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Binuclear Diiridium and Mixed-Metal Rhodium–Iridium Complexes Containing Terminal η^2-Alkynes: The Structure of $[Ir_2(CO)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-}S)(\mu\text{-}CO)(Ph_2PCH_2PPh_2)_2]\cdot CH_2Cl_2$

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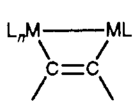
The reaction of the A-frame complex $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (DPM = $Ph_2PCH_2PPh_2$) with dimethyl acetylenedicarboxylate (DMA) or hexafluoro-2-butyne (HFB) yields complexes in which the alkyne is terminally bound to a single metal center adjacent to the sulfide bridge atom. The reaction is reversible, with stronger binding of HFB compared to DMA, and occurs with concomitant movement of one carbonyl group to the bridging site adjacent to the alkyne. An X-ray structure has been determined for the HFB complex, confirming the geometry described. The complex $[Ir_2(CO)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2]\cdot CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 20.614$ (7) Å, $b = 15.348$ (3) Å, $c = 19.890$ (5) Å, $\beta = 117.84$ (2)°, $V = 5565.0$ Å^3, and $Z = 4$. On the basis of 6806 unique observed reflections and 412 parameters varied the structure has converged at $R = 0.045$ and $R_w = 0.063$. Analogous reactions of DMA and HFB with the mixed-metal A-frame complex $[RhIr(CO)_2(\mu\text{-}S)(DPM)_2]$ give similar results as determined spectroscopically, but the alkyne is bound to the iridium center only, and bonding of the alkynes is weaker than in the corresponding diiridium complexes.

Introduction

The coordination of unsaturated organic substrates to transition-metal complexes is an important step in substrate activation during catalytic reactions. For mononuclear complexes the binding of simple substrates, such as olefins and alkynes, is well understood and can be readily rationalized based on the Dewar–Chatt–Duncanson model.[1] However, for complexes which involve more than one metal center, additional complexity is introduced owing to the presence of adjacent metals and the possibility of bridging modes involving the substrate molecules. The bridging mode is dominant for alkyne groups in binuclear complexes, with two geometries being commonly observed, in which the alkyne lies either parallel to or perpendicular to the metal–metal axis[2] (structures I and II, respectively).



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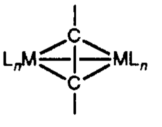
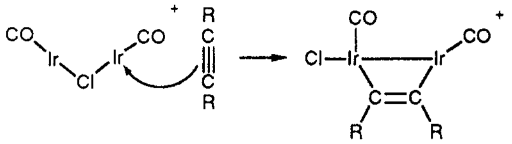


II

Interconversion of these two bonding modes has also been observed.[3] A molecular orbital analysis of both bonding types has been presented by Hoffmann and co-workers[2] in an attempt to rationalize the geometries observed in the large number of complexes which have been structurally characterized.

In DPM-bridged homo- and heterobinuclear complexes of rhodium and iridium, the parallel binding mode (I) is observed almost exclusively,[4–13] although a few examples involving the perpendicular mode (II) have recently been characterized.[14,15]

One alkyne coordination mode that apparently has not yet been identified in binuclear DPM-bridged complexes is that in which the alkyne is bonded to only one metal center in an η^2-fashion. This would be analogous to the many well-known examples of mononuclear alkyne complexes. Binuclear species containing terminally bound alkynes have been proposed as labile intermediates to explain the products observed in reactions such as that shown, in which $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ is reacted with alkynes;[4] attack in the A-frame "pocket" between the metals would be expected to yield the isomer having the bridging alkyne and the carbonyls mutually cis.



With this chloro-bridged A-frame, rearrangement is apparently extremely facile since no evidence of an intermediate containing a terminal η^2-alkyne was ever observed.

In an attempt to isolate a complex analogous to the proposed η^2-intermediate, we turned to the related complex $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ on the assumption that rearrangement to give an alkyne-bridged product should be much less facile owing to the reluctance of the sulfido group to move to a terminal site. Such a difference between chloro- and sulfido-bridged A-frames had been observed previously.[16] In the related complex $[Ir_2(CO)_2(\eta^2\text{-}C_4F_6)(P(O\text{-}t\text{-}Bu)_3)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2]$, the terminal η^2-alkyne group was found to slowly rearrange to the bridging geometry.[17]

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Table I. Spectroscopic Data for the Compounds[a]

compound	infrared, cm^{-1}		NMR[b]		
	solid[c]	soln[d]	$^{31}P\{^1H\}$ δ[e]	^1H δ	^{19}F[f] δ
$[Ir_2(CO)(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(DPM)_2]$ (**2**)	1943 (vs), 1780 (vs),[g] 1744 (st)[h]	1945 (vs), 1771 (st),[g] 1747 (med)[h]	−9.45 (m), −10.91 (m)	6.9–7.8 (m, 40 H), 4.71 (m, 2 H), 4.56 (m, 2 H)	−52.56 (q), −52.74 (q)[i] ($^5J_{F-F}$ = 4.5 Hz)
$[Ir_2(CO)(\eta^2\text{-DMA})(\mu\text{-S})(\mu\text{-CO})(DPM)_2]$ (**3**)	1933 (vs), 1770 (vs),[g] 1753 (st),[h] 1679 (st)[j]	1939 (vs), 1775 (st),[g] 1680 (med)[j]	−8.63 (m), −10.06 (m)	6.6–8.0 (m, 40 H), 4.21 (m, 2 H), 3.80 (m, 2 H)	
$[RhIr(CO)(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(DPM)_2]$ (**5**)		1959 (vs), 1814 (med),[g] 1753 (med)[h]	15.98 (dm),[k] −10.39 (m)	6.8–8.1 (m, 40 H), 5.12 (m, 2 H), 2.64 (m, 2 H)	−52.04 (q) −53.74 (br) ($^5J_{F-F}$ = 5.0 Hz)

