.41248 (13)	0.10559 (14)
	0.8436 (33)	0.2618 (12)	−0.0354 (15)	H(54)	0.22738 (33)	0.40570 (13)	0.22098 (14)
C(230)	0.39320 (13)	0.16494 (5)	0.11961 (5)	H(55)	0.31553 (34)	0.47790 (14)	0.31844 (14)
	0.4091 (38)	0.1631 (15)	0.1219 (20)	H(56)	0.50763 (34)	0.55429 (13)	0.30158 (13)
O(231)	0.34228 (17)	0.14540 (6)	0.16885 (7)	H(58)	0.83517 (36)	0.66178 (15)	0.26040 (18)
	0.3510 (24)	0.1479 (10)	0.1691 (13)	H(59)	1.02263 (42)	0.74245 (16)	0.26396 (21)
C(240)	0.46026 (13)	0.32459 (5)	0.00111 (6)	H(60)	1.25564 (36)	0.72290 (15)	0.21433 (18)
	0.4754 (50)	0.3204 (23)	0.0026 (24)	H(61)	1.29916 (31)	0.62139 (15)	0.16149 (17)
O(241)	0.44744 (17)	0.37836 (6)	−0.00643 (7)	H(62)	1.11177 (31)	0.53977 (12)	0.15684 (16)
	0.4573 (25)	0.3579 (11)	−0.0040 (13)	H(64)	0.93168 (37)	0.40881 (13)	0.19398 (14)
P	0.82497 (17)	0.53623 (7)	0.20252 (7)	H(65)	0.95311 (42)	0.34138 (14)	0.09071 (16)
	0.82348 (88)	0.53531 (35)	0.20290 (43)	H(66)	0.88040 (36)	0.38019 (13)	−0.03137 (14)
C(50)	0.64559 (13)	0.57207 (5)	0.18546 (6)	H(67)	0.78997 (36)	0.48661 (14)	−0.05010 (13)
	0.6433 (31)	0.5721 (13)	0.1875 (17)	H(68)	0.76585 (36)	0.55461 (12)	0.05131 (13)
C(51)	0.52443 (13)	0.52690 (5)	0.19380 (6)	H(70)	0.67714 (33)	0.42560 (13)	0.24534 (14)
	0.5211 (32)	0.5269 (13)	0.1939 (17)	H(71)	0.69759 (39)	0.36886 (15)	0.35872 (18)
C(52)	0.47290 (13)	0.48696 (5)	0.13879 (6)	H(72)	0.87663 (41)	0.40209 (18)	0.45951 (15)
	0.4761 (32)	0.4876 (13)	0.1405 (17)	H(73)	1.03741 (39)	0.49217 (20)	0.44633 (14)
C(53)	0.36630 (14)	0.44347 (5)	0.14866 (6)	H(74)	1.01296 (34)	0.55115 (15)	0.33521 (14)
	0.3714 (38)	0.4449 (16)	0.1514 (20)				
C(54)	0.30959 (14)	0.43998 (6)	0.21331 (6)				
	0.3151 (39)	0.4418 (16)	0.2167 (21)				

[a] For each entry, the neutron result is given on the first line and the X-ray result, if available, on the second line. [b] The numbering scheme for the $[BzPh_3]P^+$ cation is as follows. Bz: C(50)–C(56). Ph: C(57)–C(62), C(63)–C(68), C(69)–C(74). The lowest numbered C atom in each group is bonded to P.

hydrogen and after about 20 h the formation of $[H_2Ir_4(CO)_{10}]^{2-}$ [10] is observed.

Note that the deprotonation of $[HIr_4(CO)_{11}]^-$ seems to be solvent dependent. It occurs only in solvents in which OH^- is not solvated.

