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A Trinuclear Iridium Cluster Containing a Tricoordinate Bridging Hydrogen Ligand: Structural and Chemical Studies

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The first examples of trimeric iridium cluster complexes $[(IrH_2LL')_3(\mu_3\text{-}H)](BF_4)_2$ (L = PCy_3 or PPh_3; L′ = pyridine or MeCN) are described and their X-ray structures discussed. The hydrogen ligands were located from the ^{1}H NMR spectra of the complexes. Chemical studies are also discussed. The compound belongs to the space group $P1\,[C_i^1]$ No. 2 (Z = 2) with unit cell dimensions a = 14.279 (5) Å, b = 14.515 (5) Å, c = 23.173 (9) Å, α = 76.05 (3)°, β = 80.61 (3)°, and γ = 72.74 (3)°. A total of 6234 reflections were used, and the final R factors were R = 0.058 and R_w = 0.083.

Introduction

We have shown that complexes of the type [Ir(cod)(PR_3)L]X (cod = 1,5-cyclooctadiene) (**1**: R = cyclohexyl (Cy) or isopropyl (*i*-Pr); L = tertiary amine, e.g., pyridine (py) or imidazole; X = BF_4 or PF_6) are hydrogenation catalysts in noncoordinating solvents such as CH_2Cl_2.[4] They are particularly effective in the reduction of tri- and tetrasubstituted olefins, for example, those found in a variety of natural products.[5]

Their activity may be due to the formation of the dihydrido olefin complexes $[IrH_2(ol)_2(PR_3)L]^+$ (ol = olefin) because the corresponding species have been observed in the bis(phosphine) analogues (L = PR_3).[4] When the substrate concentration falls to 0 (or for olefins that are themselves poor ligands, to ca. 0.05 M), the iridium species dimerize (L = PR_3) or trimerize (L = py or nitrile) irreversibly to give catalytically inactive cluster complexes. The latter constitute the first examples of a trinuclear iridium cluster, $\{[IrH_2(PR_3)L]_3(\mu_3\text{-}H)\}X_2$ (**2a**, R = Cy; **2b**, R = *i*-Pr) on which a brief report has appeared.[6]

These complexes contain a tricoordinate bridging hydrogen ligand. Tricoordination of a hydrogen ligand was first suggested for Cp_4Rh_3H[7] and $Ru_6H_2(CO)_{18}$[8] and has recently been demonstrated for a number of cyclopentadienyl (Cp) and carbonyl complexes such as $Re_4H_4(CO)_{12}$,[9] $Cp_4Co_4H_4$,[10] and $Cp_4N_4H_3$.[11] Trimeric iridium clusters related to **2** and made by an analogous route, but containing chelating bis(phosphine) ligands, have also been recently reported.[12] We provide evidence for a tricoordinate hydrogen ligand in **2**, where the cluster is stabilized only by P and N donor ligands. We also report some chemistry of these systems and the preparation of some related compounds.

Experimental Section

Reagents. Ammonium chloroiridate was obtained from the Compagnie des Mêtaux Précieux and Johnson Matthey Inc. Ligands were purchased from Aldrich Chemical Co. or, in the case of tertiary phosphines, Strem Chemicals.

Spectroscopy. NMR spectra were recorded on a Bruker 270-MHz instrument. Chemical shifts are given as ppm relative to Me_4Si. IR spectra were recorded on a Perkin-Elmer 283 instrument.

Synthesis. Starting materials were synthesized via published procedures.[13]

(η-1,5-Cyclooctadiene)(cyanomethane)(tricyclohexylphosphine)iridium(I) Tetrafluoroborate. $IrCl(cod)(PCy_3)$ (522 mg, 0.85 mmol) was stirred for 30 min with $AgBF_4$ (170 mg, 0.87 mmol) in CH_3CN (2 mL) and CH_2Cl_2 (30 mL) at 25 °C under N_2. The supernatant was filtered from the precipitated AgCl, reduced to 5 mL in vacuo, and treated with Et_2O (5 mL) to precipitate the product: yield 494 mg, 82%; IR ν(CN) 2270 w cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) δ 4.83 (br, cod vinyl), 3.79 (br, cod vinyl), 2.5–1.2 (m, PCy_3 and MeCN). Anal. Calcd for $C_{28}H_{48}NPIrBF_4$: C, 47.50; H, 6.77. Found: C, 47.57; H, 6.65.