[a] Abbreviations used: st, strong; vs, very strong; med, medium; m, multiplet; dm, doublet of multiplets; q, quartet; br, broad. [b] In CD_2Cl_2. [c] Nujol mull. [d] CH_2Cl_2 solution. [e] Versus 85% H_3PO_4. [f] Versus $CFCl_3$. [g] $\nu(CO)$. [h] $\nu(C{\equiv}C)$ of coordinated alkyne. [i] −20 °C. [j] $\nu(C{=}O)$ of CO_2Me. [k] $^1J_{Rh-P}$ = 137.7 Hz.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. Reactions were carried out under standard Schlenk conditions using dinitrogen which had been passed through columns containing Ridox and 4A molecular sieves in order to remove traces of oxygen and water, respectively. The compounds $[Ir_2(CO)_2(\mu\text{-S})(DPM)_2]$[18] and $[RhIr(CO)_2(\mu\text{-S})(DPM)_2]$[16b] were prepared according to the reported procedures. Hexafluoro-2-butyne (HFB) was purchased from PCR Incorporated and dimethyl acetylenedicarboxylate (DMA) was obtained from Aldrich Chemical Co. The $^{31}P\{^1H\}$, ^1H, and ^{19}F NMR spectra were recorded on a Bruker WH-400 spectrometer. Infrared spectra were recorded on a Nicolet 7199 Fourier transform IR spectrometer either as solids in Nujol mulls on KBr plates or as solutions in KCl cells with 0.5-mm window path lengths. Elemental analyses were performed by the microanalytical service within the department.

Preparation of Compounds. (a) $[Ir_2(CO)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-S})(\mu\text{-CO})(DPM)_2]$ (2). A 50.0-mg sample (0.040 mmol) of $[Ir_2(CO)_2(\mu\text{-S})(DPM)_2]$ (**1**) was dissolved in 5 mL of CH_2Cl_2 under dinitrogen. Excess hexafluoro-2-butyne (HFB) was then bubbled through the solution, causing the deep purple solution to become yellow within 1 min. The solution was left under HFB for 10 min and then was concentrated to approximately 2 mL with a rapid flow of dinitrogen. The product was precipitated by the addition of 10 mL of diethyl ether, the solvent removed, and the solid dried with a rapid flow of dinitrogen. Compound **2** was isolated as an orange microcrystalline solid in 75% yield. Spectroscopic data for this and subsequent compounds are given in Table I. Anal. Calcd for $Ir_2SP_4F_6O_2C_{56}H_{44}$: C, 47.93; H, 3.16. Found: C, 47.08; H, 2.98.

(b) $[Ir_2(CO)(\eta^2\text{-}H_3CO_2CC{\equiv}CCO_2CH_3)(\mu\text{-S})(\mu\text{-CO})(DPM)_2]$ (3). A 50.0-mg sample (0.040 mmol) of $[Ir_2(CO)_2(\mu\text{-S})(DPM)_2]$ (**1**) was dissolved in 4 mL of CH_2Cl_2 under dinitrogen. To this solution was added excess dimethyl acetylenedicarboxylate (DMA) (10 μL, approximately 2 equiv) which caused an immediate color change to orange. The compound was precipitated by the addition of 10 mL of hexanes, yielding an orange-yellow powder, which was washed with two 5-mL portions of diethyl ether and dried with dinitrogen flow. Isolated yield: 85%. Anal. Calcd for $Ir_2SP_4O_6C_{58}H_{50}$: C, 50.36; H, 3.64. Found: C, 49.52; H, 3.64.

(c) $[RhIr(CO)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-S})(\mu\text{-CO})(DPM)_2]$ (5). A 10.0-mg sample of $[RhIr(CO)_2(\mu\text{-S})(DPM)_2]$ (**4**) was dissolved in 1 mL of CH_2Cl_2 under dinitrogen. Hexafluoro-2-butyne (HFB) was bubbled through the solution, causing an immediate color change from dark red to orange-yellow. In the absence of an HFB atmosphere the solution regained a dark red color and infrared spectroscopy revealed only starting material. Compound **5** was characterized in solution (see Table I) by saturating the solution with HFB and keeping it under an atmosphere of HFB.

Table II. Summary of Crystal Data and Details of Intensity Collection

compd	$[Ir_2(CO)(\eta^2\text{-}C_4F_6)(\mu\text{-S})(\mu\text{-CO})(DPM)_2]\cdot CH_2Cl_2$
formula	$Ir_2Cl_2SP_4F_6O_2C_{57}H_{46}$
fw	1488.26
cryst shape	monoclinic prism
cryst size, mm	0.63 × 0.45 × 0.29
space group	$P2_1/c$ (No. 14)
cell parameters	
a, Å	20.614 (7)
b, Å	15.348 (3)
c, Å	19.890 (5)
β, deg	117.84 (2)
V, Å^3	5565.0
Z	4
ρ(calcd), g/cm^3	1.776
temp, °C	22
radiatn (λ, Å)	graphite-monchromated Mo Kα (0.71069)
receiving aperture, mm	3.00 + (tan θ) wide × 4.00 high, 173 from crystal
takeoff angle, deg	3.00
scan speed, deg/min	variable between 6.67 and 1.54
scan width, deg	0.80 + (0.347 tan θ) in θ
no. of unique data collcd	9821 (h, k, $\pm l$)
no. of unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	6806
linear absorption coeff, μ, cm^{-1}	50.66
2θ limits, deg	$1.0 \leq 2\theta \leq 50.0$
range of transmissn factors	0.723–1.169
final no. of parameters refined	412
error in observn of unit wt	2.027
R[a]	0.045
R_w[b]	0.063

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

X-ray Data Collection. Crystals of $[Ir_2(CO)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-S})(\mu\text{-CO})(DPM)_2]\cdot CH_2Cl_2$ (**2**) were obtained by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution of the complex. A suitable crystal was wedged into a capillary tube which was flame sealed as a precaution against loss of solvent of crystallization. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections, in the range 22.2° ≤ 2θ ≤ 25.8°, which were centered in both positive and negative θ on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Automatic peak search and reflection indexing programs established a monoclinic crystal system. The systematic absences ($h0l$, l = odd; $0k0$, k = odd) were consistent with the space group $P2_1/c$.

Intensity data were collected on the CAD4 diffractometer and processed in the usual manner as described previously.[19] There was no appreciable decrease in the intensities of the three standard reflections, so no correction was applied to the data. Corrections for absorption, using the method of Walker and Stuart,[20] were applied to the data. See Table II for crystal data and details of intensity collection.

