

Concerted Motion of Carbon Monoxide and Bridging Chloride Ligands in the Heterotrinnuclear Complex $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})\{\mu\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{AsPh}\}_2][\text{BPh}_4]_2$

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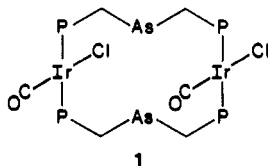
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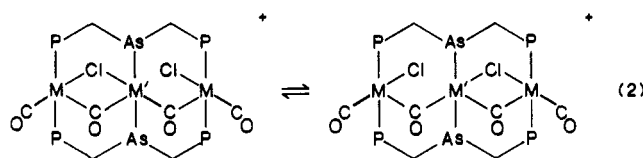
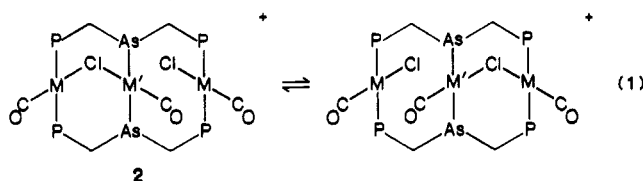
Treatment of $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}(\mu\text{-dpma})_2][\text{BPh}_4]$ (dpma is bis((diphenylphosphino)methyl)phenylarsine) with carbon monoxide in a dichloromethane/methanol mixture containing sodium tetraphenylborate yields red crystals of $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2][\text{BPh}_4]_2$. This complex crystallizes from dichloromethane/ethyl ether as a solvate with six dichloromethane molecules in the monoclinic space group $C2/c$ (No. 15) with $a = 34.896$ (4) Å, $b = 16.394$ (2) Å, $c = 23.029$ (3) Å, and $\beta = 116.12$ (2)° at 130 K. Least-squares refinement of 365 parameters using 6278 reflections yielded $R = 0.058$ and $R_w = 0.062$. The structure of the cation consists of a $\text{Ir}_2\text{Rh}(\mu\text{-dpma})_2$ core with trans bridging ligands. One Ir-Rh bond is bridged by a chloride and a carbonyl group in a double A-frame geometry, while the other is bridged by a carbonyl group. One iridium has one terminal carbonyl group while the other has two. The bridging chloride and one terminal carbonyl group are statistically disordered because the cations pack about a crystallographic C_2 axis. ^{31}P and ^{13}C NMR spectra of the cation in dichloromethane solution indicate that it undergoes a fluxional process that renders the two IrP_2 environments equivalent. A dynamic process is described which involves concerted, oscillatory motion of the bridging chloride and five carbonyl groups about the Ir_2Rh core in clockwise or counterclockwise directions.

Introduction

The rhodium and iridium metallamacrocycles **1** have central cavities that are capable of binding a third metal through a variety of interactions which may involve the two arsenic atoms, the two metal atoms, and the halide and carbonyl ligands.¹⁻⁷ Two types of complexes, **2** and



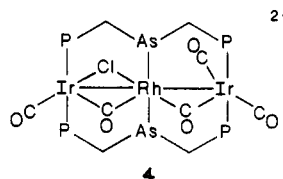
3, containing nearly linear Ir_3 , IrRhIr , RhIrRh , or Rh_3 chains have been prepared from **1**.⁴ Each type exhibits fluxional behavior that involves simple bridge/terminal halide exchange as shown in eq 1 and 2. These require



3a. M = Ir, M' = Rh
b. M = M' = Ir

relatively little movement of the ligands.^{8,9} These fluxional processes are very facile, and the exchange rates are rapid even at -80 °C. Thus no low-temperature-limiting spectra were obtained that corresponded to the solid-state structures of the complexes.

Here we describe the synthesis and structural characterization of a related complex, $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2]^{2+}$ (**4**; dpma is bis((diphenylphosphino)-



methyl)phenylarsine) which undergoes a related fluxional process at a slower rate so that low-temperature-limiting spectra are available, and an unambiguous assessment of the nature of the process can be made. Unlike the examples of eq 1 and 2, the halide ligand in **4** undergoes bridge/bridge rather than bridge/terminal conversion. This represents the first characterization of the dynamics of bridge/bridge halide exchange.

Results

Synthetic and Spectroscopic Studies. Treatment of a dichloromethane/methanol solution of $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}(\mu\text{-dpma})_2][\text{BPh}_4]$ (**3a**) and sodium tetraphenylborate with carbon monoxide results in the substitution of a carbon monoxide for the terminal chloride ligand to produce the dicationic complex $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2][\text{BPh}_4]_2$ (**4**). The complex is isolated as bright red crystals in 77% yield. The low-temperature-limiting ^{31}P NMR spectrum (recorded at -75 °C) consists of two singlets at -5.5 and -11.5 ppm, corresponding to the two inequivalent IrP_2 units seen in the solid state (vide infra). At 25 °C, the ^{31}P spectrum consists of a single broad resonance, indicating that a fluxional

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Table I. Spectroscopic Data

compound	³¹ P NMR ^a δ	¹³ C NMR ^a		IR ^b ν(CO), cm ⁻¹	UV-vis ^a λ _{max} , nm (ε, M ⁻¹ /cm ⁻¹)
		ppm	¹ J(Rh,C), Hz		
[Ir ₂ Rh(μ-CO) ₂ (CO) ₂ (μ-Cl)- Cl(μ-dpma) ₂][BPh ₄] ₂ (3)	0.7, ^c 0.1 ^d	200.1	41	1985, 1976, 1836, 1820, 1807, 1759, 1755, 1740	514 (7100), 402 (19000), 356 (16000)
[Ir ₂ Rh(μ-CO) ₂ (CO) ₃ (μ-Cl)- (μ-dpma) ₂][BPh ₄] ₂ (4)	-5.5, ^c -11.5	173.2	45	2040, 2029, 2026, 1973, 1826, 1809	520 (9200), 406 (16000), 356 (14000)
		209.1			
		195.0 174.4, 168.8, 164.5			
[Ir ₂ Rh(μ-CO) ₂ (CO) ₂ (μ-I)- I(μ-dpma) ₂][BPh ₄] ₂ (5)	-9.9, ^c -10.2 ^d			1979, 1965, 1797, 1748	524 (9300), 410 (17000), 378 (17000), 339 (15000)
[Ir ₂ Rh(μ-CO) ₂ (CO) ₂ ClI- (μ-dpma) ₂][BPh ₄] ₂ (6)	-2.5, ^c -2.7, ^d -4.4, -5.4			1966, 1811, 1800, 1745	490 (8300), 398 (19000), 364 (20000)
[Ir ₂ Rh(μ-CO) ₂ (CO) ₃ (μ-I)- (μ-dpma) ₂][BPh ₄] ₂ (7)	-5.3, ^d -12.5			2038, 1997, 1967, 1804, 1746 ^e	

^a Dichloromethane solution. ^b Nujol mulls. ^c Recorded at 25 °C. ^d Recorded at -75 °C. ^e For a mixture of 7, 6, and 5.