Preparation of the Clusters $[(IrH_2LL')_3(\mu_3\text{-}H)](BF_4)_2$ (L = PCy_3 or P(*i*-Pr)$_3$, L′ = py; L = PCy_3, L′ = MeCN). $[Ir(cod)(PCy_3)py]BF_4$ (746 mg, 1 mmol) in CH_2Cl_2 (30 mL) was treated with H_2 (1 atm, 25 °C). After 3.5 h, 3.1 mmol of H_2 (theory 3.3 mmol) was absorbed and 0.98 mmol (theory 1 mmol) of cyclooctene (GC) had been formed. A trace of precipitated pyridinium tetrafluoroborate (25 mg) was filtered off at this stage. The filtrate was reduced in volume to 5 mL and hexane added to give a yellow product. Recrystallization from CH_2Cl_2 gave yellow microcrystals: yield 190 mg, 30%; IR ν(Ir–H) 2230 m, 1770 m cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.8 (m, py), 7.8 (m, py), 2.5–1.2 (m, PCy_3), –3.9 (q, J = 50 Hz, μ_3-H), –20 (d, J = 10 Hz, IrH), –25.6 (d, J = 25 Hz, IrH). Anal. Calcd for $C_{69}H_{121}P_3N_3Ir_3B_2F_8{\cdot}CH_2Cl_2$: C, 43.81; H, 6.36. Found: C, 44.02; H, 6.11. The hexafluorophosphate salt was obtained in a similar way and in a similar yield from $[Ir(cod)(PCy_3)py]PF_6$. The IR and NMR spectra are identical with the results shown above for the BF_4 salt. Anal. Calcd for $C_{69}H_{121}P_5N_3Ir_3F_{12}{\cdot}CH_2Cl_2$: C, 41.27, H, 6.08. Found: C, 41.45; H, 5.97.

The P(*i*-Pr)$_3$ analogue was obtained in 25% yield from [Ir(cod)P(*i*-Pr)$_3$py]BF_4: IR ν(Ir–H), 2240 m, 1770 m cm^{-1}; ^{1}H NMR δ 8.8 (m, py), 7.8 (m, py), 1.3 (dd, J = 6 Hz, J = 12 Hz, Me), 1.5–2.9 (m, Me_2CH), –3.7 (q, J = 50 Hz, μ_3-H), –19.9 (d, J = 25 Hz, IrH), –21.8 (d, J = 10 Hz, IrH). Anal. Calcd for $C_{42}H_{85}P_3N_3Ir_3B_2F_8{\cdot}CH_2Cl_2$: C, 33.13; H, 5.55. Found: C, 32.85; H, 5.35.

The acetonitrile analogue, **3**, was prepared as follows: $[Ir(cod)(PCy_3)CH_3CN]BF_4$ (218 mg, 0.3 mmol) in CH_2Cl_2 (30 mL) was saturated with H_2 (0 °C, 15 min). The volume of the solution was reduced to 5 mL, and the yellow product was precipitated with ether. Recrystallization from CH_2Cl_2/Et_2O gave yellow microcrystals: yield 134 mg, 76%; IR 2240 m, 1770 m cm^{-1}; ^{1}H NMR δ 2.5–1.2 (m, PCy_3 and MeCN), –4.4 (q, J = 43 Hz, μ_3-H), –20 (d, J = 4 Hz, IrH), –25 (d, J = 23 Hz, IrH). Anal. Calcd for $C_{60}H_{115}P_3N_3Ir_3B_2F_8{\cdot}CH_2Cl_2$: C, 40.59; H, 6.43. Found: C, 40.41; H, 6.22.

Solid-State Syntheses. The precursor complexes mentioned above were exposed to H_2 (1 atm, 25 °C) for 2 days. After recrystallization, the yields of the trinuclear cluster complexes were similar to those obtained above.

Collection and Reduction of X-ray Data. Crystals of **2a** suitable for diffraction study were obtained by allowing octane to slowly diffuse into a CH_2Cl_2 solution of the hexafluorophosphate salt of the compound at room temperature. A crystal bounded by the faces (011), (011), (101), $(\bar{1}0\bar{1})$, $(43\bar{2})$, and $(\bar{4}\bar{3}2)$, with the approximate dimensions

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Table I. Experimental Data for the X-ray Diffraction Study of $[Ir_3H_7(PCy_3)_3py_3](PF_6)_2\cdot CH_2Cl_2$

(A) Crystal Parameters at 25 °C	
space group $P\bar{1}$ $[C_i^1]$ No. 2	
$a = 14.279$ (5) Å	$V = 4429$ (3) Å^3
$b = 14.515$ (5) Å	$Z = 2$
$c = 23.173$ (9) Å	fw = 2039.2
$\alpha = 76.05$ (3)°	$\rho_{calcd} = 1.529$ g cm^{-3}
$\beta = 80.61$ (3)°	
$\gamma = 72.74$ (3)°	
(B) Measurement of Intensity Data	
radiation	Mo Kα $\lambda = 0.710\,73$ Å
monochromator	graphite single crystal
takeoff angle	2.5°
detector aperture	
horiz = $A + B \tan\theta$	$A = 3.0$ mm $B = 1.0$ mm
vert	4.0 mm
crystal-detector dist	330 mm
crystal orientation	random
rflctns measd	$+h\pm k\pm l$
max 2θ	40°
scan type	couple θ (crystal)–2θ (counter)
scan speed, variable	max θ = 10.0° min^{-1} min θ = 1.1° min^{-1}
θ scan width	0.70 + 0.347 tan θ on each side of calcd position
bkgd	moving crystal-moving counter
std rflctns	3 measmt after every approx 130 data rflctns
obsd rflctns ($F^2 > 3\sigma(F^2)$)	6324
(C) Treatment of Data	
abs coeff	49.09 cm^{-1}
grid	6 × 6 × 8
transmission factors	max 0.6045 min 0.1650
ignorance factor	$p = 0.03$