Structure Solution and Refinement. The crystal structure was solved in the space group $P2_1/c$ using Patterson techniques to locate the metal atoms and by successive least-squares and difference Fourier calculations to obtain the other atom positions. The electron density in the vicinity of the solvent atoms appeared somewhat smeared out, suggesting either significant vibration or

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Table III. Positional Parameters and Isotropic Thermal Parameters[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Ir(1)	0.27694 (2)	0.06539 (2)	0.27614 (2)	2.547 (8)	C(26)	0.1641 (6)	0.2548 (8)	0.0532 (6)	5.0 (3)*
Ir(2)	0.25690 (2)	−0.07577 (2)	0.17183 (2)	2.689 (8)	C(31)	0.3248 (5)	−0.0254 (6)	0.0466 (5)	3.1 (2)*
Cl(1)[b]	0.1947 (4)	0.5243 (6)	0.0840 (5)	8.4 (2)*	C(32)	0.3429 (6)	−0.1124 (8)	0.0544 (6)	4.7 (3)*
Cl(2)[b]	0.0952 (7)	0.476 (1)	0.1315 (7)	14.2 (4)*	C(33)	0.3890 (7)	−0.1453 (9)	0.0259 (7)	6.1 (3)*
S	0.3712 (1)	−0.0101 (2)	0.2554 (1)	3.11 (6)	C(34)	0.4168 (7)	−0.0891 (9)	−0.0076 (7)	5.9 (3)*
P(1)	0.2669 (1)	0.1666 (2)	0.1832 (1)	2.97 (6)	C(35)	0.4008 (7)	−0.0071 (9)	−0.0154 (7)	6.0 (3)*
P(2)	0.2623 (1)	0.0143 (2)	0.0809 (1)	2.76 (6)	C(36)	0.3549 (6)	0.0289 (8)	0.0131 (6)	4.4 (2)*
P(3)	0.2878 (1)	−0.0362 (2)	0.3693 (1)	2.92 (6)	C(41)	0.1746 (5)	0.0332 (6)	−0.0055 (5)	3.0 (2)*
P(4)	0.2910 (1)	−0.1805 (2)	0.2657 (2)	3.32 (6)	C(42)	0.1104 (6)	0.0211 (8)	−0.0019 (6)	4.7 (3)*
F(1)	0.3944 (5)	0.2884 (5)	0.4120 (5)	9.2 (3)	C(43)	0.0434 (7)	0.0386 (9)	−0.0665 (7)	6.0 (3)*
F(2)	0.4552 (5)	0.1837 (7)	0.4147 (6)	12.2 (4)	C(44)	0.0408 (6)	0.0644 (7)	−0.1318 (6)	4.5 (2)*
F(3)	0.4080 (7)	0.1904 (7)	0.4865 (5)	19.1 (4)	C(45)	0.1035 (6)	0.0763 (7)	−0.1371 (6)	4.4 (2)*
F(4)	0.2392 (6)	0.2500 (7)	0.4212 (5)	16.6 (4)	C(46)	0.1713 (5)	0.0611 (7)	−0.0736 (5)	3.6 (2)*
F(5)	0.1909 (5)	0.2897 (6)	0.3096(5)	13.2 (3)	C(51)	0.3444 (5)	−0.0051 (6)	0.4680 (5)	2.9 (2)*
F(6)	0.1529 (5)	0.1866 (7)	0.3451 (6)	18.6 (3)	C(52)	0.3139 (6)	0.0435 (7)	0.5038 (6)	4.0 (2)*
O(1)	0.1239 (3)	−0.0063 (5)	0.1765 (3)	3.8 (2)	C(53)	0.3584 (6))	0.0733 (8)	0.5811 (7)	5.2 (3)*
O(2)	0.1473 (5)	−0.1960 (6)	0.0537 (4)	6.8 (3)	C(54)	0.4301 (6)	0.0527 (8)	0.6168 (6)	4.7 (3)*
C(1)	0.1864 (5)	−0.0006 (7)	0.2013 (5)	3.3 (2)	C(55)	0.4616 (7)	0.0021 (9)	0.5811 (7)	5.7 (3)*
C(2)	0.1869 (5)	−0.1483 (7)	0.0993 (5)	4.1 (3)	C(56)	0.4168 (6)	−0.0269 (8)	0.5050 (6)	4.7 (3)*
C(3)	0.3944 (8)	0.2029 (8)	0.4190 (7)	6.4 (4)	C(61)	0.2045 (5)	−0.0728 (7)	0.3716 (6)	3.6 (2)*
C(4)	0.3286 (6)	0.1600 (6)	0.3624 (5)	3.8 (3)	C(62)	0.2047 (6)	−0.1473 (8)	0.4104 (6)	5.2 (3)*
C(5)	0.2588 (6)	0.1634 (7)	0.3365 (5)	4.3 (3)	C(63)	0.1404 (7)	−0.172 (1)	0.4123 (7)	6.8 (4)*
C(6)	0.2084 (7)	0.2198 (9)	0.3505 (7)	7.5 (4)	C(64)	0.0792 (7)	−0.122 (1)	0.3788 (7)	6.4 (3)*
C(7)	0.2982 (5)	0.1246 (6)	0.1173 (5)	2.9 (2))	C(65)	0.0779 (8)	−0.047 (1)	0.3429 (8)	6.8 (4)*
C(8)	0.3326 (5)	−0.1337 (7)	0.3619 (5)	3.7 (3)	C(66)	0.1434 (6)	−0.0215 (8)	0.3390 (6)	4.6 (2)*
C(9)[b]	0.157 (2)	0.562 (2)	0.095 (2)	11 (1)*	C(71)	0.2194 (5)	−0.2518 (7)	0.2647 (6)	4.0 (2)*
C(11)	0.3219 (5)	0.2632 (7)	0.2191 (5)	3.6 (2)*	C(72)	0.2401 (7)	−0.3272 (9)	0.3086 (7)	6.1 (3)*
C(12)	0.2931 (6)	0.3410 (8)	0.2257 (6)	4.9 (3)*	C(73)	0.1842 (8)	−0.376 (1)	0.3139 (8)	7.7 (4)*
C(13)	0.3415 (7)	0.414 (1)	0.2585 (8)	6.6 (3)*	C(74)	0.1125 (7)	−0.352 (1)	0.2754 (8)	7.1 (4)*
C(14)	0.4142 (7)	0.403 (1)	0.2862 (8)	6.5 (3)*	C(75)	0.0920 (7)	−0.280 (1)	0.2316 (7)	6.5 (3)*
C(15)	0.4455 (7)	0.3277 (9)	0.2818 (7)	5.8 (3)*	C(76)	0.1464 (6)	−0.2292 (8)	0.2258 (6)	4.6 (3)*
C(16)	0.3972 (6)	0.2538 (8)	0.2471 (6)	5.0 (3)*	C(81)	0.3574 (5)	−0.2567 (7)	0.2664 (6)	4.0 (2)*
C(21)	0.1746 (5)	0.2091 (7)	0.1180 (5)	3.7 (2)*	C(82)	0.4279 (6)	−0.2656 (9)	0.3280 (7)	5.6 (3)*
C(22)	0.1167 (6)	0.1900 (8)	0.1324 (6)	4.6 (3)*	C(83)	0.4773 (8)	−0.327 (1)	0.3214 (8)	7.1 (4)*
C(23)	0.0471 (7)	0.218 (1)	0.0798 (1)	6.4 (3)*	C(84)	0.4571 (7)	−0.373 (1)	0.2571 (8)	7.0 (4)*
C(24)	0.0354 (7)	0.261 (1)	0.0145 (8)	6.9 (4)*	C(85)	0.3904 (8)	−0.361 (1)	0.1954 (8)	7.7 (4)*
C(25)	0.0939 (7)	0.283 (1)	0.0029 (7)	6.7 (3)*	C(86)	0.3389 (7)	−0.302 (1)	0.1995 (7)	6.5 (3)*