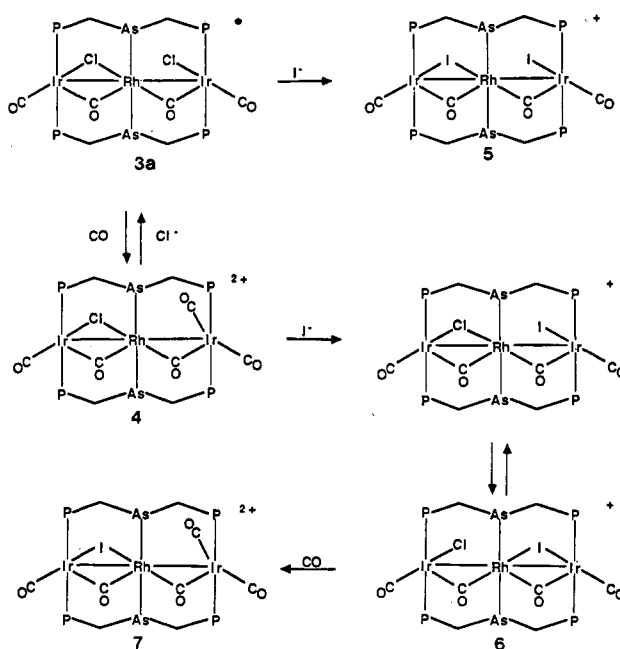
process is occurring which renders the environments of the two IrP₂ units equivalent. This process will be discussed in detail later. The carbon monoxide/chloride exchange reaction used to prepare 4 is easily reversible; thus 3a can be regenerated quantitatively from the reaction of 4 with 1 equiv of chloride ion (from [Ph₄As]Cl).

Because the replacement of chloride with iodide ligands affects the structure⁸ or exchange rate⁷ in other complexes, the synthesis of the iodide analogue of 4 was undertaken to determine if a similar rate decrease would occur with these complexes. The reaction of a dichloromethane solution of 3a with methanolic solutions of sodium iodide and sodium tetraphenylborate yields the corresponding diiodide complex [Ir₂Rh(μ-CO)₂(CO)₂(μ-I)I(μ-dpma)₂][BPh₄]₂ (5) as red crystals. Carbon monoxide was then bubbled through dichloromethane/methanol solution of 5 and sodium tetraphenylborate for 24 h, but no evidence of any carbon monoxide/iodide exchange was observed. The ³¹P NMR spectrum showed only the singlet corresponding to the diiodide complex 5 to be present. The iodide ligand is much less labile than the corresponding chloride toward carbon monoxide substitution.

An alternative route that first involves the synthesis of a mixed-halide analogue of 5 was devised. Treatment of 4 with 1 equiv of iodide ion (from [Ph₃MeAs]I) yields [Ir₂Rh(μ-CO)₂(CO)₂ClI(μ-dpma)₂][BPh₄]₂ (6). The reaction of this complex with sodium tetraphenylborate and carbon monoxide results in exchange of carbon monoxide with the remaining chloride to produce the desired [Ir₂Rh(μ-CO)₂(CO)₃(μ-I)(μ-dpma)₂][BPh₄]₂ (7) in approximately 70% yield as estimated from peak areas in the ³¹P NMR spectrum. Some unreacted 6 and the diiodide complex 5 were also present in the reaction mixture. The synthetic routes to complexes 4, 5, 6, and 7 are summarized in Chart I.

Spectroscopic data for the complexes are collected in Table I. The infrared data indicate that both of the dihalide complexes 5 and 6 have structures analogous to that reported for the dichloride complexes 3. Each complex exhibits three sets of carbonyl stretches. One group appears in the terminal carbonyl region (1965–1985 cm⁻¹), while the other two fall in the range for bridging carbonyl ligands (1797–1836 cm⁻¹ and 1740–1759 cm⁻¹, respectively). The dicationic complex 4 exhibits only two sets of carbonyl stretches, one in the terminal region and one in the bridging region. The four terminal stretching vibrations range from 1973 to 2040 cm⁻¹. The increase in the energy of these vibrations as compared to 3, 5, and 6 is probably

Chart I



due to the fact that three carbonyl groups are bound to one iridium atom, thus reducing the average amount of back-bonding from the iridium atom to each carbonyl ligand. Bridging carbonyl stretches in the 1740–1759 cm⁻¹ range are no longer present in 4, but two bridging stretches are observed at 1809 and 1826 cm⁻¹. The product isolated from the reaction of the mixed-halide complex 6 with carbon monoxide contains carbonyl stretches present in the dihalide complexes 3, 5, and 6 and in the monohalide complex 4. This is not surprising since the ³¹P spectrum showed the presence of unreacted 6 and the diiodide complex 5 along with the desired [Ir₂Rh(μ-CO)₂(CO)₃(μ-I)(μ-dpma)₂]²⁺ (7).

The ³¹P NMR spectrum of the diiodide complex 5 consists of a singlet at -9.9 ppm. This is comparable to the dichloride complex 3a, which has a single resonance at 0.7 ppm. The upfield shift of the resonance in the iodide complex, relative to the chloro complex, is also observed in other related pairs of complexes such as Ir₂(CO)₂X₂(μ-dpma)₂ (X = Cl, I).¹⁰ The structure of 5 appears to be

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2][\text{BPh}_4]_2 \cdot 6\text{CH}_2\text{Cl}_2$