0.28 mm × 0.25 mm × 0.20 mm, was selected and secured (epoxy cement) on to the tip of a thin glass fiber. The fiber was then mounted in a random orientation on a goniometer head. Diffraction data were collected at ambient temperature with an Enraf-Nonius CAD-4 automatic diffractometer. A standard peak search and autocentering program was employed to locate 25 random reflections. A least-squares treatment of these reflections provided an orientation matrix. Final unit cell parameters were obtained from a least-squares refinement of 25 reflections in the range 24° < 2θ < 40°. Inspection of the unit cell parameters revealed the triclinic nature of the cell. The space group $P\bar{1}[C_i^1]$ No. 2 was selected and later confirmed by the subsequent successful solution and refinement of the structure. A total of 8963 reflections were collected in the range 0° < 2θ < 40°, of which 6324 conformed to the relation $F^2 > 3\sigma(F^2)$ after Lorentz and polarization corrections were applied. The intensity of three reflections that were monitored during the course of data collection showed a linear decay in intensity (maximum decay was 6%). The data were corrected for this isotropic decay prior to the structure solution and refinement. A complete description of the data collection is provided in Table I.

Structure Solution and Refinement. The structure was solved by heavy-atom methods. The coordinates of three heavy atoms were obtained from a three-dimensional Patterson synthesis, and these positions were assigned to iridium atoms. Subsequent least-squares refinement produced noncredible isotropic temperature parameters but yielded the discrepancy indices R = 4.9% and R_w = 5.6%.[14] A difference Fourier synthesis followed by a distance and angle calculation suggested the misassignment of one iridium atom; relocation of this atom, followed by three cycles of isotropic least-squares refinement, now produced credible temperature factors and reduced the values of R and R_w to 0.210 and 0.282, respectively. Sequential difference Fourier followed by least-squares calculations revealed the positions of all remaining nonhydrogen atoms exclusive of the solvate molecule. At this stage of the refinement data were corrected for absorption effects by a Gaussian method, with a grid of 6 × 6 × 8. Subsequent least-squares refinement of these 92 atoms yielded the values R = 0.068 and R_w = 0.094. A difference Fourier calculation next revealed three three-atom arrangements at distances greater than 3.0 Å from any refined atomic position. Each of these three-atom arrangements showed that (1) two atoms were bound to a third, subtending an angle of ca. 105°, (2) the central atom was about one-third the size of the outer two, and (3) the outer two were the size of carbon atoms. A disorder model based on the features described was devised in which one molecule of CH_2Cl_2 was evenly disordered over three positions in the asymmetric unit. The occupancy of each of these sites was fixed at 0.33 and was not allowed to vary in the final least-squares refinement. No attempts were made to locate or refine hydrogen atoms. Due to computational constraints, the atomic parameters were partitioned into three blocks during the final stages of the refinement. The first block contained the parameters of the nonhydrogen atoms of the cation, the second, those of the anions, and the third, those of the solvate molecules. The metal, phosphorus, and nitrogen atoms were assigned anisotropic thermal parameters while the remaining nonhydrogen atoms were refined isotropically. The structure solution rapidly converged (two cycles) to give the final discrepancy indices R = 0.058 and R_w = 0.083. Exclusive of the PF_6 anions, no parameter shifted by more than 0.2 during the final cycle of refinement; the greatest parameter shift was for atom F54 (0.43σ). The goodness of fit, $[w_i(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, was 3.679. A final difference Fourier synthesis showed several small peaks in the vicinity of the methylene chloride molecule(s); however, no attempt was made to sort out this residual disorder nor was any attempt made to sort out the apparent disorder of the PF_6 anions. Atomic, positional, and thermal parameters are listed in Table II and supplementary data Table 3. Selected bond distances and intramolecular angles are presented in Tables III and IV. A tabulation of final observed and calculated structure factor amplitudes is available as supplementary material, as are complete tables of intramolecular distances and angles. The data for the Ir_3, cyclohexylphosphine P_3, and N_3 planes are given in Table 5 (supplementary data). Figure 1 shows an ORTEP diagram of the $Ir_3P_3N_3$ core of the cation, and Figure 2 shows our assignment of the coordination environment of the cluster, including hydrogen ligands.

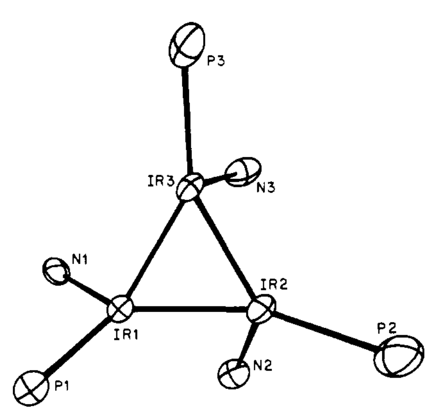

Figure 1. ORTEP diagram of the heavy-atom environment of the iridium coordination sphere. Atoms are represented by 50% probability ellipsoids.

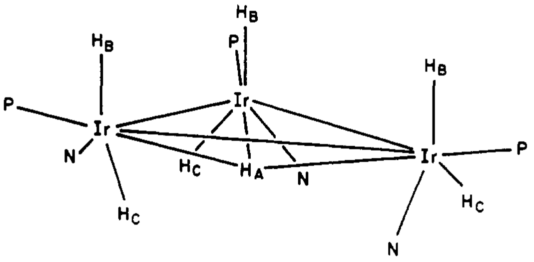

Figure 2. Our assignment of the full coordination environment of the cluster.

