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Systematic Mixed-Metal Cluster Synthesis. The Preparation, Structure, and Spectroscopic Properties of Bis((diphenylphosphino)methyl)phenylarsine-Bridged Complexes Containing Nearly Linear Rh_3, RhIrRh, IrRhIr, and Ir_3 Chains

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Because metal ions prefer binding phosphorus rather than arsenic, reaction between bis((diphenylphosphino)methyl)phenylarsine (dpma) and $Rh_2(CO)_4(\mu\text{-}Cl)_2$ or $Ir(CO)_2Cl(p\text{-toluidine})$ yields the 12-membered metallocycles $Rh_2(\mu\text{-dpma})_2(CO)_2Cl_2$ (**1**) or $Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$ (**2**) with uncoordinated arsenic atoms. Trinuclear complexes have been prepared by the addition of a metal ion to the central cavity of these metallocycles. For example, **1** reacts with $Ir(CO)_2Cl(p\text{-toluidine})$ in the presence of $NaBPh_4$ to yield $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ with the RhIrRh sequence, and **2** reacts with $Rh_2(\mu\text{-}Cl)_2(CO)_4$ and $NaBPh_4$ to form $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$ with an IrRhIr chain. Infrared, electronic, and ^{31}P and ^{13}C NMR spectra of the complexes are reported. The NMR results show that the mixed-metal chains retain their identity under normal handling in solution at room temperature. $[Rh_2Ir\{\mu\text{-}(C_6H_5)_2PCH_2As(C_6H_5)CH_2P(C_6H_5)_2\}_2(CO)_3(\mu\text{-}Cl)Cl][C(C_6H_5)_4]\cdot 2.5CH_2Cl_2$ crystallizes from dichloromethane/ethyl ether in the triclinic space group $P\bar{1}$ (No. 2) with $a = 12.618$ (2) Å, $b = 17.057$ (5) Å, $c = 22.545$ (2) Å, $\alpha = 85.23$ (2)°, $\beta = 79.73$ (2)°, and $\gamma = 77.38$ (2)° at 140 K. Least-squares refinement of 526 parameters using 7036 reflections yields $R = 0.071$ and $R_w = 0.079$. The complex consists of the RhIrRh chain bridged by trans-aligned dpma units. The carbonyl groups are all terminal, one bound to each metal. One chloride bridges one RhIr unit, and the other is a terminal ligand on the other rhodium. The nonbonded Rh···Ir separations are 3.154 (1) and 3.188 (1) Å, and the Rh–Ir–Rh angle is 156.3 (1)°. The electronic absorption spectra of this and related tricarbonyl complexes are analyzed in terms of a $d_{z^2} \rightarrow p_z$ transition.

Introduction

Polyfunctional phosphine-based ligands have proven to be versatile backbones about which bi-, tri-, and tetranuclear clusters or chains of transition-metal ions can be constructed from mononuclear components.[1-4] The selective synthesis of heterobinuclear complexes has been achieved through the capture of one metal ion by an unidentate, bifunctional phosphine bound to a second metal ion[5], by ring opening of a four-membered, chelated ring diphosphine in the presence of a second metal complex,[6] or by transmetalation of certain binuclear complexes.[7] Here we demonstrate that a series of trinuclear complexes can be assembled in which the placement of two different metal ions (Rh(I) or Ir(I)) within the chain can be controlled to produce nearly linear complexes with the sequences RhRhRh, RhIrRh, IrRhIr, and IrIrIr.

In order to do this, we utilize the preference of transition-metal ions to bind phosphorus rather than arsenic.[8] Stability constant data indicate that hard (or class a) metal ions preferentially bind to group V (15[28]) donors in the order N >> P > As > Sb while soft (or class b) metal ions bind in the order N << P > As > Sb.[8] Consequently, with the tridentate ligand bis((diphenylphosphino)methyl)-

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Table I. Infrared and Electronic Spectral Data

compd	ν(CO), cm^{-1} terminal	ν(CO), cm^{-1} bridging	UV-vis λ_{max}, nm (ϵ, M^{-1}·cm^{-1})
$[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	1987, 1973, 1952[a] 1983[b]		532 (23 500), 389 (3680)[b]
$[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	1985, 1970, 1964[a] 1986, 1975[b]		578 (24 100), 398 (4470)[b]
$[Ir_2Rh(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	1993, 1972[b]		580 (21 800), 414 (5900), 380 (8600)[b]
$[Ir_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$			634 (11 000)
$[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	1983[b]	1713[b]	532 (19 600), 391 (5330)[b]
$[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	1983[b]	1756[b]	560 (6800), 452 (10 200), 381 (18 600)[b]
$[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	1985, 1976, 1972, 1963[a] 1977[b]	1836, 1820, 1807, 1759, 1755, 1740[a]	514 (7130), 402 (18 900), 356 (16 200)[b]
$[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	1968, 1961[a] 1974[b]	1822, 1799, 1736, 1727, 1714[a] 1814, 1736[b]	430 (14 600), 369 (16 000)[b]
$Rh_2(\mu\text{-dpma})_2(CO)_2Cl_2$	1985, 1974[a] 1977[c]		367 (9570)[c]
$Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$	1974, 1964[a] 1964[c]		432 (1900), 383 (16 000)[c]

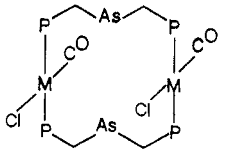
[a] Nujol mull. [b] Dichloromethane. [c] Toluene solution.