Preparation of $[Ir_4(CO)_{11}]^{2-}$. A sample of 0.191 g (0.13 mmol) of $[Ph_4P]^+[HIr_4(CO)_{11}]^-$ was dissolved in 8 mL of Me_2SO. A solution (0.097 N) of *t*-BuOK in Me_2SO was added dropwise. The reaction was monitored by IR spectroscopy and was complete after the addition of 1.7 mL of the *t*-BuOK solution. $[Ir_4(CO)_{11}]^{2-}$ can also be made via the reaction of $[Ir_4(CO)_{11}(COOR)]^-$ (R = Me, Et) with sodium or potassium hydroxide in dry 2-propanol.[2a]

Crystallographic Section

Orange crystals of $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$ were mounted in glass

Table III. Selected Bond Distances (A) in the $[HIr_4(CO)_{11}]^-$ Anion[a]

	neutron (80 K)	X-ray (298 K)		neutron (80 K)	X-ray (298 K)
		Ir-Ir			
Ir(1)-Ir(2)	2.716 (1)	2.704 (2)	Ir(2)-Ir(4)	2.719 (1)	2.714 (2)
Ir(1)-Ir(3)	2.712 (1)	2.703 (2)	Ir(3)-Ir(4)	2.800 (1)	2.795 (2)
Ir(1)-Ir(4)	2.714 (1)	2.710 (2)	mean	2.736 (14)	2.728 (15)
Ir(2)-Ir(3)	2.753 (1)	2.740 (2)			
		Ir-H			
Ir(3)-H(1)	1.821 (3)		mean	1.834 (13)	
Ir(4)-H(1)	1.847 (3)				
		Ir-C(terminal)			
Ir(1)-C(10)	1.919 (1)	1.88 (4)	Ir(3)-C(30)	1.901 (2)	1.84 (4)
Ir(1)-C(12)	1.917 (1)	1.76 (4)	Ir(3)-C(32)	1.868 (1)	1.78 (3)
Ir(1)-C(14)	1.907 (1)	1.85 (3)	Ir(4)-C(40)	1.874 (1)	1.76 (3)
Ir(2)-C(20)	1.892 (2)	1.94 (4)	Ir(4)-C(42)	1.889 (2)	1.88 (5)
Ir(2)-C(22)	1.883 (1)	1.91 (3)	mean	1.894 (6)	1.84 (2)
		C-O(terminal)			
C(10)-O(11)	1.137 (2)	1.14 (5)	C(30)-O(31)	1.138 (2)	1.18 (5)
C(12)-O(13)	1.140 (2)	1.26 (5)	C(32)-O(33)	1.144 (2)	1.16 (4)
C(14)-O(15)	1.140 (2)	1.12 (4)	C(40)-O(41)	1.143 (2)	1.24 (5)
C(20)-O(21)	1.143 (2)	1.03 (5)	C(42)-O(43)	1.139 (2)	1.16 (5)
C(22)-O(23)	1.144 (2)	1.08 (4)	mean	1.141 (1)	1.15 (2)
		Ir-C(bridging)			
Ir(2)-C(230)	2.191 (1)	2.25 (3)	Ir(3)-C(230)	1.998 (1)	1.99 (4)
Ir(2)-C(240)	2.143 (1)	2.10 (5)	Ir(4)-C(240)	2.041 (1)	1.96 (5)
mean	2.167 (24)	2.18 (8)	mean	2.020 (22)	1.98 (5)
		C-O(bridging)			
C(230)-O(231)	1.177 (2)	1.16 (4)	mean	1.179 (2)	1.20 (5)
C(240)-O(241)	1.181 (2)	1.23 (5)			

[a] Esd's of mean values are calculated as $\sigma(\bar{x}) = [\Sigma_{i=1}{}^{n}(x_i - \bar{x})^2/n(n-1)]^{1/2}$, except for $n = 2$, when the larger of $\sigma(\bar{x})$ and the individual esd's is used.