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(14) The refinements were of the full-matrix type; the function minimized in the least-squares analysis was $w(|F_o| - |F_c|)^2$, where $w = \sigma(F_o)^{-2}$. Atomic scattering factors were corrected for the real and imaginary components of anomalous scattering. See: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.3.1.

Table II. Atomic Coordinates for Crystalline $[Ir_3H_7(PCy_3)_3py_3](PF_6)_2 \cdot CH_2Cl_2$

atom	x/a	b/y	c/z	atom	x/a	y/b	z/c
Ir1	0.23555 (6)	0.25577 (5)	0.23710 (3)	C131	0.070 (1)	0.315 (1)	0.1264 (9)
Ir2	0.30262 (6)	0.28237 (6)	0.33616 (3)	C132	0.014 (1)	0.238 (1)	0.1654 (9)
Ir3	0.43190 (6)	0.17846 (6)	0.25738 (3)	C133	−0.013 (2)	0.184 (2)	0.1225 (10)
P1	0.1321 (4)	0.3669 (4)	0.1715 (2)	C134	−0.079 (2)	0.260 (2)	0.0748 (11)
P2	0.3091 (4)	0.4019 (4)	0.3832 (2)	C135	−0.032 (2)	0.341 (2)	0.391 (11)
P3	0.5727 (4)	0.1725 (4)	0.1940 (2)	C136	−0.003 (2)	0.394 (2)	0.0858 (10)
P4	0.7567 (7)	0.7883 (9)	0.0648 (3)	C211	0.244 (2)	0.387 (2)	0.4611 (9)
P5	0.2499 (7)	0.8384 (6)	0.4249 (4)	C212	0.284 (2)	0.287 (2)	0.5018 (10)
N1	0.241 (1)	0.130 (1)	0.2028 (7)	C214	0.100 (2)	0.352 (2)	0.5943 (12)
N2	0.176 (1)	0.248 (1)	0.3888 (9)	C215	0.165 (2)	0.560 (2)	0.5522 (12)
N3	0.504 (1)	0.080 (1)	0.3316 (7)	C216	0.239 (2)	0.470 (2)	0.4948 (10)
F41	0.867 (2)	0.771 (2)	0.072 (1)	C221	0.437 (2)	0.408 (1)	0.3835 (9)
F42	0.228 (2)	0.203 (2)	0.004 (1)	C222	0.495 (2)	0.315 (2)	0.4281 (11)
F43	0.675 (2)	0.876 (2)	0.060 (1)	C223	0.610 (2)	0.311 (2)	0.4137 (12)
F44	0.734 (2)	0.774 (2)	0.133 (1)	C224	0.624 (2)	0.405 (2)	0.4252 (14)
F45	0.795 (2)	0.674 (2)	0.067 (1)	C225	0.563 (2)	0.501 (2)	0.3869 (13)
F46	0.663 (3)	0.749 (3)	0.055 (2)	C226	0.450 (2)	0.504 (2)	0.3960 (11)
F51	0.362 (2)	0.778 (2)	0.431 (1)	C231	0.252 (1)	0.529 (1)	0.3475 (9)
F52	0.264 (2)	0.886 (2)	0.477 (1)	C232	0.296 (2)	0.555 (2)	0.2823 (11)
F53	0.275 (2)	0.929 (2)	0.379 (1)	C233	0.261 (2)	0.670 (2)	0.2551 (12)
F54	0.242 (3)	0.795 (2)	0.372 (2)	C234	0.142 (2)	0.698 (2)	0.2602 (13)
F55	0.780 (2)	0.247 (2)	0.527 (1)	C235	0.088 (2)	0.669 (2)	0.3297 (13)
F56	0.137 (2)	0.900 (2)	0.421 (1)	C236	0.135 (2)	0.552 (2)	0.3525 (11)
C11	0.222 (2)	0.051 (2)	0.2467 (11)	C311	0.677 (1)	0.068 (1)	0.2197 (9)
C12	0.226 (2)	−0.039 (2)	0.2290 (12)	C312	0.776 (2)	0.066 (2)	0.1831 (11)
C13	0.247 (2)	−0.042 (2)	0.1666 (12)	C313	0.862 (2)	−0.010 (2)	0.2199 (13)
C14	0.272 (2)	0.036 (2)	0.1261 (11)	C314	0.838 (2)	−0.113 (2)	0.2344 (13)
C15	0.269 (1)	0.120 (1)	0.1450 (9)	C315	0.733 (2)	−0.111 (2)	0.2699 (11)
C21	0.084 (2)	0.314 (2)	0.3900 (10)	C316	0.658 (2)	−0.035 (1)	0.2305 (9)
C22	0.003 (2)	0.287 (2)	0.4251 (12)	C321	0.622 (1)	0.283 (1)	0.1851 (8)
C23	0.014 (2)	0.193 (2)	0.4635 (14)	C322	0.652 (1)	0.290 (1)	0.2444 (9)
C24	0.110 (2)	0.122 (2)	0.4592 (15)	C323	0.698 (2)	0.392 (2)	0.2314 (10)
C25	0.190 (2)	0.156 (2)	0.4224 (11)	C324	0.623 (2)	0.479 (2)	0.2064 (11)
C31	0.570 (2)	0.107 (2)	0.3576 (10)	C325	0.587 (2)	0.468 (2)	0.1451 (11)
C32	0.608 (2)	0.044 (2)	0.4114 (11)	C326	0.544 (2)	0.378 (1)	0.1613 (9)
C33	0.578 (2)	−0.039 (2)	0.4368 (11)	C331	0.511 (1)	0.177 (1)	0.1152 (9)
C34	0.515 (2)	−0.066 (2)	0.4080 (12)	C332	0.529 (2)	0.079 (1)	0.1087 (9)
C35	0.477 (2)	−0.004 (2)	0.3550 (10)	C333	0.491 (2)	0.097 (2)	0.0473 (10)
C111	0.042 (1)	0.458 (1)	0.2106 (9)	C334	0.573 (2)	0.123 (2)	−0.0034 (11)
C112	−0.043 (2)	0.410 (2)	0.2514 (10)	C335	0.599 (2)	0.215 (2)	0.0026 (11)
C113	−0.113 (2)	0.485 (2)	0.2898 (11)	C336	0.637 (2)	0.202 (2)	0.0656 (10)
C114	−0.160 (2)	0.583 (2)	0.2500 (11)	C1	0.515 (4)	0.793 (4)	0.1985 (26)
C115	−0.081 (2)	0.630 (2)	0.2131 (11)	C2	0.952 (5)	0.045 (5)	0.3711 (32)
C116	−0.009 (2)	0.558 (2)	0.1702 (10)	C3	0.039 (5)	0.879 (5)	0.0655 (29)
C121	0.195 (1)	0.444 (1)	0.1117 (9)	Cl11	0.465 (1)	0.734 (1)	0.1662 (8)
C122	0.252 (2)	0.501 (2)	0.1381 (10)	Cl12	0.500 (2)	0.769 (2)	0.2760 (11)
C123	0.292 (2)	0.575 (2)	0.0856 (10)	Cl21	0.904 (2)	0.154 (2)	0.3291 (10)
C124	0.366 (2)	0.520 (2)	0.0395 (11)	Cl22	0.895 (2)	−0.040 (2)	0.3809 (10)
C125	0.313 (2)	0.456 (2)	0.0147 (12)	Cl31	0.088 (2)	0.804 (2)	0.1240 (10)
C126	0.267 (2)	0.383 (2)	0.0687 (10)	Cl32	0.122 (2)	0.943 (2)	0.0229 (11)