Table II. Nuclear Magnetic Resonance Data for Complexes in Dichloromethane Solution

compd	^{31}P δ	^{31}P J(Rh,P), Hz	^{13}C δ	^{13}C ^1J(Rh,C), Hz	^{13}C ^2J(P,C), Hz
$[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	24.2	119.6	187.4[a]	78.0	
			187.7[b]	73.0	15.0
$[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	22.7	118.8	168.8[a]		
			188.9[b]	76.1	14.5
$[Ir_2Rh(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	14.3				
$[Ir_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	12.6				
$[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	24.5	118.0			
$[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	25.2	103.0	192.2[c]		
			188.6	77.0	15.0
$[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	0.7		200.1[c]	41	
			173.2		
$[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$	−0.7		184.0[c]		
			173.6		10.1
$Rh_2(\mu\text{-dpma})_2(CO)_2Cl_2$	24.6	120.0	187.9	75.5	15.0
$Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$	18.4		172.1		9.3

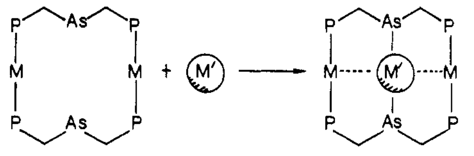
[a] Intensity 1. [b] Intensity 2. [c] Bridging carbon monoxide

phenylarsine[9] (dpma) metal ions are expected to preferentially coordinate to the end phosphorus donors. We use this preference, along with the ability of the metal–ligand fragments $Rh^I(CO)$ and $Ir^I(CO)$ to direct the location of other π-acceptor ligands (like phosphines) away from the site trans to the carbonyl group,[10] to create metallomacrocycles with a central cavity. Thus, the reaction of dpma with $Rh_2(\mu\text{-Cl})_2(CO)_4$ or with $Ir(CO)_2Cl(p\text{-toluidine})$[11] yields the metallomacrocycles 1 and 2. These



1, M = Rh
2, M = Ir

complexes contain 12-membered rings which have two uncoordinated arsenic atoms available for binding another metal as shown in eq 1. We have previously demonstrated the binding of palladium(II) to the central cavity of 1 and 2.[9]


(1)

Results

Synthetic Studies. The synthetic aspects are summarized in Scheme I. Treatment of dpma with $Rh_2(\mu\text{-Cl})_2(CO)_4$ yields yellow $Rh_2(\mu\text{-dpma})_2(CO)_2Cl_2$ (1) in 77% yield. The spectroscopic properties for this and other new complexes are collected in Tables I and II. The solid-state structure of this metallomacrocycle has been established by an X-ray diffraction study.[9] The reaction between dpma and $Ir(CO)_2Cl$ (p-toluidine) yields the analogous iridium complex $Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$ (2). Both the iridium and the rhodium complex form in high yields without recourse to high dilution techniques that are necessary for the synthesis of many macrocycles.

With these metallomacrocycles in hand, it is possible to go about inserting the central metal in a systematic fashion as shown in Scheme I. Two series of cationic products are obtained. These differ in the number (three or four) of carbonyl groups present. In some cases the two series are reversibly interconverted. Cations of both series have