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. [b] Atoms Cl(1), Cl(2), and C(9) are those of the CH_2Cl_2 solvent molecule.

slight disorder in this group, and consequently the thermal parameters are quite large. All hydrogen atoms were located but were assigned idealized positions on the basis of the geometry of their attached carbon atom and by using C–H distances of 0.95 Å; thermal parameters were fixed at 1.2 times that of the attached carbon atom. The hydrogen atoms were included as fixed contributions in the least-squares calculations and were not refined.

Refinement was carried out by using full-matrix least-squares techniques,[21] minimizing the function $\sum w(|F_o| - |F_c|)^2$, with $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral atom scattering factors[22,23] and anomalous dispersion terms[24] used in the structure determination programs were obtained from the usual sources. Although a few low-angle reflections (particularly 102 and 011) appeared to suffer from extinction effects, most other intense low-angle reflections were unaffected. Attempts to refine the secondary extinction parameter also did not help the few relevant reflections, so no correction was applied.

The positional and isotropic thermal parameters for the final model are given in Table III. In the final difference Fourier map, the 10 highest residual peaks were in the range 2.63–0.71 e/Å^3 and were located mainly in the vicinities of the CH_2Cl_2 solvent atoms. Refinement converged at R = 0.045 and R_w = 0.063.

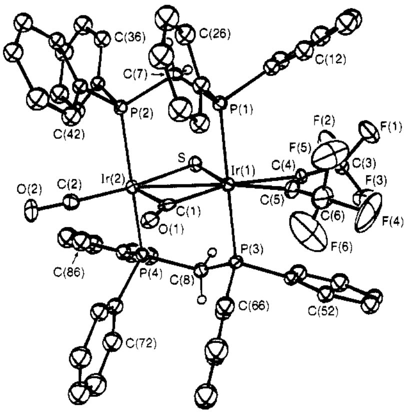

Figure 1. A perspective view of [$Ir_2(CO)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2$] showing the numbering scheme. Thermal ellipsoids are shown at the 20% level except for the methylene hydrogens, which are shown artificially small, and the phenyl hydrogens, which are omitted.

Results and Discussion

(a) Description of Structure. The complex [$Ir_2(CO)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2$] (**2**) crystallizes in the space group $P2_1/c$ with one complex molecule and one CH_2Cl_2 solvent molecule in the asymmetric unit. The solvent molecule displays the expected geometry and is not involved in any unusual contacts with the complex. A perspective view of the complex including the numbering scheme is shown in Figure 1. Selected bond distances and

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(21) All computing was carried out on a Digital PDP11/23 PLUS computer using the programs of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to some local programs by R. G. Ball.

(22) Cromer, D. T.; Waber, J. F. *International Tables for X-Ray Crystallography*; Kynock: Birmingham, England, 1974; Vol. IV, Table 2.2A.

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

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Table IV. Selected Distances (Å) in $[Ir_2(CO)(\eta^2\text{-}HFB)(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2]$

Ir(1)–Ir(2)	2.8929 (4)	P(3)–C(8)	1.799 (8)
Ir(1)–S	2.457 (2)	P(4)–C(8)	1.839 (8)
Ir(1)–P(1)	2.350 (2)	F(1)–C(3)	1.33 (1)
Ir(1)–P(3)	2.351 (2)	F(2)–C(3)	1.33 (1)
Ir(1)–C(1)	2.032 (8)	F(3)–C(3)	1.26 (1)
Ir(1)–C(4)	2.117 (7)	F(4)–C(6)	1.33 (1)
Ir(1)–C(5)	2.065 (8)	F(5)–C(6)	1.29 (1)
Ir(2)–S	2.381 (2)	F(6)–C(6)	1.21 (1)
Ir(2)–P(2)	2.320 (2)	O(1)–C(1)	1.148 (8)
Ir(2)–P(4)	2.311 (2)	3(2)–C(2)	1.155 (9)
Ir(2)–C(1)	2.141 (8)	C(3)–C(4)	1.45 (1)
Ir(2)–C(2)	1.860 (8)	C(4)–C(5)	1.28 (1)
P(1)–C(7)	1.827 (7)	C(5)–C(6)	1.47 (1)
P(2)–C(7)	1.854 (7)		

Table V. Selected Angles (deg) in $[Ir_2(CO)(\eta^2\text{-}HFB)(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2]$