Table III. Selected Intramolecular Distances (Å) for Crystalline $[Ir_3H_7(PCy_3)_3py_3](PF_6)_2 \cdot CH_2Cl_2$

Ir1–Ir2	2.775 (1)	Ir1–Ir3	2.776 (1)	Ir2–Ir3	2.755 (1)
Ir1–P1	2.286 (3)	Ir2–P2	2.291 (3)	Ir3–P3	2.281 (3)
Ir1–N1	2.140 (8)	Ir2–N2	2.134 (8)	Ir3–N3	2.144 (9)
P1–C111	1.844 (3)	P2–C211	1.886 (3)	P3–C311	1.837 (3)
P1–C131	1.877 (3)	P2–C221	1.857 (3)	P3–C321	1.885 (3)
N1–C11	1.390 (9)	N2–C21	1.371 (9)	N3–C31	1.391 (9)
N1–C15	1.363 (9)	N2–C25	1.349 (8)	N3–C35	1.345 (9)
P1–C121	1.852 (3)	P2–C231	1.829 (3)	P3–C331	1.885 (3)

Results and Discussion

A number of novel trinuclear iridium hydrides can be obtained by reaction 1 (coa = cyclooctane). For example, **2** can

$$\underset{\mathbf{1}}{3[\mathrm{Ir(cod)LL'}]^+} + 10\mathrm{H_2} \rightarrow \underset{\mathbf{2}}{[(\mathrm{IrLL'H_2})_3(\mu_3\text{-H})]^{2+}} + \mathrm{H^+} + 3\mathrm{coa} \quad (1)$$

$$\mathbf{a}\text{: } L = PCy_3;\ L' = C_5H_5N$$

$$\mathbf{b}\text{: } L = P(i\text{-Pr})_3;\ L' = C_5H_5N$$

be isolated in moderate yield (30%) from CH_2Cl_2 solutions of **1** that have been treated with hydrogen for 3.5 h at 0 °C. The solution absorbs 3.1 mol of H_2/mol of Ir (theory 3.3 mol) and 0.98 mol/mol of Ir (theory 1.0 mol) of cyclooctane is formed, as judged by manometry and GLC, respectively. The complexes were recrystallized from acetone/ethanol and crystals prepared for a diffraction study by liquid diffusion (CH_2Cl_2/octane). The complexes were both air stable and thermally stable, as were the precursors **1**.

Unexpectedly, the precursors $[Ir(cod)LL']BF_4$ also reacted with H_2 in the solid state to give the trinuclear complexes **2** in similar yields after recrystallization. $[Ir(cod)(PPh_3)_2]BF_4$ also gave the known[4] $[Ir_2H_5(PPh_3)_4]BF_4$ under these conditions.