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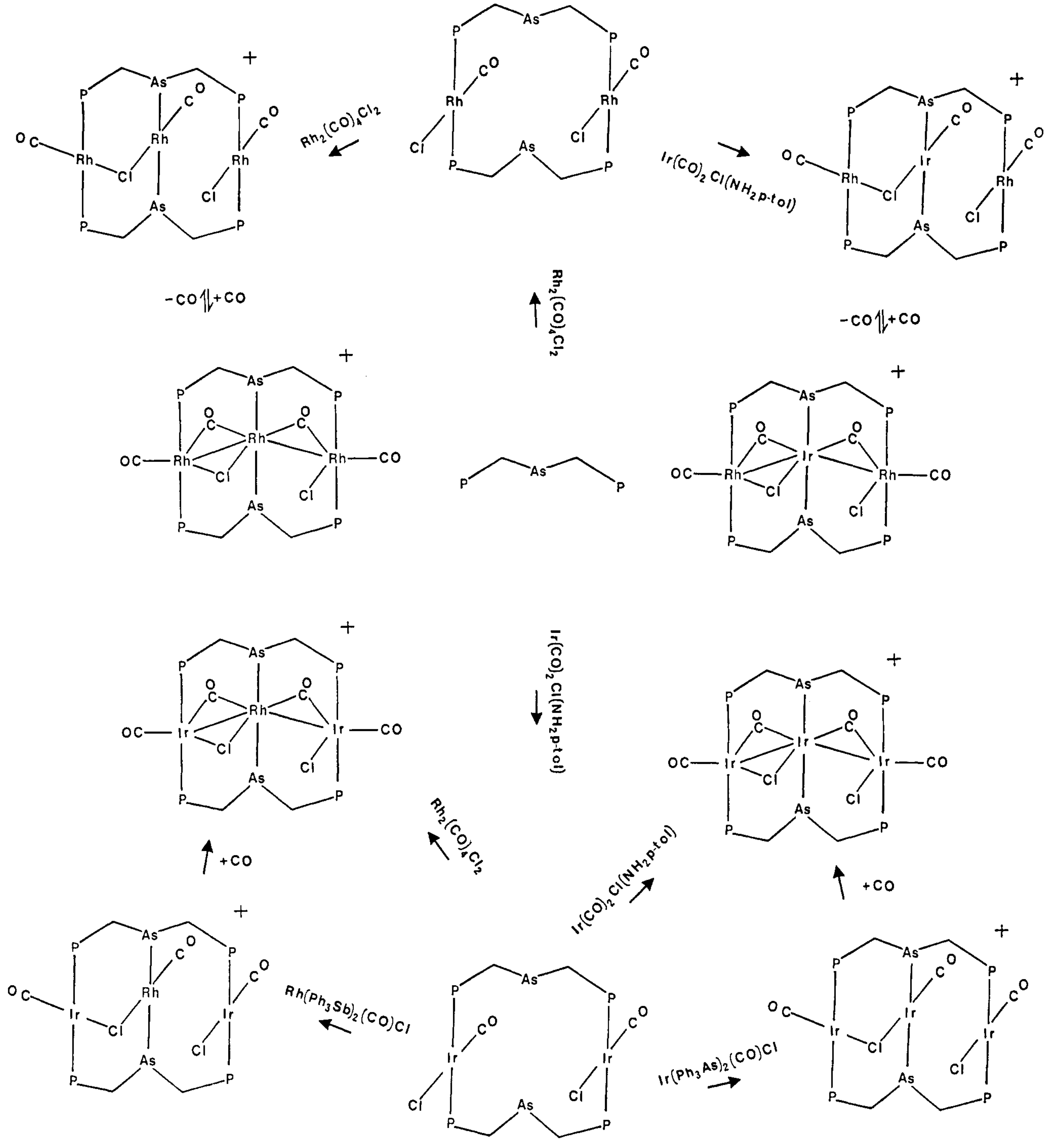
Scheme I



been isolated as the tetraphenylborate salts.

Addition of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ to 1 yields rose-colored $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$, which has also been obtained in a single step by the reaction between dpma and $Rh_2(\mu\text{-}Cl)_2(CO)_4$.[12] Treatment of a dichloromethane solution of $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ with carbon monoxide (1 atm) produces spectral changes indicative of the formation of the corresponding tetracarbonyl. However, the additional carbon monoxide ligand is exceedingly weakly held, and the tetracarbonyl was not isolated.

The reaction between $Rh_2(\mu\text{-dpma})_2(CO)_2Cl_2$ and $Ir(CO)_2Cl$(*p*-toluidine) yields blue-purple $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$. Addition of carbon monoxide to this tricarbonyl yields a red solution of $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+$ which has been thoroughly characterized in solution. This tetracarbonyl also loses carbon monoxide easily, so an analytically pure sample has not been isolated.

Treatment of $Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$ with $Rh_2(\mu\text{-}Cl)_2(CO)_4$ and sodium tetraphenylborate yields red $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$. In this case the tetracarbonyl is readily isolated and does not lose carbon monoxide easily or cleanly. In order to obtain the corresponding tricarbonyl, it is necessary to introduce the rhodium from a reagent containing only a single carbon monoxide ligand. This has been accomplished by using $Rh(SbPh_3)_2(CO)Cl$[13] as the source of the Rh(CO) unit. The

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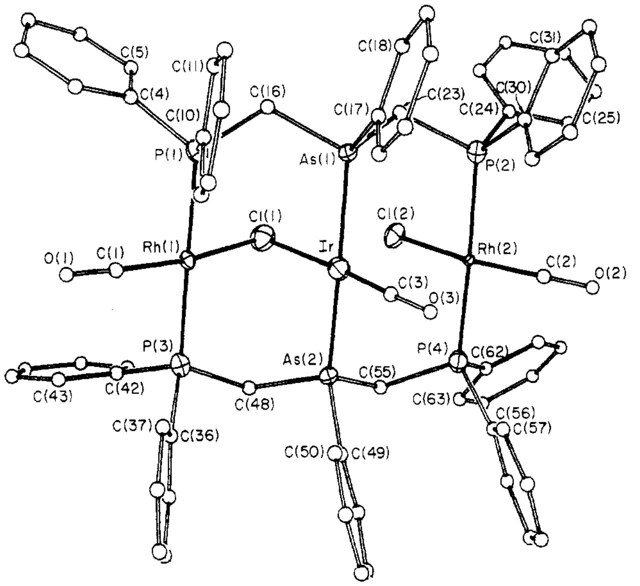

Figure 1. A perspective view of $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ using 50% probability thermal ellipsoids for the anisotropically refined atoms and uniform arbitrarily sized circles for other atoms.

substitution of arsenic for antimony occurs facilely, and blue $[Ir_2Rh(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ is isolated from the reaction. Exposure of solutions of blue $[Ir_2Rh(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ to carbon monoxide rapidly turns them red, and red crystals of $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$ can be isolated through the addition of ethyl ether.