	x	y	z	U		x	y	z	U
Ir	330 (1)	7456 (1)	6569 (1)	18 (1) ^a	C(31)	1833 (4)	6856 (8)	7982 (6)	31 (3)
Rh	0	7229 (1)	7500	15 (1) ^a	C(32)	2113 (4)	6207 (8)	8149 (6)	35 (3)
As	-721 (1)	7264 (1)	6648 (1)	17 (1) ^a	C(33)	1973 (4)	5454 (8)	7885 (6)	35 (3)
Cl(1)	130 (2)	8608 (3)	7036 (3)	22 (2) ^a	C(34)	1552 (4)	5352 (8)	7429 (6)	39 (3)
P(1)	-348 (1)	7455 (2)	5669 (1)	19 (1) ^a	C(35)	1262 (4)	6005 (7)	7253 (6)	27 (3)
P(2)	1048 (1)	7632 (2)	7347 (1)	18 (1) ^a	C(36)	3559 (4)	4674 (7)	1112 (5)	21 (3)
O(1)	-231 (3)	5747 (5)	8019 (4)	26 (2)	C(37)	3970 (4)	4991 (7)	1239 (5)	25 (3)
O(2)	668 (3)	6815 (5)	5658 (4)	38 (2)	C(38)	4351 (4)	4781 (8)	1750 (6)	33 (3)
O(3)	227 (6)	9347 (11)	6677 (8)	39 (5)	C(39)	4346 (4)	4199 (8)	2198 (6)	33 (3)
C(1)	-202 (3)	6449 (6)	7987 (5)	17 (2)	C(40)	3951 (4)	3859 (8)	2101 (6)	38 (3)
C(2)	539 (4)	7049 (7)	6008 (6)	28 (3)	C(41)	3580 (4)	4100 (8)	1580 (6)	33 (3)
C(3)	270 (7)	8653 (14)	6641 (11)	24 (5)	C(42)	2786 (4)	5056 (7)	847 (5)	25 (3)
C(4)	-387 (4)	8112 (7)	5021 (5)	25 (3)	C(43)	2860 (4)	5673 (8)	1297 (6)	33 (3)
C(5)	-387 (4)	7789 (9)	4459 (6)	43 (4)	C(44)	2614 (4)	5792 (8)	1646 (6)	36 (3)
C(6)	-452 (5)	8270 (10)	3947 (8)	65 (5)	C(45)	2280 (4)	5237 (8)	1540 (6)	38 (3)
C(7)	-494 (5)	9133 (9)	3391 (8)	52 (4)	C(46)	2196 (4)	4629 (8)	1085 (6)	38 (3)
C(8)	-477 (4)	9455 (8)	4536 (6)	40 (3)	C(47)	2438 (4)	4519 (7)	750 (6)	28 (3)
C(9)	-418 (4)	8959 (8)	5056 (6)	34 (3)	C(48)	2932 (4)	4144 (7)	-5 (5)	26 (3)
C(10)	-553 (4)	6474 (7)	5291 (5)	24 (3)	C(49)	3093 (4)	3356 (8)	126 (6)	36 (3)
C(11)	-979 (4)	6418 (8)	4832 (6)	38 (3)	C(50)	2903 (5)	2710 (9)	-296 (7)	46 (4)
C(12)	-1147 (5)	5670 (8)	4569 (7)	45 (4)	C(51)	2537 (4)	2836 (9)	-872 (7)	41 (3)
C(13)	-907 (4)	4987 (8)	4712 (6)	40 (3)	C(52)	2376 (4)	3617 (8)	-1016 (7)	40 (3)
C(14)	-475 (4)	5038 (8)	5164 (6)	33 (3)	C(53)	2576 (4)	4241 (8)	-593 (6)	34 (3)
C(15)	-296 (4)	5766 (7)	5454 (6)	27 (3)	C(54)	3132 (4)	5729 (7)	108 (6)	28 (3)
C(16)	-754 (3)	7848 (6)	5887 (5)	16 (2)	C(55)	2916 (4)	6453 (7)	54 (6)	30 (3)
C(17)	-1054 (4)	6287 (7)	6302 (5)	24 (3)	C(56)	2929 (4)	7103 (8)	-325 (6)	37 (3)
C(18)	-850 (4)	5515 (7)	6464 (5)	21 (3)	C(57)	3178 (4)	7050 (8)	-654 (6)	34 (3)
C(19)	-1094 (4)	4827 (8)	6200 (6)	30 (3)	C(58)	3404 (4)	6349 (7)	-615 (6)	33 (3)
C(20)	-1518 (4)	4890 (8)	5771 (6)	34 (3)	C(59)	3376 (4)	5695 (7)	-239 (6)	29 (3)
C(21)	-1710 (4)	5628 (8)	5618 (6)	36 (3)	B	3109 (4)	4894 (8)	517 (6)	21 (3)
C(22)	-1479 (4)	6337 (8)	5874 (6)	30 (3)	Cl(2)	1636 (2)	7000 (4)	2050 (3)	94 (3) ^a
C(23)	-1087 (4)	7947 (7)	6878 (5)	23 (3)	Cl(3)	2175 (2)	8410 (3)	2584 (2)	65 (2) ^a
C(24)	1307 (4)	8412 (7)	7086 (5)	23 (3)	Cl(4)	779 (2)	8601 (3)	4933 (3)	105 (4) ^a
C(25)	1281 (4)	9222 (7)	7217 (6)	28 (3)	Cl(5)	759 (3)	7116 (3)	4280 (3)	151 (6) ^a
C(26)	1484 (4)	9809 (8)	6995 (6)	34 (3)	Cl(6)	584 (2)	5853 (3)	1427 (2)	64 (2) ^a
C(27)	1690 (4)	9575 (8)	6634 (6)	36 (3)	Cl(7)	510 (4)	6773 (7)	2400 (4)	255 (10) ^a
C(28)	1713 (4)	8770 (8)	6496 (6)	38 (3)	C(60)	2192 (5)	7383 (9)	2389 (8)	63 (5)
C(29)	1522 (4)	8164 (8)	6718 (6)	36 (3)	C(61)	714 (7)	8156 (12)	4254 (10)	96 (7)
C(30)	1409 (4)	6759 (7)	7538 (5)	20 (2)					

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

identical with that of **3a**, with two bridging and two terminal carbonyl ligands, a bridging iodide, and a terminal iodide ligand. Although the environments of the two IrP_2 units are not identical in the solid state, a simple bridge/terminal iodide exchange, identical with that reported for complex **3** and shown in eq 1,⁹ renders the two IrP_2 units equivalent. The mixed-halide complex **6** also appears to be isostructural with complexes **3** and **5**. Because the complex contains two different halide ligands, bridge/terminal halide exchange will not make the two IrP_2 units equivalent. Thus two singlets, at -2.5 and -4.4 ppm, are observed in the ^{31}P NMR spectrum of **6**. It is quite likely that bridge/terminal exchange is occurring in this complex, although the NMR data do not require it.

The visible spectra of the complexes are all very similar. Thus, exchanging chloride for iodide or carbonyl for halide ligands does not perturb the electronic structure of the complexes to a great extent. In particular, the spectra of $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}(\mu\text{-dpma})_2]^+$ (**3a**) and $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2]^{2+}$ (**4**) are nearly identical.