Description of the Structure. $[Ir_3H_7(PCy_3)_3py_3](PF_6)_2 \cdot CH_2Cl_2$ (**2a**) was structurally characterized. The crystallographic data are presented in Tables I–IV and supplementary data Tables 1–7. The structure shows that discrete cations and anions are present, and the CH_2Cl_2 of solvation appears to be disordered over three sites. There are no unusually short contacts. Figure 1 shows the ORTEP diagram of the heavy-atom core of the dication of **2a**. A nearly equilateral triangle of iridium atoms dominates the structure. The Ir–Ir distances

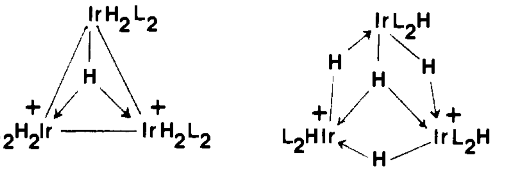
Table IV. Selected Bond Angles (Deg) for Crystalline $[Ir_3H_7(PCy_3)_3py_3](PF_6)_2 \cdot CH_2Cl_2$

Ir2-Ir1-Ir3	59.64 (1)	Ir1-Ir2-Ir3	60.01 (1)	Ir1-Ir3-Ir2	60.35 (1)
Ir2-Ir1-P1	129.42 (7)	Ir1-Ir2-P2	142.33 (8)	Ir1-Ir3-P3	131.41 (7)
Ir2-Ir1-N1	134.3 (2)	Ir1-Ir2-N2	88.7 (2)	Ir1-Ir3-N3	132.7 (2)
Ir3-Ir1-P1	142.92 (8)	Ir3-Ir2-P2	134.04 (8)	Ir2-Ir3-P3	144.36 (7)
Ir3-Ir1-N1	90.0 (2)	Ir3-Ir2-N2	127.7 (2)	Ir2-Ir3-N3	89.1 (2)
P1-Ir1-N1	95.7 (2)	P2-Ir2-N2	96.9 (2)	P3-Ir3-N3	94.9 (2)
Ir1-P1-C111	109.8 (1)	Ir2-P2-C211	111.5 (1)	Ir3-P3-C311	113.5 (1)
Ir1-P1-C121	113.5 (1)	Ir2-P2-C221	112.4 (1)	Ir3-P3-C321	113.5 (1)
Ir1-P1-C131	116.7 (1)	Ir2-P2-C231	116.1 (11)	Ir3-P3-C331	111.6 (1)
C111-P1-C121	103.2 (1)	C211-P2-C221	111.4 (1)	C311-P3-C321	103.1 (1)
C111-P1-C131	111.5 (1)	C211-P2-C231	104.4 (1)	C311-P3-C331	111.6 (1)
C121-P1-C131	101.1 (1)	C221-P2-C231	100.3 (1)	C321-P3-C331	102.8 (1)
Ir1-N1-C11	113.5 (5)	Ir2-N2-C21	123.2 (5)	Ir3-N3-C31	119.9 (5)
C11-N1-C15	120.9 (6)	C21-N2-C25	120.7 (6)	C31-N3-C35	121.8 (6)
Ir1-N1-C15	126.3 (5)	Ir2-N2-C25	116.5 (5)	Ir3-N3-C35	120.0 (5)

of 2.755 (1), 2.776 (1), and 2.775 (1) Å suggest that the Ir–Ir bond order is unity (Ir–Ir = 2.68 Å in $Ir_4(CO)_{12}$[15]). The Ir_3, P_3, and N_3 planes are parallel to within 3°. The center of the P_3 plane is 1.17 Å above and the N_3 plane 1.35 Å below the Ir_3 plane, as depicted in Figure 1.

A difference Fourier map failed to reveal the hydrogen ligands, and their positions were deduced from the ^1H NMR spectrum (see below). The assignment we propose for the coordination of the hydrogen ligands is shown in Figure 2. A bridging hydrogen, H_A, is equidistant from the three metal atoms. If a reasonable M–H distance (ca. 1.7 Å[11]) is assumed, this hydrogen is probably 0.6–0.8 Å above or below the Ir_3 plane. Further evidence (see below) suggests that latter assignment, with H_A on the same side of the Ir_3 plane as are the pyridine groups. H_B and H_c seem to be unexceptional terminal hydrogen ligands. The bonding of the unique hydrogen ligand must involve a four-center, two-electron interaction.

The relationship of this structure to that of $[Ir_3H_7(Ph_2P(CH_2)_3PPh_2)_3](BF_4)_2 \cdot CH_2Cl_2$ has been fully discussed by Wang and Pignolet in a recent report.[12] A point not mentioned by these authors is that both isomers can be described by the electron counting scheme of Green et al.[16] Each would then



be an 18-electron Ir(III) complex, a result in accord with the stability and other chemical properties of the clusters. The choice of a bridging or terminal position for the hydrogen ligands in these complexes is a delicate one, and it is not yet clear exactly what dictates it.

^{1}H NMR Spectra. The complexes **2a,b** were studied by ^1H NMR spectroscopy and proved to have almost identical characteristics. For example, for **2a**, a quartet at −3.9 ppm is assigned to H_A. The coupling constant $^2J(P,H \text{ trans})$ is 50 Hz, or about one-third of the values usually observed in mononuclear complexes (130–160 Hz[17]). This reduction may be related to the fractional bond order of the Ir–H bonds in the clusters $Ir_n(\mu_n\text{-}H)$, since we found[4] values of $^2J(P,H \text{ trans})$ of 60–85 Hz, or half the normal value, in the binuclear complex $\{[IrH(PPh_3)_2]_2(\mu\text{-}H)_3\}BF_4$ (**4**).