Mixing $Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$ with $Ir(CO)_2Cl(p\text{-toluidine})$ yields the orange tetracarbonyl $[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl]^+$. This tetracarbonyl has also been isolated directly from the reaction between dpma and $Ir(CO)_2Cl(p\text{-toluidine})$,[14] but the yield is better when the two-step process is used. Like $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl]^+$, this tetracarbonyl does not lose carbon monoxide easily. The corresponding tricarbonyl $[Ir_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ has been prepared in solution through the addition of $Ir(AsPh_3)_2(CO)Cl$ (as the source of Ir(CO)) to $Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$. A deep green solution with spectral characteristics indicative of the formation of $[Ir_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ is slowly formed, but the very air-sensitive complex was not isolated in pure form. Treatment of this green solution with carbon monoxide leads to the quantitative formation of $[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl]^+$.

The stability of solutions of the tetracarbonyl cations toward carbon monoxide loss of 25 °C shows a systematic and pronounced variation that depends on the metals present. $[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl]^+$ loses carbon monoxide within a matter of seconds after removal of the carbon monoxide atmosphere used for its preparation. $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl]^+$ is somewhat more stable and undergoes carbon monoxide loss over a matter of minutes. With $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl]^+$ there is a gradual loss of carbon monoxide from the cation in solution over a period of hours with some $[Ir_2Rh(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ production (as monitored by ^{31}P NMR). $[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl]^+$, however, shows no evidence for carbon monoxide loss for up to 1 day. These differences in stability are reflected in the stability of corresponding mononuclear complexes. $Ir(PPh_3)_2(CO)_2Cl$ is a known compound which is formed reversibly from $Ir(PPh_3)_2(CO)Cl$,[15] while $Rh(PPh_3)_2(CO)_2Cl$ is unknown and does not form in detectable quantities upon addition of carbon monoxide to $Rh(PPh_3)_2(CO)Cl$.[16]

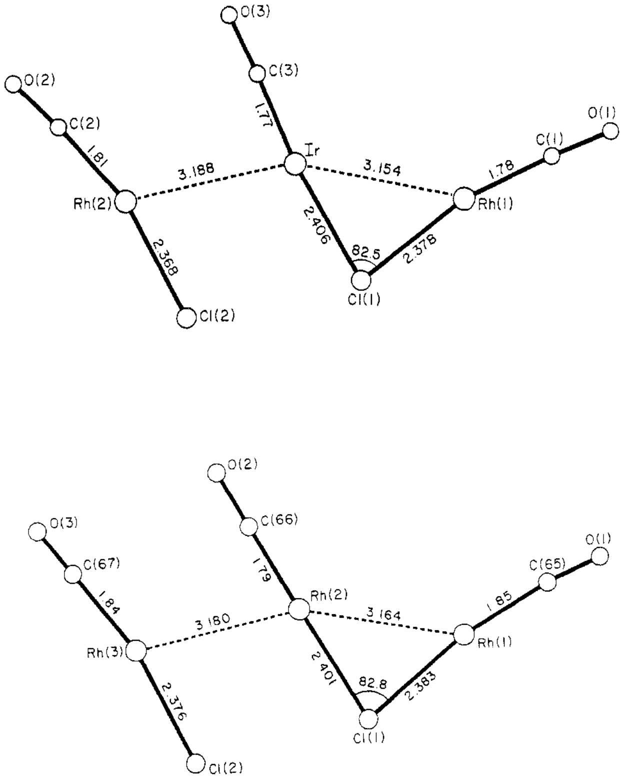

Figure 2. A comparison of some of the in-plane dimensions for $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ (top) and $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ (bottom).[3]

The X-ray Crystal Structure of $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]\cdot2.5CH_2Cl_2$. The solid contains one cation, a normal tetraphenylborate, one ordered dichloromethane molecule, and three other partially occupied dichloromethane sites. There are no unusual contacts between these components. The numbering scheme of the cation is shown in Figure 1. Atomic positional parameters are given in Table III. Tables IV and V present selected interatomic distances and angles.

The structure of the cation reveals the presence of the anticipated, nearly linear RhIrRh unit. The Rh···Ir separations are considerably longer than what would be expected for Rh–Ir single bonds (ca. 2.7–2.8 Å). Consequently, the structure may be viewed as a planar $Ir(CO)ClP_2$ unit sandwiched between two planar $Rh(CO)ClP_2$ units. Within each of these planar units, the geometry is quite comparable to that of other complexes which contain the $M(CO)ClP_2$ or $M(CO)ClAs_2$ units. The P–Rh–P angles, 179.4 (2) and 172.7 (2)°, and the As–Ir–As angle, 172.7 (1)°, are nearly linear. Likewise, the Cl–Ir–CO angle, 173.3 (7)°, is nearly linear while the Cl–Rh–CO angles, 167.2 (6) and 165.3 (6)°, show some bending of the CO groups away from the central Ir–CO group.