The X-ray Crystal Structure of $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2][\text{BPh}_4]_2 \cdot 6\text{CH}_2\text{Cl}_2$. Well-formed crystals were obtained by slow diffusion of diethyl ether into a carbon monoxide saturated, dichloromethane solution of **4**. The asymmetric unit consists of half of the cation, a tetraphenylborate anion, and three dichloromethane molecules. The numbering scheme for the cation

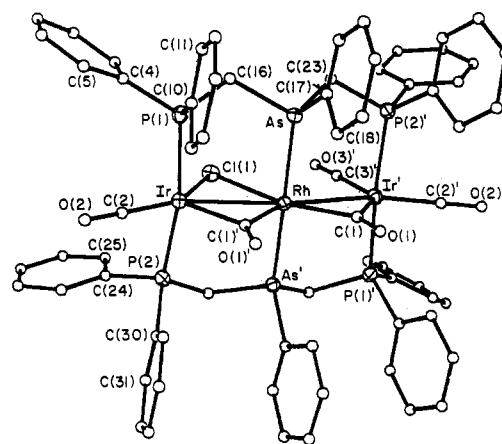


Figure 1. A perspective view of $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2]^{2+}$ (**4**) showing 50% thermal ellipsoids for heavy atoms and uniform, arbitrarily sized circles for carbon atoms.

is shown in Figure 1. Atomic positional parameters are given in Table II. Bond distances and angles are presented in Table III. The cations are packed about a crystallographic twofold axis which passes through the rhodium atom and is perpendicular to the RhAs_2Ir_2 plane. This twofold axis requires that there be a statistical disorder in the $\text{C}(3)\text{-O}(3)$ ligand and $\text{Cl}(1)$, and these atoms were refined at 0.5 occupancy. A similar form of disorder was observed in $[\text{Ir}_3(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}(\mu\text{-dpma})_2]^+$ (**3b**), although in this case the occupancies of the carbonyl and

(11) Balch, A. L.; Olmstead, M. M.; Oram, D. E.; Reedy, P. E., Jr., to be submitted for publication.

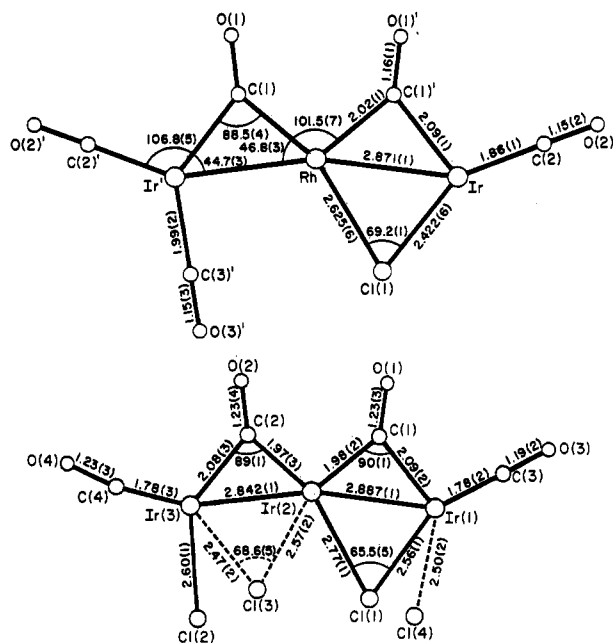


Figure 2. Comparison of the inner cores of top, [Ir₂Rh(μ-CO)₂(CO)₃(μ-Cl)(μ-dpma)₂]²⁺ (**4**), and bottom, [Ir₃(μ-CO)₂(CO)₂(μ-Cl)Cl(μ-dpma)₂]⁺ (**3b**) (the dashed lines connect the atoms from the minor, disordered form).

chloride ligands were not exactly 0.5, and a twofold axis was not present.⁹

The overall geometry of **4** is nearly identical with **3b** with the central iridium atom and terminal chloride in **3b** replaced with a rhodium atom and terminal carbonyl in **4**. This can be best appreciated in Figure 2 which compares planar sections of the two complexes. Since iridium and rhodium are nearly the same size due to the lanthanide contraction, comparisons between **4** and **3b** are quite useful. The Ir-Rh bond distances in **4** (see Figure 3) of 2.871 Å are nearly identical with the Ir-Ir bond lengths in **3b** of 2.842 and 2.887 Å. These are in the range normally observed for metal-metal single bonds in phosphine-bridged Rh(I) and Ir(I) complexes. The presence of the two Ir-Rh bonds are necessary to provide an 18-electron count at each of the three metals. Complex **4** is nearly linear, with an Ir-Rh-Ir angle of 165.1°. This is comparable to the Ir(1)-Ir(2)-Ir(3) angle of 166.0° reported for **3b**.⁹ There is a virtual (noncrystallographic) mirror plane which contains the three metal atoms, five carbonyl ligands, and the chloride of **4**. In solution this renders the environments of the two pairs of trans phosphorus atoms equivalent, resulting in the observed two singlets in the low-temperature-limiting ³¹P NMR spectrum. The geometry about the two iridium atoms is a distorted octahedron, while that of rhodium is a distorted pentagonal-bipyramid. The Ir-P and Rh-As bond distances are comparable to those in **3b** and other bi- and trinuclear phosphine- and arsine-bridged complexes.²⁻⁹ The distances of the carbonyl carbons from the metals are significantly longer in this complex as compared to related dpma-bridged trinuclear species. The Ir-CO distances in **3b**, [Ir₂(SnCl)(CO)₂Cl₂(μ-dpma)₂]⁺, and Ir₂Ag(CO)₂Cl₃(μ-dpma)₂ range from 1.768 to 1.82 Å for terminal carbonyl ligands,¹¹ while in **4** these distances are 1.865 Å for Ir-C(2) and 1.987 Å for Ir'-C(3). This weakening of the metal-carbonyl bonds is probably due to the large number of carbonyl ligands (five) competing for electron density at the metals.

The Fluxional Behavior of [Ir₂Rh(μ-CO)₂(CO)₃(μ-Cl)(μ-dpma)₂]²⁺ (4**).** Both the ³¹P and ¹³C NMR spectra of **4** indicate that it is fluxional. Representative ³¹P NMR

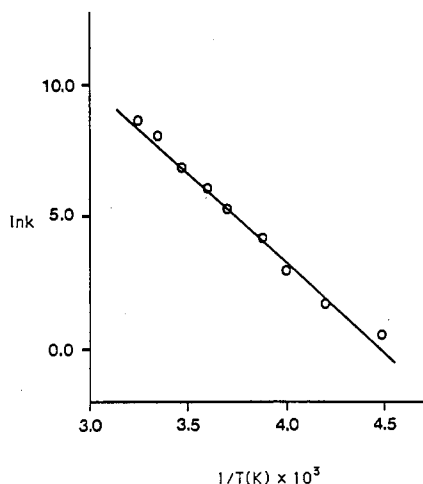
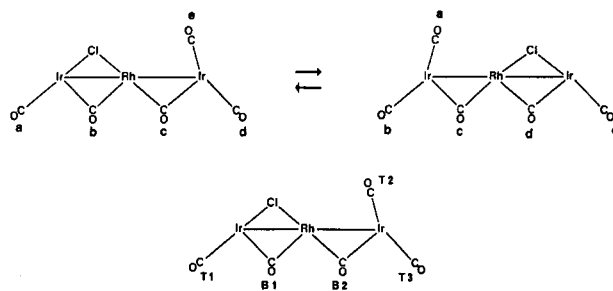


Figure 3. A plot of ln *k* vs 1/*T* for **4** obtained from ³¹P NMR data in dichloromethane solution.