A doublet at −20.1 ppm [$^2J(P,H \text{ cis}) = 10$ Hz] and another at −25.6 ppm [$^2J(P,H \text{ cis}) = 25$ Hz],[17] each having 3 times the intensity of the quartet, are assigned to H_B and H_C. Curiously, no sign of fluxional behavior was observed. The unusual chemical shift of H_A may result from the bridging arrangement. In the case of **4**, the bridging hydrides also resonate ca. 15 ppm downfield from the terminal resonances. IR spectroscopy showed a terminal Ir–H stretching frequency at 2230 cm^{-1} as well as an absorption at 1770 cm^{-1} which might be the μ_3-hydride stretch.

The possibility that H_A is mono- or dicoordinate and fluxional, which would be consistent with the ^1H NMR spectrum, was rejected on the basis of the close approach of the cluster to 3-fold symmetry in the solid state and the absence of abnormal thermal parameters indicating disorder of a possible $Ir_3(\mu\text{-}H)$ structure. In addition such a hydrogen ligand would be expected to be more cis than trans to the PCy_3 group, leading to a $^2J(P,H)$ coupling constant nearer 10 than 50 Hz.[18] In addition, the complexes of Pignolet et al., which are thought to have dicoordinate hydrogens, have IR and ^1H NMR spectral properties quite different from those of **2**.

Reactions of the Complex 2a. The complex reacted readily with a variety of reagents, e.g., CO and C_2H_4, but in some cases a mixture of cationic products was obtained that was difficult to separate or characterize. We imagine that at the temperatures required for reaction (60–80 °C) some metalation of the tricyclohexylphosphine groups occurs,[18] complicating the chemistry considerably. At 20 °C, $NaBH_4$ reacts with **2** in THF to give a mixture of neutral hydride complexes, which are soluble in pentane but could not be separated or characterized.

Analogous Complexes. $[Ir(cod)(MeCN)(PCy_3)]BF_4$ (**5**) can be easily obtained from $[IrCl(cod)(PCy_3)]$ in MeCN on treatment with $AgBF_4$. On hydrogenation in CH_2Cl_2, **5** gives a yellow solution, from which $[Ir_3H_7(PCy_3)_3(MeCN)_3](BF_4)_2$ was crystallized in good yield. The complex appeared entirely analogous to **2** from ^1H NMR and IR measurements.

Conclusions

We have described the first examples of trinuclear iridium clusters.[19] Our work[6] together with Wang and Pignolet's[12] suggests that there is very little energy difference between terminal and bridging hydrogen positions since a small change in the coligands causes a structural change from one to the other.

This work also suggests that NMR coupling constants may be useful in distinguishing terminal and bridging hydrogen ligands.

The ratio of hydrogen ligands to metal atoms (2.33) is unusually high for a cluster.

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E. I. du Pont de Nemours for fellowships (R.H.C.), which enabled this work to be done. We also thank the Compagnie des Mêtaux Prêcieux and Johnson Matthey and Co. for loans of iridium and the donors of the Petroleum Research Fund, administered by the American Chemical society, and NSF for partial funding.

Registry No. **1a**, BF_4 salt, 80409-82-1; **1a**, PF_6 salt, 64536-78-3; **1b**, BF_4 salt, 80409-83-2; **2a**, BF_4 salt, 80446-89-5; **2a**, PF_6 salt, CH_2Cl_2 adduct, 69044-44-6; **2b**, BF_4 salt, 80446-31-7; **3**, 80409-85-4; **5**, 80409-87-6; $IrCl(cod)(PCy_3)$, 64536-83-0.

Supplementary Material Available: Table 1 (observed and calculated structure factor amplitudes), Table 2 (bond angles), Table 3 (thermal parameters), Tables 4 and 5 (further intramolecular distances), Table 6 (various unweighted least-squares planes, including dihedral angles and equations of planes), and a figure (unit cell) (31 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie des Polymères Inorganiques and the Laboratoire de Chimie des Mêtaux de Transition (ERA 608), Universitê Pierre et Marie Curie, 75230 Paris Cedex 05, France

Synthesis and Structure of the First Tungsten Complex Having the $W_2S_4^{2+}$ Core: $[P(C_6H_5)_4]_2W_4S_{12}$

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Acidification of tetrathiotungstate $(WS_4)^{2-}$ produces doubly bridged polynuclear complexes. The first complex $[(W_2S_4)(WS_4)_2]^{2-}$ having the central $W_2S_4^{2+}$ core is generated from acidification of $(WS_4)^{2-}$ in anhydrous medium by acetic acid. The structure of the syn isomer has been determined by X-ray crystallography. The syn isomer crystallizes in space group $P\bar{1}$, with $a = 19.278$ (6) Å, $b = 21.244$ (2) Å, $c = 14.929$ (6) Å, $\alpha = 89.43$ (6)°, $\beta = 89.73$ (6)°, $\delta = 78.23$ (1)°, and $Z = 2$. Least-squares refinement of the structure led to a value of the conventional R index (on F) of 0.067 for the 3518 reflections. In the central $W_2S_4^{2+}$ core, each tungsten has a tetragonal sulfur environment. The apex of each pyramid is occupied by a sulfido group. The equatorial plane is formed by sulfido bridging groups and by sulfur atoms of the $(WS_4)^{2-}$ ligands. The geometries of the $W_2S_4^{2+}$ or $Mo_2S_4^{2+}$ cores are very similar. Strong W–W interactions exist, resulting in a 2.911 (16) Å short distance. Moreover, the complex is diamagnetic. The tetranuclear species is a mixed W(V)–W(VI) valence compound.