The cation can be considered to be made up of two units which are similar to those found in binuclear complexes bridged by bis(diphenylphosphino)methane (dpm). The left portion, including Rh(1) and its ligands and Ir and its ligands, forms a chloro-bridged A-frame unit like that in $Rh_2(\mu\text{-dpm})_2(\mu\text{-Cl})(CO)_2^+$.[17] The right side, including Rh(2) and its ligands and Ir and its ligands, form a face-

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Table III. Atom Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^3)

atom	x	y	z	U	atom	x	y	z	U
Ir	2734 (1)	−29 (1)	2389 (1)	24 (1)[a]	C(37)	5191 (15)	−1864 (12)	3713 (9)	31 (5)
Rh(1)	3366 (1)	187 (1)	3649 (1)	13 (1)[a]	C(38)	5983 (17)	−2592 (12)	3660 (9)	34 (5)
Rh(2)	1137 (1)	62 (1)	1426 (1)	7 (1)[a]	C(39)	5745 (17)	−3300 (13)	3814 (9)	38 (5)
As(1)	2937 (1)	1321 (1)	2072 (1)	14 (1)[a]	C(40)	4687 (16)	−3375 (12)	4064 (8)	30 (5)
As(2)	2297 (2)	−1302 (1)	2766 (1)	17 (1)[a]	C(41)	3863 (17)	−2686 (12)	4135 (9)	32 (5)
P(1)	3779 (4)	1415 (3)	3274 (2)	22 (2)[a]	C(42)	2378 (15)	−1061 (11)	4819 (8)	21 (4)
P(2)	1290 (4)	1372 (3)	1152 (2)	18 (2)[a]	C(43)	2987 (18)	−1117 (12)	5241 (9)	37 (5)
P(3)	2959 (4)	−1054 (3)	4015 (2)	22 (2)[a]	C(44)	2542 (18)	−1007 (13)	5837 (10)	42 (6)
P(4)	767 (4)	−1185 (3)	1771 (2)	22 (2)[a]	C(45)	1434 (15)	−866 (11)	6032 (9)	28 (5)
Cl(1)	1644 (4)	535 (3)	3301 (2)	31 (2)[a]	C(46)	803 (26)	−808 (18)	5609 (13)	83 (9)
Cl(2)	−12 (4)	564 (3)	2321 (2)	27 (2)[a]	C(47)	1297 (24)	−948 (18)	5005 (14)	82 (9)
Cl(3)	2193 (5)	1070 (4)	6280 (3)	48 (2)[a]	C(48)	1970 (14)	−1362 (10)	3632 (7)	17 (4)
Cl(4)	1274 (6)	1363 (5)	5170 (4)	84 (4)[a]	C(49)	3316 (16)	−2303 (11)	2566 (9)	28 (5)
Cl(5)	4193 (13)	5273 (10)	−896 (7)	50	C(50)	4408 (15)	−2302 (12)	2389 (8)	27 (5)
Cl(6)	3074 (13)	4456 (10)	161 (7)	50	C(51)	5170 (20)	−3020 (14)	2233 (10)	49 (6)
Cl(7)	6304 (15)	4477 (11)	4484 (8)	50	C(52)	4785 (20)	−3713 (15)	2261 (11)	55 (7)
Cl(8)	5548 (15)	4466 (11)	3458 (8)	50	C(53)	3731 (18)	−3726 (14)	2436 (10)	47 (6)
Cl(9)	8974 (14)	3154 (11)	4917 (8)	50	C(54)	2930 (17)	−3026 (12)	2590 (9)	34 (5)
Cl(10)	7785 (14)	4420 (11)	5705 (8)	50	C(55)	912 (14)	−1443 (11)	2561 (8)	22 (4)
O(1)	5207 (11)	−20 (8)	4319 (6)	38 (4)	C(56)	1591 (14)	−2097 (11)	1408 (8)	20 (4)
O(2)	1957 (12)	−467 (9)	192 (7)	46 (4)	C(57)	2679 (15)	−2128 (12)	1136 (8)	27 (5)
O(32)	4263 (10)	−746 (8)	1329 (6)	30 (3)	C(58)	3315 (15)	−2817 (11)	893 (8)	24 (5)
C(1)	4491 (15)	46 (12)	4051 (8)	25 (5)	C(59)	2867 (18)	−3499 (13)	930 (10)	40 (6)
C(2)	1682 (14)	−267 (10)	670 (8)	21 (4)	C(60)	1817 (17)	−3491 (13)	1195 (9)	38 (5)
C(3)	3667 (15)	−460 (11)	1764 (8)	25 (5)	C(61)	1146 (17)	−2771 (12)	1434 (9)	32 (5)
C(4)	3605 (15)	2161 (11)	3848 (8)	26 (5)	C(62)	−651 (14)	−1240 (10)	1744 (7)	16 (4)