capillaries under a nitrogen atmosphere. The compound crystallizes in the monoclinic space group $P2_1/c$, with unit cell parameters given in Table I. X-ray data were collected on a Nicolet/Syntex P2$_1$ diffractometer with Mo Kα radiation up to a 2θ(max) of 45°. A decrease (≤10%) in the intensities of the three standard reflections [$(\bar{4}0\bar{3})$, $(\bar{6}53)$, $(0,18,\bar{1})$] was accompanied by a noticeable decomposition (darkening) of the crystal during data collection, thus necessitating a decay correction of the raw intensities. After further corrections for Lorentz–polarization and absorption effects, 3714 reflections with $I > 3\sigma(I)$ were retained for the subsequent structure analysis. The positions of the four Ir atoms were obtined by direct methods,[12] and the rest of the model (i.e., the non-hydrogen atom positions) was generated by Fourier techniques.[13] Full-matrix least-squares refinement (in which the Ir and P atoms were refined anisotropically) resulted in final agreement factors[14] of $R(F) = 0.072$ and $R(wF) = 0.084$.

Table IV

	neutron	X-ray		neutron	X-ray
(A) Displacement (in A) of Atoms from the Noncrystallographic Mirror Plane in the $[HIr_4(CO)_{11}]^-$ Anion					
Ir(1)	0.06	0.05	C(20)	−0.02	−0.03
Ir(2)	0.02	0.01	O(21)	−0.01	0.01
C(12)	−0.01	−0.05	C(22)	0.04	0.04
O(13)	−0.03	0.01	O(23)	−0.04	−0.04
(B) Displacement (in A) of Atoms from the Basal Plane in $[HIr_4(CO)_{11}]^-$					
Ir(2)	0.18	0.11	O(231)	−0.10	−0.11
Ir(3)	0.01	−0.01	C(240)	−0.00	0.05
Ir(4)	−0.02	−0.03	O(241)	−0.08	−0.08
C(230)	0.01	0.08	H(1)	−0.01	

[a] All atoms listed here were assigned unit weights in the least-squares planes calculation.

For the neutron diffraction analysis, a rod-shaped crystal (approximate dimensions 0.7 × 0.9 × 1.8 mm) was mounted roughly along the *a* axis on an aluminum pin and placed under an atmosphere of nitrogen inside a closed-cycle helium refrigerator.[15] Data were collected at 80 K at the Brookhaven High Flux Beam Reactor, on a four-circle diffractometer operated under the Reactor Experimental Control Facility.[16] The unit cell parameters at 80 K are given in Table I. One quadrant of data was collected by using neutrons of wavelength 1.161 73 (8) Å[17] up to a 2θ(max) of 104.5°. After corrections for Lorentz and absorption[18] effects, 9627 unique reflections (including those with $F_o^2 < 0$) were retained for the ensuing structure analysis. The model obtained from the earlier X-ray study was used to phase the neutron data, and a series of difference-Fourier maps[13] revealed the positions of all H atoms. Least-squares refinement[19]

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(12) MULTAN: A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data [Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368].

(13) For the X-ray portion of this work, major computations were performed on the USC IBM 370-158 computer using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology. For the neutron diffraction analysis, calculations were performed on CDC 6600 and 7600 computers using programs described by: Berman, H. M.; Bernstein, F. C.; Bernstein, H. J.; Koetzle, T. F.; Williams, G. J. B. Informal Report 21714; Brookhaven National Laboratory: Upton, NY, 1976.

(14) $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R(wF) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $R(F^2) = \sum|F_o^2 - |F_c|^2|/\sum|F_o^2|$; $R(wF^2) = [\sum w(F_o^2 - |F_c|^2)^2/\sum wF_o^4]^{1/2}$.

(15) Air products and Chemicals, Inc., DISPLEX Model CS-202.

(16) (a) Dimmler, D. G.; Greenlaw, N.; Kelley, M. A.; Potter, D. W.; Rankowitz, S.; Stubblefield, F. W. *IEEE Trans. Nucl. Sci.* **1976**, *23*, 398. (b) McMullan, R. K.; Andrews, L. C.; Koetzle, T. F.; Reidinger, F.; Thomas, R.; Williams, G. J. B. NEXDAS Neutron and X-Ray Data Acquisition System (unpublished).