Chart II



spectra recorded in dichloromethane solution are shown in the supplementary material. At -50 °C the spectrum consists of two equally intense singlets, as expected from the solid state structure of **4**. When the sample is warmed to -15 °C, the resonances are still well-resolved but exhibit substantial broadening. At 35 °C, the two singlets coalesce into a single broad peak. Warming the sample above 35 °C results in decomposition of the sample, but below that, the temperature-dependent behavior is reversible. To account for these observations, a process must occur in which the environments of the two IrP₂ units are exchanged. Since variations in the concentration of **4** do not affect the exchange rate at fixed temperatures, the process must be intramolecular. The spectra have been simulated and analyzed to give rate constants for the two-site exchange process. An Arrhenius plot of the data is shown in Figure 3. From this, an *E_a* value of 15.0 (0.9) kcal/mol was determined. From an Eyring plot, values of Δ*G*[‡] = 12.9 (2), Δ*H*[‡] = 14.1 (9) kcal/mol, and Δ*S*[‡] = 4.3 (3) eu were determined. The small positive value of 4.3 eu suggests that the transition state in the process is similar to the solid-state structure. This low value also rules out a dissociative process for the exchange of the chloride and carbonyl ligands. That would result in a much larger positive entropy of activation. The iodo analogue **7** shows similar behavior. The two ³¹P resonances coalesce at 25 °C and at that temperature Δ*G*[‡] = 13.2 (4) kcal/mol. Thus, the behavior of **4** and **7** are very similar.

An exchange process that satisfies the experimental data (i.e., a nondissociative, intramolecular process) is shown in Chart II. This involves the oscillatory motion of the five carbonyl ligands and the chloride ligand in a concerted fashion about the trimetallic core in clockwise or counterclockwise directions. Migration of these ligands completely around the cation is prohibited by the need to have the chloride ligand occupy a bridging site where it can

Table III. Bond Distances (Å) and Angles (deg) for $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2][\text{BPh}_4]_2 \cdot 6\text{CH}_2\text{Cl}_2$

Bond Distances			
Ir-Rh	2.871 (1)	Ir-Cl(1)	2.422 (6)
Ir-P(1)	2.361 (2)	Ir-P(2)	2.368 (2)
Ir-C(2)	1.865 (15)	Ir-C(3)	1.987 (23)
Ir-C(1)'	2.093 (12)	Rh-As	2.415 (1)
Rh-Cl(1)	2.625 (6)	Rh-C(1)	2.021 (12)
As-C(16)	1.956 (12)	As-C(17)	1.933 (11)
As-C(23)	1.940 (14)	P(1)-C(4)	1.797 (13)
P(1)-C(10)	1.819 (11)	P(1)-C(16)	1.816 (13)
P(2)-C(24)	1.816 (14)	P(2)-C(30)	1.828 (11)
P(2)-C(23)'	1.804 (13)	O(1)-C(1)	1.161 (13)
O(2)-C(2)	1.146 (19)	O(3)-C(3)	1.155 (29)
Bond Angles			
Rh-Ir-Cl(1)	58.7 (2)	Rh-Ir-P(1)	94.5 (1)
Cl(1)-Ir-P(1)	91.0 (1)	Rh-Ir-P(2)	95.1 (1)
Cl(1)-Ir-P(2)	89.1 (1)	P(1)-Ir-P(2)	168.8 (1)
Rh-Ir-C(2)	151.6 (4)	Cl(1)-Ir-C(2)	149.7 (4)
P(1)-Ir-C(2)	86.5 (3)	P(2)-Ir-C(2)	87.8 (3)
Rh-Ir-C(3)	88.5 (8)	P(1)-Ir-C(3)	88.4 (5)
P(2)-Ir-C(3)	86.1 (6)	C(2)-Ir-C(3)	119.9 (9)
Rh-Ir-C(1)'	84.7 (3)	Cl(1)-Ir-C(1)'	103.5 (4)
P(1)-Ir-C(1)'	94.6 (3)	P(2)-Ir-C(1)'	96.3 (3)
C(2)-Ir-C(1)'	106.8 (5)	C(3)-Ir-C(1)'	133.3 (9)
Ir-Rh-As	90.4 (1)	Ir-Rh-Cl(1)	52.1 (1)
As-Rh-Cl(1)	87.4 (1)	Ir-Rh-C(1)	148.1 (3)
As-Rh-C(1)	88.4 (3)	Cl(1)-Rh-C(1)	159.5 (4)
Ir-Rh-Ir'	165.1 (1)	Cl(1)-Rh-Ir'	113.0 (1)
C(1)-Rh-Ir'	46.8 (3)	Ir-Rh-As'	89.2 (1)
As-Rh-As'	177.3 (1)	Cl(1)-Rh-As'	90.3 (1)
C(1)-Rh-As'	93.2 (3)	Cl(1)-Rh-C(1)'	98.8 (4)
C(1)-Rh-C(1)'	101.5 (7)	Rh-As-C(16)	111.6 (3)
Rh-As-C(17)	122.6 (3)	C(16)-As-C(17)	104.4 (5)
Rh-As-C(23)	111.5 (3)	C(16)-As-C(23)	100.1 (5)
C(17)-As-C(23)	104.0 (5)	Ir-Cl(1)-Rh	69.2 (1)
Ir-P(1)-C(4)	114.1 (4)	Ir-P(1)-C(10)	116.9 (3)
C(4)-P(1)-C(10)	105.2 (5)	Ir-P(1)-C(16)	111.1 (3)
C(4)-P(1)-C(16)	103.5 (6)	C(10)-P(1)-C(16)	104.8 (6)
Ir-P(2)-C(24)	110.5 (3)	Ir-P(2)-C(30)	118.3 (3)
C(24)-P(2)-C(30)	103.9 (6)	Ir-P(2)-C(23)'	112.1 (4)
C(24)-P(2)-C(23)'	107.1 (6)	C(30)-P(2)-C(23)'	104.0 (5)
Rh-C(1)-O(1)	136.4 (11)	Rh-C(1)-Ir'	88.5 (4)
O(1)-C(1)-Ir'	135.1 (11)	Ir-C(2)-O(2)	178.6 (11)
Ir-C(3)-O(3)	178.7 (15)		

function as a four-electron donor. Further evidence in support of this mechanism can be obtained from ^{13}C NMR spectra. In Chart II, the five carbonyl ligands are labeled a-e for clarity. During the exchange process carbonyl a moves into the position formerly occupied by e and carbonyl e moves into the position of a. Thus, as the temperature is increased, the resonances for these two carbonyl groups should broaden and coalesce. Similar exchange takes place with carbonyls b and d; thus, their resonances should also coalesce at elevated temperatures. Carbonyl c remains in same bridging environment throughout the process. Consequently the resonance corresponding to c should not change as a function of temperature.