C(5)	2637 (17)	2662 (12)	4043 (9)	36 (5)	C(63)	−1318 (16)	−1607 (12)	2193 (9)	33 (5)
C(6)	2534 (19)	3167 (14)	4498 (10)	46 (6)	C(64)	−2378 (16)	−1654 (12)	2130 (9)	33 (5)
C(7)	3422 (19)	3248 (15)	4729 (11)	55 (7)	C(65)	−2753 (16)	−1321 (11)	1606 (8)	29 (5)
C(8)	4405 (21)	2718 (15)	4568 (11)	61 (7)	C(66)	−2142 (17)	−976 (12)	1173 (10)	36 (5)
C(9)	4534 (19)	2203 (13)	4098 (10)	44 (6)	C(67)	−1067 (16)	−928 (11)	1230 (9)	30 (5)
C(10)	5149 (13)	1378 (10)	2865 (7)	14 (4)	C(68)	−318 (21)	5259 (16)	1915 (12)	59 (7)
C(11)	5456 (16)	2105 (12)	2586 (9)	31 (5)	C(69)	−860 (18)	5995 (14)	1829 (11)	47 (6)
C(12)	6478 (17)	2089 (13)	2239 (9)	39 (6)	C(70)	−1176 (21)	6352 (16)	1274 (11)	62 (7)
C(13)	7268 (17)	1349 (12)	2177 (9)	35 (5)	C(71)	−878 (22)	5885 (17)	716 (13)	70 (8)
C(14)	6988 (16)	640 (12)	2456 (9)	32 (5)	C(72)	−364 (22)	5014 (17)	779 (13)	74 (8)
C(15)	5950 (15)	646 (11)	2784 (8)	26 (5)	C(73)	−66 (21)	4764 (16)	1362 (11)	62 (7)
C(16)	2888 (14)	1969 (10)	2750 (7)	16 (4)	C(74)	−443 (21)	4014 (15)	2685 (11)	56 (7)
C(17)	4175 (14)	1535 (10)	1500 (7)	17 (4)	C(75)	−1554 (22)	4145 (16)	2571 (12)	64 (8)
C(18)	4144 (16)	2304 (11)	1190 (8)	27 (5)	C(76)	−2124 (23)	3446 (16)	2761 (12)	68 (8)
C(19)	5002 (15)	2480 (12)	782 (9)	29 (5)	C(77)	−1566 (26)	2719 (20)	3033 (14)	91 (10)
C(20)	5947 (16)	1886 (11)	652 (8)	28 (5)	C(78)	−462 (22)	2651 (17)	3136 (12)	70 (8)
C(21)	6008 (15)	1138 (11)	952 (8)	27 (5)	C(79)	9 (17)	3302 (12)	2973 (9)	32 (5)
C(22)	5125 (13)	991 (10)	1375 (7)	15 (4)	C(80)	1458 (15)	4528 (11)	2429 (8)	20 (4)
C(23)	1626 (14)	1906 (10)	1759 (8)	17 (4)	C(81)	2063 (19)	4342 (13)	2896 (11)	45 (6)
C(24)	34 (14)	1994 (11)	965 (8)	20 (4)	C(82)	3103 (26)	4141 (18)	2888 (15)	84 (9)
C(25)	−326 (14)	1812 (11)	462 (8)	20 (4)	C(83)	3737 (23)	4116 (15)	2341 (12)	63 (7)
C(26)	−1222 (15)	2305 (11)	259 (9)	28 (5)	C(84)	3349 (20)	4243 (15)	1820 (12)	56 (7)
C(27)	−1819 (17)	2938 (12)	580 (9)	36 (5)	C(85)	2111 (21)	4487 (15)	1879 (12)	61 (7)
C(28)	−1481 (18)	3115 (13)	1103 (10)	41 (6)	C(86)	−237 (20)	5438 (14)	3067 (11)	51 (7)
C(29)	−592 (15)	2646 (11)	1283 (9)	27 (5)	C(87)	−1048 (22)	5356 (17)	3549 (12)	67 (8)
C(30)	2323 (13)	1567 (9)	501 (7)	11 (4)	C(88)	−1400 (24)	5905 (18)	4022 (14)	80 (9)
C(31)	2219 (15)	2300 (11)	177 (8)	24 (4)	C(89)	−1021 (21)	6608 (17)	3954 (12)	66 (8)
C(32)	3042 (14)	2455 (11)	−298 (8)	22 (4)	C(90)	−163 (26)	6779 (21)	3540 (15)	97 (11)
C(33)	3960 (16)	1875 (11)	−436 (9)	28 (5)	C(91)	137 (25)	6134 (18)	3053 (14)	81 (9)
C(34)	4095 (16)	1138 (11)	−116 (8)	27 (5)	C(92)	2447 (18)	1168 (14)	5472 (10)	46 (6)
C(35)	3290 (14)	981 (11)	358 (8)	21 (4)	C(93)	3480 (52)	4761 (39)	−387 (28)	50
C(36)	4073 (16)	−1948 (12)	3952 (9)	29 (5)	B	125 (22)	4803 (16)	2555 (12)	45 (7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