(17) The neutron wavelength was calibrated with a standard KBr crystal (a = 6.6000 Å at 295 K). The beam was monochromated with a Ge(220) crystal.

(18) Observed intensities were corrected for absorption by numerical integration over an 8 × 16 × 16 Gaussian grid [see: Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035]. The absorption coefficient for the title compound, $\mu = 2.176$ cm^{-1}, was calculated assuming a contribution for hydrogen given by the empirical expression $(\mu/\rho)_H = (10.055 + 14.117\lambda)$ [Koetzle, T. F.; McMullan, R. K., unpublished work] and tabulated mass absorption coefficients for non-hydrogen atoms ["International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III, p 197].

resulted in the agreement factors[14] $R(F^2) = 0.074$ and $R(wF^2) = 0.059$. A final difference map was essentially featureless.

Discussion

A view of the $[HIr_4(CO)_{11}]^-$ anion is shown in Figure 2. The final atomic coordinates and selected bond distances are given in Tables II and III, respectively. The geometry of the $[BzPh_3]^+$ cation is entirely normal. Complete results from the X-ray and neutron analyses are available as supplementary material (see paragraph at end of paper).

In the preliminary X-ray analysis of $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$, it was predicted[20] that the H atom would bridge the Ir(3)–Ir(4) edge of the tetrahedron, partly because of the Ir(3)–Ir(4) distance [2.795 (2) Å] being significantly longer than the others [mean 2.714 (7) Å] and partly because of the distortions of the Ir–Ir–C (terminal) angles about the Ir(3)–Ir(4) bond.[21] This prediction is confirmed by the present neutron analysis (Figure 2), which locates the hydride ligand in a nearly symmetrical position about this bond [Ir(3)–H(1) = 1.821 (3) Å, Ir(4)–H(1) = 1.847 (3) Å], making an Ir–H–Ir angle of 99.5 (1)°.

The anion has approximate C_s symmetry, with the pseudo mirror plane passing through Ir(1), Ir(2), H(1), C(12), O(13), C(20), O(21), C(22), and O(23) (Table IV). The two bridging carbonyl groups [C(230)O(231) and C(240)O(241)] are signficantly asymmetric, as has been found in other Ir_4 carbonyl complexes such as $[H_2Ir_4(CO)_{10}]^{2-}$ [10] and $[Ir_4(CO)_{11}Br]^-$.[9] The pattern of asymmetry, according to standard arguments,[9,22] suggests that the negative charge of the anion is predominantly associated with the Ir(2) atom.

The Ir–H(bridging) distance found here [average 1.834 (13) Å] is the most precise measured to date for a bond of this type. An earlier measurement by neutron diffraction, on the complex $[(C_5Me_5)Ir(\mu\text{-}H)_3Ir(C_5Me_5)]^+$, yielded an Ir–H(bridging) distance of 1.75 (3) Å,[23] but that value is probably less reliable because of disorder problems involving the $Ir(\mu\text{-}H)_3Ir$ portion of the molecule.

The structural analysis of the $[HIr_4(CO)_{11}]^-$ anion now completes the list of known structures of the isoelectronic series $Ir_4(CO)_{12}$, $[HIr_4(CO)_{11}]^-$, and $[H_2Ir_4(CO)_{10}]^{2-}$. All have different ligand arrangements about a common Ir_4 tetrahedral core: $Ir_4(CO)_{12}$ has exclusively terminal carbonyls;[3,4] $[HIr_4(CO)_{11}]^-$ has a bridging hydride ligand along with two bridging carbonyl groups, and $[H_2Ir_4(CO)_{10}]^{2-}$ has three bridging carbonyls but terminal hydrides.[10] Of the existing family of hydride/carbonyl Ir_4 clusters, only $H_2Ir_4(CO)_{11}$[1] remains structurally uncharacterized.