As shown in Figure 4, the temperature dependence of the ^{13}C NMR spectra is in good agreement with these predictions. At -50°C , the three singlets corresponding to the terminal carbonyl groups and the two doublets corresponding to the bridging carbonyls are clearly resolved. The coupling of the two, high-frequency (low-field) ^{13}C resonances to ^{103}Rh (spin, $1/2$; natural abundance, 100%) provides convincing evidence for the assignment of these to the bridging carbonyl groups. The coupling constants of 42 and 47 Hz for these doublet are approximately half as large as normally observed for terminal carbonyl ligands bound to Rh(I).^{4,8,12} At 0°C the three terminal resonances and the upfield bridging resonance

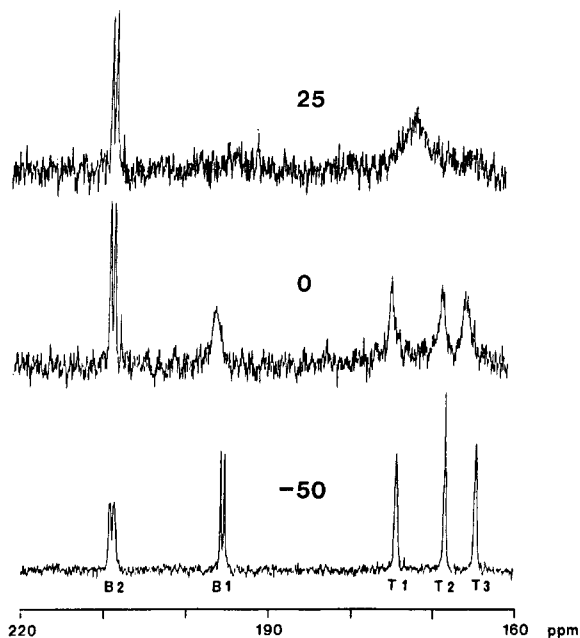


Figure 4. The variable-temperature ^{13}C NMR spectra of ^{13}CO -enriched 4 in dichloromethane solution. Resonance assignments of the low-temperature spectrum correspond to the labeling given in Chart II. The assignments of resonances T1 and T2 may be reversed with respect to the locations in Chart II.

show significant broadening, while the downfield doublet is unchanged. The similarity in broadening of resonances B1 and T3 allows these to be assigned as a pair of interchanging groups, while resonances T1 and T2 show a different degree of broadening and represent a second pair of interchanging groups. When the temperature is increased to 25°C , the T1 and T2 resonances have coalesced into a broad singlet while B1 and T3 resonances have nearly broadened into the baseline. From these data it is clear that the upfield doublet corresponds to carbonyl B1, while the downfield doublet represents carbonyl B2.

The ^{31}P and ^{13}C NMR data are consistent with a single process that is responsible for the observed temperature-dependent changes. Thus the rate data generated from the ^{31}P NMR spectra indicate that resonances T1 and T2 should coalesce at 12°C , which is in agreement with our data, and the resonances B1 and T3 should coalesce at 55°C (which we also observe when the sample is warmed in dichloroethane).

The difference in the rate of fluxionality for 3 and 4 is significant. If the separation in ^{31}P resonances for 3 is similar to that in 4 at the low temperature limit, then we can estimate that the rate constant for eq 2 is at least 2 orders of magnitude faster than for the process shown in Chart II. The enhanced rate for eq 2 can be attributed to the presence of the terminal chloro ligand whose lone pairs allow for a simultaneous bond-making/bond-breaking process during the bridge/terminal exchange of these ligands. For 4 the corresponding bridge/bridge chloride exchange is not assisted by a nearby nucleophile. Hence, it requires breaking of the Cl-Ir bond before forming the new Ir-Cl bond and possibly greater distortion of the Ir-RhIr core in order to facilitate movement of the chloro ligand along the chain.

Experimental Section

Preparation of Compounds. $[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}(\mu\text{-dpma})_2][\text{BPh}_4]$ was prepared as described previously.⁴

$[\text{Ir}_2\text{Rh}(\mu\text{-CO})_2(\text{CO})_3(\mu\text{-Cl})(\mu\text{-dpma})_2][\text{BPh}_4]_2$ (4). A solution of 100 mg (0.31 mmol) of sodium tetraphenylborate in 1 mL of methanol was added to a solution of 155 mg (0.074 mmol) of

[Ir₂Rh(μ-CO)₂(CO)₂(μ-Cl)Cl(μ-dpma)₂][BPh₄]₂ in 10 mL of dichloromethane. The resultant red solution was purged with carbon monoxide for 3 h, during which time the solution became lighter red in color. The addition of 10 mL of methanol caused the product to precipitate as bright red needles. The product was collected by filtration and washed successively with methanol and diethyl ether; yield 140 mg, 79%. Anal. Calcd for C₁₁₇H₉₈As₂B₂Cl₂Ir₂O₅P₄Rh: C, 58.50; H, 4.11; Cl, 1.47. Found: C, 58.04; H, 4.02; Cl, 1.60.

[Ir₂Rh(μ-CO)₂(CO)₂(μ-I)I(μ-dpma)₂][BPh₄]₂ (5). A solution of 70 mg (0.47 mmol) of sodium iodide in 1 mL of methanol was added with stirring to a cold solution (-20 °C) of 100 mg (0.048 mmol) of [Ir₂Rh(μ-CO)₂(CO)₂(μ-Cl)Cl(μ-dpma)₂][BPh₄]₂ in 5 mL of dichloromethane. Additional methanol was added to precipitate the product as the iodide salt. The red crystalline solid was collected by filtration and washed with methanol. The product was converted to the tetraphenylborate salt by dissolving it in a minimum amount of dichloromethane and adding to it a solution of 100 mg (0.31 mmol) of sodium tetraphenylborate in 2 mL of methanol. After filtration, addition of excess methanol to the solution caused red crystals to precipitate. The product was collected by filtration and washed successively with methanol and diethyl ether; yield 75 mg, 69%. Anal. Calcd for C₉₂H₇₈As₂BI₂Ir₂O₄P₄Rh: C, 48.61; H, 3.46; I, 11.16. Found: C, 48.86; H, 3.32; I, 10.59.