to-face "dimeric" unit much like that found in $Rh_2(\mu$-dpm$)_2(CO)_2Cl_2$.[18]

The structure is also extremely similar to that of the trirhodium complex $[Rh_3(\mu$-dpmp$)_2(CO)_3(\mu$-$Cl)Cl]^+$.[3] A comparison of the nearly planar sections containing the three metal ions, the three carbon monoxide ligands, and the two chloride ligands is shown in Figure 2. The structural parameters within this section are very similar. Even small details, such as the slightly shorter nonbonded M···M separations between the chloro-bridged metals and the bending of the terminal carbonyl groups away from the central M–CO unit, are preserved in both structures. Because of the lanthanide contraction, iridium and rhodium have similar sizes, and consequently, there are no significant differences in the metal–ligand distances within this planar section.

Spectroscopic Data and the Structure of the Complexes in Solution. The spectroscopic features for the metallomacrocycles **1** and **2** indicate that they contain planar, noninteracting $M(CO)ClP_2$ units. For **1** the values of ν(CO) and ^1J(Rh,P) are typical of those of a number of complexes containing the $Rh(CO)ClP_2$ unit.[19] The yellow color (λ_{max} 367 nm) gives further indication that the rho-

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[18] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.

[19] Balch, A. L.; Guimerans, R. R.; Linehan, J. *Inorg. Chem.* **1985**, *24*, 290 and references therein.

Table IV. Selected Interatomic Distances (Å) for $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$

	At Ir		
Ir···Rh(1)	3.154 (1)	Ir···Rh(2)	3.188 (1)
Ir–As(1)	2.408 (2)	Ir–As(2)	2.407 (2)
Ir–Cl(1)	2.407 (5)	Ir–C(3)	1.76 (2)
	At Rh(1)		
Rh(1)–P(1)	2.324 (5)	Rh(1)–P(3)	2.336 (5)
Rh(1)–Cl(1)	2.378 (5)	Rh(1)–C(1)	1.78 (2)
Rh(1)···Ir	3.154 (1)		
	At Rh(2)		
Rh(2)–P(2)	2.308 (5)	Rh(2)–P(4)	2.318 (5)
Rh(2)–Cl(2)	2.368 (4)	Rh(2)–C(2)	1.81 (2)
Rh(2)···Ir	3.188 (1)		
	Within Carbon Monoxide		
O(1)–C(1)	1.15 (2)	O(2)–C(2)	1.13 (2)
O(3)–C(3)	1.19 (2)		

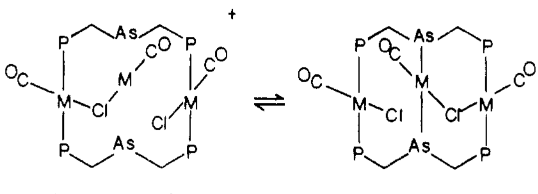
Table V. Selected Interatomic Angles (deg) in $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$

	At Ir		
As(1)–Ir–As(2)	172.7 (1)	As(1)–Ir–Cl(1)	86.4 (1)
As(2)–Ir–Cl(1)	87.6 (1)	As(1)–Ir–C(3)	93.7 (6)
As(2)–Ir–C(3)	92.7 (6)	Cl(1)–Ir–C(3)	173.3 (7)
Rh(1)···Ir···Rh(2)	156.3 (1)	Ir–C(3)–O(3)	177.3 (17)
	At Rh(1)		
P(1)–Rh(1)–P(3)	179.4 (2)	P(1)–Rh(1)–Cl(1)	90.8 (2)
P(3)–Rh(1)–Cl(1)	89.2 (2)	P(1)–Rh(1)–C(1)	88.1 (7)
P(3)–Rh(1)–C(1)	92.1 (7)	Cl(1)–Rh(1)–C(1)	167.2 (6)
Rh(1)–C(1)–O(1)	177.7 (18)		
	At Rh(2)		
P(2)–Rh(2)–P(4)	172.7 (2)	P(2)–Rh(2)–Cl(2)	87.1 (2)
P(4)–Rh(2)–Cl(2)	86.4 (2)	P(2)–Rh(2)–C(2)	92.5 (6)
P(4)–Rh(2)–C(2)	92.9 (6)	Cl(2)–Rh(2)–C(2)	165.3 (6)
Rh(2)–C(2)–O(2)	175.7 (17)		
	At Bridging Chloride		
Ir–Cl(1)–Rh(1)	82.5 (1)		
	At Methylene Carbons		
As(1)–C(16)–P(1)	110.6 (8)	As(1)–C(23)–P(2)	112.5 (8)
As(2)–C(48)–P(3)	115.1 (9)	As(2)–C(55)–P(4)	114.2 (9)

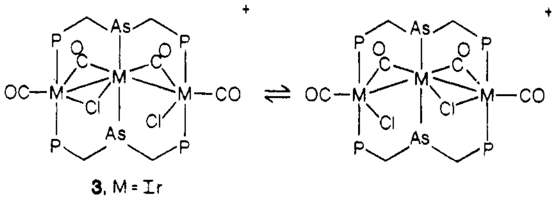
dium centers are widely separated (vide infra).[20] The observation of only a single ^{31}P NMR resonance for both **1** and **2** indicates that they have sufficient conformational flexibility in solution so that the two $M(CO)ClP_2$ environments become equivalent, although in the solid state for **1** they are not equivalent.[9]

The data for each of the four tricarbonyl cations indicate that they have analogous structures. The infrared spectra both in solution and in the solid state show absorption bands for terminal, but not bridging, carbonyl groups. The electronic spectra show similar features for solution samples as well as samples prepared by suspending the solid complexes in a mull. Consequently, we believe that the solid-state structural framework found for both $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ and $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ is the framework present in solutions of the four tricarbonyl species.

In order to accommodate the NMR observations in Table II, it is necessary to postulate that the dynamic process shown in eq 2 is rapidly occurring for these cations. This process renders the two terminal MP_2 units equivalent and accounts for the observation of only a single ^{31}P NMR resonance for each of the tricarbonyls. It also makes the two end M–CO units equivalent and accounts for the presence of only two ^{13}CO resonances in the ^{13}C NMR spectra of the tricarbonyls $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ and $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$. This process has been described in greater detail for $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ and related compounds.[12]



Likewise, the four tetracarbonyls appear to have similar structures. The infrared data indicate the presence of both terminal and bridging carbon monoxide ligands. The structure of $[Ir_3(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$ has been established as **3** through an X-ray diffraction study,[14] and an X-ray analysis of $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$ indicates that it has a similar structure. The latter analysis was begun because $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$ lacks the carbonyl absorption at ca. 1820 cm^{-1} that is found in $[Ir_3(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$. However, refinement of the X-ray data was only carried to the point where we were certain that both structures were essentially identical.