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Registry No. $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$, 92984-97-9; $[Ph_4P]^+[HIr_4(CO)_{11}]^-$, 92984-99-1; $[Ir_4(CO)_{11}]^{2-}$, 92984-98-0.

Supplementary Material Available: Listings of the anisotropic temperature factors (Table A), a complete set of interatomic distances (Table B) and bond angles (Table C), and the final observed and calculated squared structure factors for the neutron structural analysis (Table D) (62 pages). Ordering information is given on any current masthead page.

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[19] Other details of the neutron least-squares refinement: Due to the large number of variable parameters (677), parameters were grouped in blocks of ca. 225, and these blocks refined alternately to convergence. The isotropic extinction parameter, g, converged to a value of 0.49 (2) × 10^4 [see: Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558], with the most significant extinction correction being 0.864 dividing F_o^2 for the (163) reflection. Neutron-scattering lengths ($b \times 10^{-12}$ cm) used in the refinement were $b_{Ir} = 1.06$, $b_P = 0.513$, $b_C = 0.6648$, $b_O = 0.5803$, and $b_H = -0.3741$ [see: Koester, L. In "Neutron Physics"; Koester, L., Steyerl, A., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1977; p 36].

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[21] The use of molecular distortions to infer H positions in metal hydride complexes is common. See, for example: Churchill, M. R.; Bird, P. H.; Kaesz, H. D.; Bau, R.; Fontal, B. *J. Am. Chem. Soc.* **1968**, *90*, 7135.

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[23] (a) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *Adv. Chem. Ser.* **1978**, *No. 167*, 73. (b) Teller, R. G. Ph.D. Dissertation, University of Southern California, 1978, Chapter 3.

[24] The molecular drawing was generated by the program ORTEP-II: Johnson, C. K. "ORTEP-II", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Contribution from the Department of Chemistry
and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Preparation, Structure, and Properties of the Polar Dirhodium(II) Tetrakis(6-fluoro-2-oxypyridinate) Molecule

F. Albert Cotton,* Scott Han, and Wenning Wang

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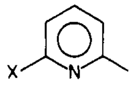
Since the discovery[1] of the $M_2(mhp)_4$ compounds (M = Cr, Mo, W; mhp = **1b**), it has been found that ligands of type **1**, which are derivatives or relatives of the 2-oxypyridinate ion (or that ion itself), are broadly useful for stabilizing dimetal units with a wide range of metallic elements and metal–metal bonds of orders from 1 to 4.[2]



1a (X=H), hp
1b (X=CH_3), mhp
1c (X=Cl), chp
1d (X=F), fhp

We recently reported[3] the first compounds containing the ligand **1d**, fhp, these being the three $M_2(fhp)_4(C_4H_8O)$ molecules in which M = Cr, Mo, and W. While in virtually all previous cases the arrangement of the four ligands on the M_2 core was such that each metal atom formed two M–N bonds and two M–O bonds (the only exceptions being a few cases where the ligand orientations were in a 3:1 ratio), the $M_2(fhp)_4(C_4H_8O)$ molecules had the fhp ligands all oriented in the same direction. This results in one metal atom having only M–N bonds while the other has four M–O bonds, plus an axial bond to the tetrahydrofuran molecule. It was not (and still is not) evident why this completely polar arrangement occurs. Since in the first study we dealt only with the quadruply bonded group 6 M_2^{4+} units, we felt it would be of value to determine how the fhp ligand would behave with an entirely different, but nevertheless stable and important, dimetal unit, namely, Rh_2^{4+}. We have succeeded in preparing several $Rh_2(fhp)_4L$ compounds, where L is C_2H_5OH, C_4H_8O, or $(CH_3)_2SO$, and have studied them structurally and spectroscopically.

Experimental Section

Preparation. A solution of the sodium salt of the 6-fluoro-2-hydroxypyridine anion (Na(fhp)) was prepared by dissolving 0.082

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