[Ir₂Rh(μ-CO)₂(CO)₂ClI(μ-dpma)₂][BPh₄]₂ (6). A solution of 9.0 mg (0.021 mmol) of methyltriphenylarsonium iodide in 0.25 mL of methanol was added slowly to a cold solution (-20 °C) of 50 mg (0.021 mmol) of 5 in 3 mL of dichloromethane. The solution became lighter red in color, and after a few minutes of stirring, red crystals began to precipitate. An additional 2 mL of methanol was added to ensure complete precipitation of the product. The product was collected by filtration and washed successively with methanol and diethyl ether. The product was purified by dissolving it in a minimum amount of dichloromethane, filtering, and slowly adding diethyl ether; yield 35 mg, 76%. Anal. Calcd for C₉₂H₇₈As₂BClI₂Ir₂O₄P₄Rh: C, 50.65; H, 3.60. Found: C, 49.79; H, 3.46.

[Ir₂Rh(μ-CO)₂(CO)₃(μ-I)(μ-dpma)₂][BPh₄]₂ (7). A solution of 25 mg (0.08 mmol) of sodium tetraphenylborate in 1 mL of methanol was added to a solution of 30 mg (0.014 mmol) of 6 in 10 mL of dichloromethane. The resultant solution was purged with CO for 2 h at which time the volume was reduced to approximately 4 mL. The addition of methanol caused red crystals to precipitate. The product was collected by filtration and washed successively with methanol and diethyl ether; yield 20 mg, 59%. Spectroscopic data indicated that the product was contaminated with quantities of 5 and 6. Purification was not possible.

Physical Measurements. The ³¹P NMR spectra were recorded with proton decoupling on a Nicolet NT-200 Fourier transform spectrometer operating at 81 MHz. ¹³C NMR spectra were recorded at 90.5 MHz on a Nicolet NT-360 FT spectrometer. The references were as follows: ³¹P, external 85% phosphoric acid; ¹³C, internal tetramethylsilane. The high-frequency-positive convention, recommended by IUPAC, has been used in reporting all chemical shifts. Line-shape analyses of ³¹P NMR spectra were performed by using an iterative analysis program, DNMR5,^{13,14} on a VAX/VMS computer. Infrared spectra were recorded from mineral oil mulls or dichloromethane solutions with a Perkin-Elmer 180 or IBM IR32 spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8450A spectrophotometer.

X-ray Structure Determination and Refinement. Well-formed, air-stable crystals of [Ir₂Rh(μ-CO)₂(CO)₃(μ-Cl)(μ-dpma)₂][BPh₄]₂·6CH₂Cl₂ were obtained by layering a dichloromethane solution of the compound with diethyl ether in a thin tube. The dichloromethane had been previously saturated with carbon monoxide. A suitable crystal was mounted on a glass fiber by using silicone grease and positioned in the cold stream of the diffractometer with the long dimension of the crystal parallel to φ. No decay in the intensities of three standard reflections was

Table IV. Crystal Data and Data Collection Parameters, Solution, and Refinement for [Ir₂Rh(μ-CO)₂(CO)₃(μ-Cl)(μ-dpma)₂][BPh₄]₂·6CH₂Cl₂

formula	C ₁₂₀ H ₉₆ As ₂ BCl ₁₃ Ir ₂ O ₆ P ₄ Rh
fw	2850.85
color and habit	pale red-brown parallelepipeds
cryst system	monoclinic
space group	C2/c
a, Å	34.896 (4)
b, Å	16.394 (2)
c, Å	23.029 (3)
β, deg	116.12 (2)
V, Å ³	11829 (2)
T, K	130
Z	4
cryst dimens, mm	0.25 × 0.37 × 0.50
d _{calcd} , g cm ⁻³	1.60
radiatn, Å	Mo Kα (λ = 0.710 69)
μ(Mo Kα), cm ⁻¹	59.7
range of transmissn factors	0.14–0.29
diffractometer	P2 ₁ , graphite monochromator
scan method	ω, 1.4° range, 1.0° offset for bkgd
scan speed, deg min ⁻¹	60
2θ range, deg	0–50
octants collected	h, k, ±l
no. of data collected	11 032
no. of unique data	10 267, R(merge) = 0.007
no. of data used in refinement	6278 [I > 3σ(I)]
no. of parameters refined	365
R ^a	0.058
R _w ^a	0.062 [w = 1/(σ ² (F _o))]

$$^a R = \sum ||F_o| - |F_c|| / |F_o| \text{ and } R_w = \sum ||F_o| - |F_c|| w^{1/2} / \sum |F_o| w^{1/2}.$$

observed during the course of data collection. Data collection parameters are given in Table IV.

The usual corrections for Lorentz and polarization effects were applied to the data. Crystallographic programs used were those of SHELXTL, version 4, installed on a Data General Eclipse computer. Scattering factors and corrections for anomalous dispersion were from the standard source.¹⁵ Solution of the structure was accomplished by Patterson methods. An absorption correction was applied.¹⁶ In the final cycles of refinement, Ir, Rh, As, Cl, and P atoms were assigned anisotropic thermal parameters. Two low-angle reflections affected by extinction were removed from the set of reflections used for refinement. In the final difference map, the largest feature was 2.3 e Å⁻³ in height, in the vicinity of one of the dichloromethane chlorines. There were numerous other spurious features in the vicinity of the dichloromethanes, but none were larger than 1.3 e Å⁻³. These features are probably due to disorder, but no reasonable model for the disorder could be constructed.

The molecule packs about a crystallographic twofold axis that passes through the rhodium atom and is perpendicular to the Rh–As–Ir plane. This twofold axis requires there to be a statistical disorder in the C(3)–O(3) ligand and Cl(1). Since the systematic absences are also consistent with the lower symmetry space group Cc, refinement was attempted in this space group to see if the disorder would be removed. The disorder persisted in Cc, and therefore refinement was continued in C2/c using a disordered model in which C(3), O(3), and Cl(1) were refined at 0.5 occupancy. Crystallization in the higher symmetry space group in a disordered fashion is physically quite reasonable. The disorder affects only two ligands, Cl(1) and C(3)–O(3), which are located within the interior of a large cation. Since packing is determined by the external shape of the molecule and is dominated by the positions of the 10 phenyl rings which protrude from the central core, it is in no way surprising that a disordered solid forms during crystal growth. A analogous situation occurs with [Ir₃(μ-CO)₂(CO)₂(μ-Cl)Cl(μ-dpma)₂][BPh₄]₂, cation 3b, where disorder in CO and Cl positions occurs and a higher symmetry space group (P $\bar{1}$ rather than P1) is found.⁹

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(16) The absorption correction is made by using program XABS (H. Hope and B. Moezzi). The program obtains an absorption tensor from F_o – F_c differences.