Ir(2)–Ir(1)–S	52.09 (4)	P(2)–Ir(2)–C(2)	93.2 (3)
Ir(2)–Ir(1)–P(1)	90.01 (5)	P(4)–Ir(2)–C(1)	98.2 (2)
Ir(2)–Ir(1)–P(3)	89.85 (5)	P(4)–Ir(2)–C(2)	92.5 (3)
Ir(2)–Ir(1)–C(1)	47.7 (2)	C(1)–Ir(2)–C(2)	98.9 (3)
Ir(2)–Ir(1)–C(4)	160.8 (3)	Ir(1)–S–Ir(2)	73.43 (5)
Ir(2)–Ir(1)–C(5)	163.5 (3)	Ir(1)–P(1)–C(7)	113.6 (2)
S–Ir(1)–P(1)	88.03 (7)	Ir(2)–P(2)–C(7)	113.3 (2)
S–Ir(1)–P(3)	91.57 (7)	Ir(1)–P(3)–C(8)	110.5 (3)
S–Ir(1)–C(1)	99.8 (2)	Ir(2)–P(4)–C(8)	112.8 (2)
S–Ir(1)–C(4)	108.8 (3)	Ir(1)–C(1)–Ir(2)	87.7 (3)
S–Ir(1)–C(5)	144.4 (3)	Ir(1)–C(1)–O(1)	144.6 (7)
P(1)–Ir(1)–P(3)	179.58 (7)	Ir(2)–C(1)–O(1)	127.6 (6)
P(1)–Ir(1)–C(1)	92.3 (2)	Ir(2)–C(2)–O(2)	175.2 (8)
P(1)–Ir(1)–C(4)	90.6 (2)	F(1)–C(3)–F(2)	99.5 (9)
P(1)–Ir(1)–C(5)	90.2 (2)	F(1)–C(3)–F(3)	105 (1)
P(3)–Ir(1)–C(1)	87.9 (2)	F(1)–C(3)–C(4)	114 (1)
P(3)–Ir(1)–C(4)	89.4 (2)	F(2)–C(3)–F(3)	107 (1)
P(3)–Ir(1)–C(5)	90.1 (2)	F(2)–C(3)–C(4)	114.7 (9)
C(1)–Ir(1)–C(4)	151.4 (3)	F(3)–C(3)–C(4)	116 (1)
C(1)–Ir(1)–C(5)	115.9 (3)	Ir(1)–C(4)–C(3)	150.7 (8)
C(4)–Ir(1)–C(5)	35.7 (3)	Ir(1)–C(4)–C(5)	70.0 (5)
Ir(1)–Ir(2)–S	54.48 (4)	C(3)–C(4)–C(5)	139.3 (9)
Ir(1)–Ir(2)–P(2)	94.01 (5)	Ir(1)–C(5)–C(4)	74.3 (5))
Ir(1)–Ir(2)–P(4)	93.08 (5)	Ir(1)–C(5)–C(6)	150.6 (9)
Ir(1)–Ir(2)–C(1)	44.6 (2)	C(4)–C(5)–C(6)	135 (1)
Ir(1)–Ir(2)–C(2)	143.5 (3)	F(4)–C(6)–F(5)	103 (1)
S–Ir(2)–P(2)	84.27 (6)	F(4)–C(6)–F(6)	102 (1)
S–Ir(2)–P(4)	84.36 (7)	F(4)–C(6)–C(5)	112 (1)
S–Ir(2)–C(1)	99.1 (2)	F(5)–C(6)–F(6)	109 (1)
S–Ir(2)–C(2)	162.0 (3)	F(5)–C(6)–C(5)	112.6 (9)
P(2)–Ir(2)–P(4)	159.60 (7)	F(6)–C(6)–C(5)	117 (1)
P(2)–Ir(2)–C(1)	100.2 (2)	P(1)–C(7)–P(2)	113.1 (3)
		P(3)–C(8)–P(4)	113.7 (4)

angles are given in Tables IV and V, respectively.

The complex molecule has the usual trans arrangement of DPM ligands and a doubly bridged A-frame geometry in which the metals are bridged by sulfur and by CO. One iridium center has a terminal CO, and the other has an η^2-bound hexafluoro-2-butyne (HFB) group. The overall geometry of the complex is very similar to that of $[Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2]$,[18] which is related to compound 2 by substitution of the alkyne by a terminal CO ligand. The DPM methylene groups are tilted toward the anionic bridging group as is most often the case in such A-frame complexes, minimizing interactions between the phenyl rings and atoms in the equatorial plane. The unsymmetrical structure results in somewhat different geometries at the metals.

The coordination at Ir(2) is very similar to both metal environments in $[Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2]$,[18] having a square-pyramidal geometry with the two phosphorus atoms, the sulfur bridge atom and C(2) at the base, and the bridging carbonyl group at the apex. Angles involving the pseudo trans-related basal groups (P(2)–Ir(2)–P(4) = 159.60 (7)°, S–Ir(2)–C(2) = 162.0 (3)°) are in better mutual agreement than are the corresponding angles in the tricarbonyl species (166.7 (1)°, 151.5 (4)°). The Ir–P distances at Ir(2) (2.320 (2), 2.311 (2) Å) are virtually identical with those of the tricarbonyl complex, and the Ir(2)–C(2) distance is only slightly longer than in the tricarbonyl species (1.860 (8) Å versus 1.80 (1) Å). The C–O distances in both of the carbonyl groups are normal.

At Ir(1) the coordination can be considered as either distorted trigonal-bipyramidal or octahedral, depending on whether one views the alkyne as occupying one or two coordination sites. The Ir(1)–P distances (2.350 (2), 2.351 (2) Å) are in excellent mutual agreement but are slightly longer than those at Ir(2), probably due to the increased steric requirements of the alkyne compared to the terminal carbonyl. The sulfido ligand bridges the two metals in an unsymmetrical fashion, with Ir(I)–S (2.457 (2) Å) being longer than Ir(2)–S (2.381 (2)Å). The opposite situation is evident at the bridging carbonyl, where the Ir(1)–C(1) distance (2.032 (8) Å) is shorter than Ir(2)–C(1) (2.141 (8) Å). The asymmetry in the parameters of the bridging groups is clearly the result of differences between the alkyne group on Ir(1) and the carbonyl on Ir(2). On the basis of the large size difference in these groups, it would appear that steric effects will be significant, particularly when it is noted that four phenyl rings (groups 2, 4, 6, and 7) are also thrust into the regions between the bridging carbonyl, the terminal carbonyl, and the alkyne. However the reasons for the asymmetry are not readily identified since the bridging carbonyl has van der Waals[25] interactions with ortho hydrogens on all four adjacent phenyl groups and these interactions are quite symmetrical (O(1)–H(22) = 2.53 Å, O(1)–H(42) = 2.50 Å, O(1)–H(66) = 2.63 Å, O(1)–H(76) = 2.62 Å). In any case it is noteworthy that the asymmetry occurs in a compensating fashion, with Ir(1) being bound more strongly to C(1) than is Ir(2), but being bound more weakly to the sulfur bridge. The Ir(1)–C(1)–Ir(2) angle (87.7(3)°) is not unusual for a bridging carbonyl associated with a metal–metal bond.[18,26] The Ir(1)–Ir(2) separation of 2.8929 (4) Å corresponds to a normal single bond and is comparable to other diiridium species which are metal–metal bonded.[4,18,26,27]