Introduction

In the development of structural and biological redox models, interest has grown in sulfur-containing compounds or molybdenum.[2a] Emphasis has been placed on binuclear di-μ-sulfido-bridged Mo(V) species, especially on complexes having the $Mo_2S_4^{2+}$ core. As recently pointed out,[2b] the thiomolybdate series $(MoO_xS_{4-x})^{2-}$ has been useful in synthesis; however, such complexes were still unknown in the thiotungstate series $(WO_xS_{4-x})^{2-}$. By use of the appropriate medium, the reactions involving tungsten were generally slow enough (in contrast to those of molybdenum) to control the generation of many new complexes. This present work is concerned with one of these new thio compounds having the $M_2S_4^{2+}$ core in the syn conformation.

Experimental Section

Synthesis of $[N(CH_3)_4]_2WS_4$. An excess of hydrogen sulfide was bubbled into an aqueous solution (250 mL) of Na_2WO_4 (25 mmol) up to pH 5.5, yielding a mixture of 80% $(WOS_3)^{2-}$ and 20% $(WS_4)^{2-}$. In this pH range, $(WS_4)^{2-}$ is the stable species, but the kinetics conversion from $(WOS_3)^{2-}$ is slow. Thus the solution was kept at 60 °C under H_2S-saturated atmosphere for about 4 days, leading to the complete interconversion of $(WOS_3)^{2-}$ into $(WS_4)^{2-}$. A solution of tetramethylammonium chloride (2/1 Me/W) was added and the mixture stirred. The solution was cooled to 0 °C for about 2 h. Orange needles were isolated, washed with ethanol, and dried with diethyl ether.

Synthesis of $[P(C_6H_5)_4]_2WS_4$. The tetraphenylphosphonium salt was prepared by cation exchange from a solution of tetramethylammonium tetrathiotungstate. A solution of $P(C_6H_5)_4Cl$ (2 mmol) in ethanol (10 mL) was added with stirring in an aqueous solution of $[N(CH_3)_4]_2WS_4$, resulting in the precipitation of the orange $WS_4[P(C_6H_5)_4]_2$. The mixture was filtered off, washed with ethanol and ether, and vacuum-dried.

Synthesis of $[P(C_6H_5)_4]_2W_4S_{12}$. The tungsten(VI) tetrathiotungstate $[P(C_6H_5)_4]_2WS_4$ was reacted with an excess of acetic acid in dichloromethane. The acidification by acetic acid was dependent on tungsten and acid concentrations.

Dilute Tungsten Medium. A 0.35-mol quantity of acetic acid was added with stirring to a solution of 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ in 100 mL of dichloromethane. An orange to red color change was observed immediately upon addition of acid. At the same time, the $(WS_4)^{2-}$ spectrum changed to a new characteristic spectrum. A steady absorbance was reached within 2 h. After about 4 h a red crystalline product was isolated. Powder-diffraction photographs, indexed by the use of cell parameters determined from a monocrystal study, proved that the red crystalline powder contained only one species. The crystal formula determined from chemical analysis data[3] was $[(WS_3)_2P(C_6H_5)_4]_n$. Anal. Calcd for $[P(C_6H_5)_4(WS_3)_2]_n$: W, 40.9; S, 21.35; C, 32.03. Found: W, 40.8; S, 20.90; C, 32.10. The n value was determined by ultracentrifuge methods ($n = 2$) and was confirmed by X-ray data. The filtrate did not contain any other species, since the crystal electronic spectra (in DMF solution) (Figure 1) were identical with the spectra of the filtrate and of the mother solution.

Keeping a dilute tungsten medium, we then added variable amounts of acid to 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ in 100 mL of dichloromethane. With the addition of more than 0.35 mol of acid, only $(W_4S_{12})^{2-}$ was present in solution as revealed by absorbance recording in the 500–200-nm range. With lower acid concentration $(WS_4)^{2-}$ was present in solution with the tetranuclear complex.

Concentrated Tungsten Medium. In concentrated tungsten medium, the formation of another compound was observed. In high acidic medium, 0.35 mol of acetic acid was added to a solution of 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ in 10 mL of dichloromethane, producing a red precipitate. The solid was washed with ethanol and dried with diethyl ether. The solid was identified as $[P(C_6H_5)_4]_2W_3S_9$ by the chemical analysis (Anal. Calcd: W, 36.8; S, 19.2; C, 38.4. Found: W, 36.10; S, 18.7; C, 37.7.), electronic spectrum, and IR absorption. These results were confirmed by indexing powder-diffraction photographs using the $[P(C_6H_5)_4]_2W_3S_9$ cell parameters previously reported.[4] In the filtrate, a transient species was observed owing to its characteristic

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