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thyltriphenylarsonium iodide, 1499-33-8.

Supplementary Material Available: Listings of all bond distances, all bond angles, hydrogen atom positions, and anisotropic thermal parameters and ³¹P NMR spectra for 4 (7 pages); a listing of structure factor amplitudes for 4 (37 pages). Ordering information is given on any current masthead page.

Tungsten and Molybdenum Alkylidyne Complexes Containing Bulky Thiolate Ligands

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Complexes of the type Mo(C-*t*-Bu)(TMT)₃ and Mo(C-*t*-Bu)(TIPT)₃ (TMT = 2,4,6-trimethylbenzenethiolate; TIPT = 2,4,6-triisopropylbenzenethiolate) can be prepared by adding 3 equiv of LiSAr (SAr = TMT or TIPT) to Mo(C-*t*-Bu)Cl₃(dme). The TMT derivative is believed to be dimeric on the basis of NMR spectra. Reactions between M(C-*t*-Bu)Cl₃(dme) (M = Mo or W), ArSH, and NEt₃ yield complexes of the type [Et₃NH][M(C-*t*-Bu)(SAr)₃Cl]. W(C-*t*-Bu)(SAr)₃ complexes can be prepared by removing chloride ion from the [Et₃NH][W(C-*t*-Bu)(SAr)₃Cl] species with zinc chloride. M(C-*t*-Bu)(SAr)₃ complexes do not react with 3-hexyne, 2-butyne, or phenylacetylene, and only minute traces of 3-heptyne metathesis products are observed after 3 days at 25 °C. The reaction between W(C₃Me₃)Cl₃ and LiTIPT yields W(C₃Me₃)(TIPT)₃ (in situ), the reaction between W(C₃Me₃)Cl₃, TIPT₃H, and NEt₃ (or that between W(C₃Me₃)(TIPT)₃ and Et₃NHCl) gives [Et₃NH][W(CMe)(TIPT)₃Cl], and the reaction between the η³-cyclopropenyl complex W(C₃-*t*-BuMe₂)Cl₃(py)₂ and LiTMT yields a mixture of W(CMe)(TMT)₃(py) and W(C-*t*-Bu)(TMT)₃(py). Both Mo(CPr)(TIPT)₃ and W(CMe)(TIPT)₃ are stable and isolable. We conclude from these studies that M(CR)(SAr)₃ complexes react too slowly with ordinary acetylenes to be active catalysts, either because coordination of sulfur (in a dimer) competes effectively with coordination of the acetylene or because the metal is simply not electrophilic enough, or both.

Introduction

We have discovered that some complexes of the type M(CR)(OR')₃ (M = Mo, W; R = alkyl; OR' = (e.g.) O-*t*-Bu, OCM₂(CF₃)₂, O-2,6-C₆H₃-*i*-Pr₂) will metathesize internal acetylenes.¹ This activity depends sensitively upon M and OR'. For example, Mo(C-*t*-Bu)(O-*t*-Bu)₃ does not react with internal acetylenes,^{1b} while W(C-*t*-Bu)(O-*t*-Bu)₃ reacts extremely rapidly to give a new alkylidyne complex derived from half the acetylene.^{1a,e} If more electron-withdrawing alkoxide ligands are employed, then molybdenum species such as Mo(C-*t*-Bu)[OCMe(CF₃)₂]₂ become active catalysts.^{1b} Metallacyclobutadiene intermediates sometimes can be observed, and some tungsten complexes are quite stable;^{1c} in the case of W(C₃R₂)(O-2,6-C₆H₃-*i*-Pr₂)₃, the rate-limiting step of the acetylene metathesis reaction consists of loss of an acetylene from the metallacyclic ring.

An important question is how the behavior of other complexes of the type M(CR)X₃ (X = (e.g.) halide, amide, thiolate) compare with that observed for the alkoxide complexes. So far we know that tungsten halide derivatives will form tungstacyclobutadiene complexes² but will not in general metathesize ordinary acetylenes; cyclo-

Table I. Selected ¹³C NMR Data for Thiolate Complexes^a

compound	δ(C _α)
[Mo(C- <i>t</i> -Bu)(TMT) ₃] ₂	336.0
[Et ₃ NH][Mo(C- <i>t</i> -Bu)(TMT) ₃ Cl]	316.3
Mo(C- <i>t</i> -Bu)(TIPT) ₃	341.5
Mo(CPr)(TIPT) ₃	333.6
[W(C- <i>t</i> -Bu)(TMT) ₃] ₂	324.3
W(C- <i>t</i> -Bu)(TIPT) ₃	329.4
W(CMe)(TIPT) ₃	312.1
W(CMe)(TMT) ₃ (py)	308.2
[Et ₃ NH][W(C- <i>t</i> -Bu)(TMT) ₃ Cl]	304.0 ^b
[Et ₃ NH][W(C- <i>t</i> -Bu)(TIPT) ₃ Cl]	306.9
[Et ₃ NH][W(CMe)(TIPT) ₃ Cl]	294.8

^a Solvent = CD₂Cl₂ at T = 298 K unless otherwise noted. ^b J_{CW} = 216 Hz.

pentadienyl complexes are formed instead.^{2,3} We also know that W(CEt)(NMe₂)₃ will not metathesize ordinary acetylenes,⁴ although it is not known whether steric or electronic factors are the primary cause of the lower activity. M(C-*t*-Bu)(CH₂-*t*-Bu)₃^{1b,5} complexes also will not

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(4) (a) It has been shown that W(C-*t*-Bu)(NMe₂)₃⁵ and related complexes (e.g., W(C-*t*-Bu)(N-*i*-Pr)₃^{4b}) will metathesize 3-heptyne erratically, if such species are prepared from W(C-*t*-Bu)(dme)Cl₃. Impurities such as "W(C-*t*-Bu)(NR₂)₂Cl" must be responsible since W(CEt)(NMe₂)₃ prepared from W(CEt)(O-*t*-Bu)₃ is inactive.^{4c} (b) Leigh, G. J.; Rahman, M. T.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* 1982, 541. (c) M. L. Listemann, Ph.D. Thesis, M.I.T., 1985.

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