The coordinated alkyne moiety lies in the equatorial plane of the molecule, with the midpoint of the C≡C bond almost directly trans to the Ir—Ir bond. The Ir–C distances (2.117 (7), 2.065 (8) Å) are comparable to those found in diiridium complexes with bridging alkyne groups[4,12] and in a related triiridium complex, which contains both terminal and bridging HFB groups.[28] The C(4)–C(5) distance (1.28 (1) Å) is not unusual for terminal π-bound alkynes in mononuclear group VIII compounds[29-34] in which typical C–C distances range from 1.19 to 1.32 Å. The angles at which the CF_3 groups are bent back (139.3 (9)°, 135 (1)°) are somewhat acute, as typical bend-back angles are in the range 168–140°.[34] The slightly

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(25) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row, New York, 1983; pp 258–259 and references therein.

(26) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 2324.

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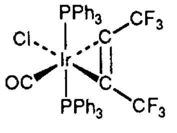
greater bending back of the CF_3 group containing C(6) appears to result from a stronger binding of this end of the alkyne, as indicated by the slightly shorter Ir(1)–C(5) distance given above. Stronger π-back-donation to C(5) would result in a shorter distance and a greater degree of rehybridization of C(5) toward sp^2. The stronger π-back-donation to C(5) than to C(4) is consistent with the former being opposite the good electron-donating sulfido group and C(4) being opposite the π-accepting carbonyl group (C(1)O(1)). Steric factors may also be important, since this bending relieves the shortest nonbonded contact between F(6) and H(66) (2.43 Å). The C—C distance in this terminal alkyne complex is notably shorter than those observed for bridging alkynes in related species such as $[Ir_2Cl_2(CO)_2(\mu\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(DPM)_2]$ (1.344 (8) Å)[4] and $[Rh_2Cl(CNMe)_2(\mu\text{-}F_3CC{\equiv}CCF_3)(DPM)_2]$ (1.32 (1) Å),[8] where distances and angles at the unsaturated carbons are very similar to normal alkenes. Accordingly, the $C{\equiv}C{-}CF_3$ angles in complex 2 are greater than corresponding angles found in these complexes (average 124.8°). The $C{-}CF_3$ distances (1.45 (1), 1.47 (1) Å) are in the range expected for such bonds adjacent to a carbon–carbon triple bond,[35] slightly shorter than those found in a dirhodium HFB-bridged complex.[8]

(b) Description of Chemistry. The addition of hexafluoro-2-butyne (HFB) to a solution of the A-frame complex $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (1) causes a color change from deep purple to yellow. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution displays two complex multiplets at δ −9.45 and −10.91, indicating an unsymmetrical species, 2, having two sets of chemically inequivalent phosphorus atoms. The infrared spectrum of the solution reveals new bands at 1945, 1771, and 1747 cm^{-1}. The absence of an acetylenic stretch in the region 1645–1490 cm^{-1}, expected for either the parallel or perpendicular bridging modes,[4] suggests a different bonding mode in this species which is confirmed by the structure determination (vide supra). The CO stretch at 1945 cm^{-1} is attributed to the terminal carbonyl in complex 2, while the stretches at 1771 and 1747 cm^{-1} are attributed to $\nu(CO)$ of the bridging carbonyl and $\nu(C{\equiv}C)$ of the coordinated alkyne, respectively. These bands are unambiguously assigned by preparation of the ^{13}CO-enriched product, in which the carbonyl stretches are shifted to 1898 cm^{-1} and approximately 1740 cm^{-1} (underneath the $C{\equiv}C$ stretch).

Compound 2 can be compared to the mononuclear HFB complex, diagrammed below, which is formed upon reaction of Vaska's compound, $[IrCl(CO)(PPh_3)_2]$, with HFB.[36]



The infrared spectrum of this mononuclear species exhibits a stretch at 1773 cm^{-1} for the coordinated alkyne which is significantly higher than that observed for compound 2. This is consistent with the sulfido ligand in compound 2 providing a more electron-rich metal, thereby being able to better reduce the C–C bond order through π-back-donation. (Note that carbonyl stretches in the IR spectrum of the precursor $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (1) were found to be rather low (1935, 1920 cm^{-1})[14] compared to the chloro-bridged analogue, also indicating electron-rich metal centers.) A $C{\equiv}C$ stretch at 1765 cm^{-1} was observed in a related binuclear iridium complex containing a terminal η^2-HFB group, $[Ir_2(CO)_2(\eta^2\text{-}C_4F_6)(P(O\text{-}t\text{-}Bu)_3)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2]$.[17] The relatively high value for $\nu(C{\equiv}C)$ in 2, compared to the same stretch in diiridium complexes containing HFB in a bridging position (range 1549–1573 cm^{-1}),[4] is an indication of the significant carbon–carbon triple-bond character remaining in the coordinated HFB group of 2. Accordingly, the bonding between the alkyne and the iridium center of 2 is somewhat weaker than in these cis-dimetallated olefin species, which are rather stable toward alkyne loss.[4] Compound 2 is stable in solution, even under N_2 purge, but loses HFB upon refluxing in CH_2Cl_2 to regenerate the dark purple color of $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (1).

The ^{19}F NMR spectrum of 2 displays an interesting temperature dependence. Although only one resonance (singlet, δ −52.62) is observed at 22 °C, lowering the temperature causes this resonance to split and resolve into two multiplets by 5 °C; at −20 °C they are well separated and appear as two partially resolved quartets (δ −52.56, −52.74 ($^5J_{F\text{-}F}$ = 4.5 Hz)). No broadening or collapse of the resonances is observed, arguing against a fluxional process which averages the environments of the fluorine atoms. It would appear, instead, that the chemical shift of each set of fluorine nuclei is temperature dependent, being accidentally coincident at 22 °C but moving away from each other at slightly different rates as the temperature is decreased. A similar effect has been observed in the $^{31}P\{^1H\}$ NMR spectra of $[Ir_2Cl(CO)_3(\mu\text{-}H_3CO_2CC{\equiv}CCO_2CH_3)(DPM)_2][BF_4]$.[4]

Compound 1 also reacts with excess dimethyl acetylenedicarboxylate (DMA), giving an immediate color change to orange-yellow. The spectral parameters (Table I) are very similar to those of the HFB adduct, suggesting the analogous formulation, $[Ir_2(CO)(\eta^2\text{-}DMA)(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2]$ (3). The acetylenic stretch for 3 is obscured by the carboxylate band of free DMA in solution but is clearly visible (at 1753 cm^{-1}) in the infrared spectrum of solid samples of 3. The $C{\equiv}C$ stretch for the HFB adduct drops by 553 cm^{-1} from that of the free alkyne,[37] whereas the drop observed for the DMA adduct is only 397 cm^{-1}, corresponding to less reduction in the $C{\equiv}C$ bond order in the latter, caused by less π-back-donation by the metal into the π^* orbital of the alkyne. This is not surprising on the basis of the greater electronegativity of the CF_3 group compared to CO_2Me[38] and is consistent with the ease of reversibility demonstrated by these complexes. As with complex 2, the formation of 3 is revesible, but in this case alkyne loss is much more facile. A solid sample of 3 that is redissolved in CH_2Cl_2 immediately gives a dark red solution signifying the presence of a large amount of compound 1. The solution IR spectrum confirms the presence of 1, along with free DMA, while a small amount of 3 remains. Likewise, reaction of 1 with only 1 equiv of DMA results in an equilibrium mixture of 1 and 3. These results are again consistent with less π-back-donation to the DMA group, thus giving weaker metal–alkyne bonding in 3 than in 2.

The products resulting from the reaction of $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (1) with HFB and DMA are somewhat surprising on the basis of the virtually exclusive observation of the bridging mode displayed by the products in all

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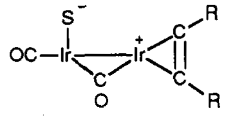
(35) MacGillavry, C. H., Rieck, G. D., Eds. *International Tables for X-ray Crystallography*; Kynock: Birmingham, England, 1968; Vol. III, Table 4.2.2.

(36) Parshall, G. W.; Jones, F. N. *J. Am. Chem. Soc.* **1965**, *87*, 5356.

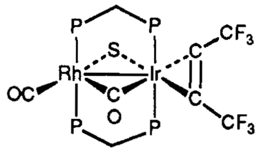
(37) The $C{\equiv}C$ stretch in free HFB is 2300 cm^{-1} and in DMA is 2150 cm^{-1}. See: Masklowsky, E. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 262 and references therein.

(38) Kosower, E. M. *An Introduction to Physical Organic Chemistry*; Wiley: New York, 1968; p 49.

previous reactions involving similar DPM-bridged binuclear complexes.[5-13] However, attack of the alkyne at an outside site of the A-frame (as in complexes **2** and **3**) has been proposed[4] in order to justify the observed products, without having to invoke ligand loss and subsequent recoordination. The rearrangement would then only require movement of the anionic bridge ligand to a terminal position and replacement by the coordinated alkyne. In the sulfido-bridged species, the reluctance of the dianionic sulfide group to move to a terminal site on one metal inhibits such rearrangement and allows the isolation of the presumed initial η^2-alkyne complex. The species isolated reveals that subsequent movement of the carbonyl ligand adjacent to the alkyne moiety to the bridging position has occurred, which is clearly advantageous sterically and furthermore provides both metals with stable 18-electron configurations. Attempts were made to induce rearrangement to the alkyne-bridged form by the addition of polar solvents to CH_2Cl_2 solutions of **2**. This would possibly stabilize a dipolar intermediate such as that shown which might then allow the alkyne to migrate to the bridge position. These attempts were unsuccessful, leading only to precipitation of the complex. In comparison, conversion of the terminal HFB group in $[Ir_2(CO)_2(\eta^2\text{-}C_4F_6)(P(O\text{-}t\text{-}Bu)_3)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2]$[17] to the bridged form, as was observed in that system, does not require cleavage of a metal–sulfur bond because the molecule is stereochemically nonrigid.



On the basis of the results of the reactions of the diiridium complex **1** with alkynes, an extension to the mixed-metal "RhIr" analogue was expected to give a similar result, except that metal-specific attack of the alkyne at iridium was anticipated due to its greater ability for π-back-bonding. Solutions of the A-frame complex $[RhIr(CO)_2(\mu\text{-}S)(DPM)_2]$ (**4**) react immediately with excess HFB; however, the resulting compound **5** persists in solution only when kept under atmosphere of HFB, rapidly reverting to compound **4** in its absence. The $^{31}P\{^1H\}$ NMR spectrum of an HFB-saturated solution of compound **5** is typical of DPM-bridged "RhIr" complexes, having a doublet of multiplets due to the rhodium-bound phosphorus atoms (δ 15.98 $^1J_{Rh-P}$ = 137.7 Hz) and a multiplet for the iridium-bound phosphorus atoms (δ −10.39). Notably, the chemical shift of the iridium-bound phosphorus atoms in **5** is significantly different from that of the precursor **4**, whereas the rhodium-bound phosphorus signal is only slightly changed. The infrared spectrum of a solution containing **5** displays carbonyl stretches at 1959 and 1814 cm^{-1}, and a C≡C stretch due to the coordinated alkyne at 1753 cm^{-1}. Again, the stretches are unambiguously assigned by preparation of the ^{13}CO-enriched species. The $^{13}C\{^1H\}$ NMR spectrum of **5** displays a doublet of triplets at δ 194.50 ($^1J_{Rh-C}$ = 71.7 Hz, $^2J_{P-C}$ = 15.1 Hz), which clearly results from a terminal CO on rhodium, and a partially resolved multiplet at δ 189.92 for the bridging carbonyl group.



5

The above information suggests a formulation for complex **5** which is quite analogous to the previously discussed diiridium species, having the coordinated alkyne on the iridium center and the terminal carbonyl on rhodium. The infrared stretch at 1959 cm^{-1} in **5** is somewhat higher than that in **2** in which the carbonyl is associated with the more basic iridium center. This structure is not surprising since coordination of the alkyne at iridium should be favored due to an expected stronger bonding through increased π-back-donation from the more basic metal. Consistent with the facile reversibility of this reaction compared to the diiridium analogue, the C≡C stretch for the coordinated HFB is several wavenumbers higher than that of compound **2**, again demonstrating less π-back-bonding to the alkyne. The difference in lability of the diiridium compound **2** and the mixed-metal complex **5** is somewhat surprising, given that the alkyne is bound to iridium in both cases, in what is apparently an identical local environment. Clearly, the replacement of the distal iridium by rhodium has a noticeable affect on the Ir–alkyne bonding, such that weaker binding of the alkyne arises from a less basic metal in this position.

The ^{19}F NMR spectrum of compound **5** exhibits one partially resolved quartet (δ −52.04 ($^5J_{F-F}$ = 5.0 Hz)) and an unresolved resonance (δ −53.74), integrating 1:1. Although the chemical shifts of the two inequivalent CF_3 groups are not coincident as in **2**, the shifts are similarly temperature dependent; however, in this case the resonances gradually move toward one another such that at −40 °C the resonances occur at δ −52.26 and −53.62.

The mixed-metal A-frame **4** also reacts with DMA, as evidenced by a color change to light orange in the vicinity of the reagent addition. Although a gradual change in the solution color occurs, after 10 molar equiv of DMA are added to an CH_2Cl_2 solution of **4**, the infrared spectrum only displays carbonyl stretches due to **4** and a strong band at 1725 cm^{-1} due to free DMA. A shoulder on the latter (1680 cm^{-1}) is likely due to the carboxylate of coordinated DMA. The $^{31}P\{^1H\}$ NMR spectrum under these conditions reveals a new species at δ 15.82 (Rh-bound phosphorus atoms) and −11.71 (Ir-bound phosphorus atoms), similar to the resonances found for **3**. On the basis of the infrared data, these resonances may represent an average environment for the phosphorus atoms in **4** and the η^2-DMA complex, but the two species have not been frozen out in the NMR as the spectrum does not change down to −80 °C. Clearly, the equilibrium established in this case strongly favors reactants. Compared to the stability of complex **5**, this result is not unexpected, given the trend already observed in going from HFB to DMA in complexes **2** and **3**.

Although the sulfido A-frames **1** and **4** demonstrate an affinity toward activated alkynes, neither reacts with activated olefins such as tetrafluoroethylene or dimethyl maleate nor do they react with unactivated alkyne or olefin substrates such as 2-butyne or ethylene.

Conclusions

The intermediacy of terminal π-bound alkyne species has previously been postulated in the reactions of binuclear DPM-bridged complexes with alkynes,[4,39] but until now their characterizations have not been possible due to facile rearrangement to rather stable species in which the alkyne group bridged the two metal centers. The complexes described herein clearly show that the alkyne in each case is coordinated on the outside of the complex, presumably at the initial site of attack. As such, these species function as models for the elusive intermediates which for other

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A-frames rearrange immediately to the alkyne-bridged species. These observations are consistent with the relative ease by which the monoanionic halide ligand can move to a terminal position relative to the dianionic sulfide group.

Comparison of the "Ir_2"–alkyne complexes to analogous "RhIr"–alkyne complexes suggests that the strength of the metal–alkyne bond is strongly influenced by the nature of the adjacent metal center. Such metal–metal cooperativity may be useful for "tailoring" the electronic environment at a metal center in order to enhance its catalytic activity. Oro and co-workers[40] have found, for example, that certain binuclear "RuRh" and "RuIr" complexes are more active than their mononuclear parent compounds in catalyzing the reduction of cyclohexene and that the "RuIr" complex is more active than the "RuRh" complex.

Although binuclear complexes that contain alkynes bound as cis-dimetalated olefins have been observed to give hydrogenated products upon reaction with H_2,[41] somewhat elevated temperatures appear necessary. In DPM-bridged complexes the bridging alkyne is quite stable and similar reactions have generally not been observed, whereas reaction of alkynes with hydride precursors is much more favorable.[41] This may be an indication that species containing terminal η^2-alkynes are more important in the hydrogenation of alkynes catalyzed by binuclear complexes. In that case, species of the type discussed herein may be useful since alkyne bridge formation is inhibited, and alkyne coordination is reversible, so that oxidative addition of H_2 can be more competitive, if such a route is favored.

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Supplementary Material Available: Tables of the anisotropic thermal parameters, distances and angles involving the phenyl and CH_2Cl_2 groups, and hydrogen atom parameters (4 pages); a listing of the observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

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Multiple Bonds between Main-Group Elements and Transition Metals. 67.[†] Synthesis of Novel Half-Sandwich Rhenium(V) Complexes of Mono- and Bidentate Sulfur-Containing Ligands: X-ray Crystal Structure of the Xanthate-*S*,*S* Complex (η^5-C_5Me_5)$ReCl_3$(S_2CO-c-C_6H_{11})

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The d^2 rhenium(V) complex (η^5-C_5Me_5)Re(O)Cl_2 (**1**) reacts with thiolates under ambient conditions to yield the *disubstituted* complexes **2** of composition (η^5-C_5Me_5)Re(O)(SR^1)$_2$ [R^1 = ethyl (**2a**), phenyl (**2c**), 2-pyridyl (**2d**)]. Bulkier ligands such as 2-methylpropane-2-thiolate give rise to formation of *monosubstituted complexes*, e.g., (η^5-C_5Me_5)Re(O)(Cl)(S-*t*-C_4H_9) (**3**) at room temperature, while disubstitution occurs in refluxing toluene with formation of compound **2b** (R^1 = *t*-C_4H_9). The reactions of (η^5-C_5Me_5)$ReCl_4$ (**4**) with sodium cyclohexylxanthate or with lithium *N*,*N*-diethyldithiocarbamate yield *monosubstituted* derivatives of formula (η^5-C_5Me_5)$ReCl_3$(S_2CR^2) (**5a**,**b**). A single-crystal X-ray diffraction study of the xanthate complex (η^5-C_5Me_5)$ReCl_3$(S_2CO-*c*-C_6H_{11}) (**5a**, R^2 = O-*c*-C_6H_{11}) shows an octahedral coordination sphere around the rhenium, with the sulfur atoms of the bidentate ligand being bonded to the metal atom in an equatorial and in an axial position.

Introduction

There has been continuing interest in the coordination chemistry of transition-metal complexes of sulfur-containing ligands because of the importance of such compounds in bioinorganic chemistry. In the case of rhenium, the interest stems partly from the use of the metastable isomer of its congener technetium (^{99m}Tc) in radiopharmaceuticals as well as from the properties of ^{186}Re and ^{188}Re, which isotopes may provide radiopharmaceuticals designed by analogy to existing Tc agents.[2,3] Although simple thiolato and sulfido rhenium complexes in high

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