3, M = Ir

In solution these tetracarbonyls are also fluxional. They undergo the bridge/terminal chloride exchange shown in eq 3. This process has been described in detail previously for $[Ir_3(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+$ and some related compounds.[14] In the present examples, the process accounts for the presence of only one ^{31}P NMR resonance for each of the tetracarbonyls and for the observations of only two (not four) carbonyl environments in the ^{13}C NMR spectra of $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+$, $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+$, and $[Ir_3(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+$. Cooling does not freeze out the motion of either of the fluxional processes shown in eq 2 or 3.

The ^{31}P and ^{13}C NMR data are of particular importance in determining the location of the two different metal ions in these complexes. Since naturally abundant rhodium is 100% spin $^1/_2$ ^{103}Rh, the resonances of Rh-bound phosphorus or carbon atoms will appear as doublets, whereas no comparable splitting due to Ir will be found. Consequently, the complexes containing the RhRhRh and RhIrRh chains show doublets in their ^{31}P NMR spectra due to $^1J(Rh,P)$, while the IrRhIr and IrIrIr chains produce singlets. Likewise, the ^{13}C NMR spectra reveal the location of the different metals. The ^{13}C NMR spectrum of $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ shows a singlet for the Ir-bound carbon monoxide and a doublet of triplets (due to $^1J(Rh,C)$ and $^2J(P,C)$) for the two carbon monoxide groups bound to rhodium. Similarly, the ^{13}C NMR spectrum of $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+$ shows a doublet of triplets for the Rh-bound terminal carbon monoxide ligands and a broad resonance for the bridging carbon monoxides (with the expected lower values of $^1J(Rh,C)$ and $^2J(P,C)$ not resolved). With $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+$, $^1J(Rh,C)$ for the bridging carbonyl is resolved, and, as expected, it is about half of that found for terminal carbon monoxide ligands. In this compound the terminal, Ir-bound carbonyl resonance is

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[20] Balch, A. L.; Tulyathan, B. *Inorg. Chem.* **1977**, *16*, 2840.

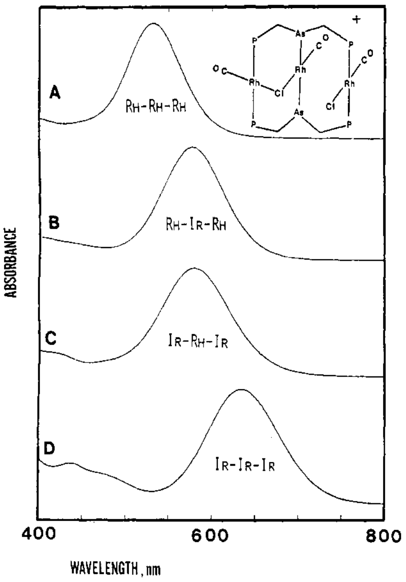

Figure 3. Electronic absorption spectra of dichloromethane solutions of A, $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$, B, $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$, C, $[Ir_2Rh(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$, and D, $[Ir_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$.

a singlet with ^2J(P,C) unresolved.

The ^{31}P and ^{13}C chemical shifts also show systematic effects of iridium or rhodium binding. Thus the ^{31}P resonances for Ir-bound phosphorus atoms are all shifted upfield of their Rh-bound counterparts. Likewise, the ^{13}C resonances for Ir-bound carbon monoxide are all shifted upfield of their Rh-bound counterparts.

Finally and importantly, the NMR results indicate that the mixed-metal chain complexes retain their structures in solution and that, during normal handling, they do not undergo rearrangement or redistribution of the different metal ions within the chains.

Electronic Spectra. The electronic spectra of these complexes are particularly useful for identification of these compounds. Moreover, the electronic spectra of the tricarbonyl complexes, which are shown in Figure 3, can be understood via a simple model. These tricarbonyls can be viewed as an idealized stack (along the z axis) of three planar ML_4 units. To do this we must disregard the bridging ligands (particularly the bridging chloride), the differences between the various ligands, and the bending of the chain. The principle interaction within such a stack will involve the out-of-plane metal orbitals (d_{z^2} and p_z), and our analysis is confined to these orbitals. The d_{z^2} orbital is known to be the highest occupied molecular orbital in planar d^8 complexes with π-acceptor ligands while the p_z orbital is empty.[21] A diagram showing the interaction of the d_{z^2} orbitals and the p_z orbitals in D_{4h} symmetry is shown in Figure 4. The d_{z^2} band is filled, and the p_z band is empty. For binuclear complexes of the type $[Rh_2(\mu\text{-dpm})_2(CNR)_4]^{2+}$, the lowest energy, proximity-shifted,[20] electronic transition has been analyzed in terms of a $d_{z^2} \rightarrow p_z$ transition[22] ($a_{2u} \rightarrow a_{1g}$ in Figure 4) and similar $d_{z^2} \rightarrow p_z$ assignments are likely for other related binuclear and trinuclear complexes. In the spectra of the tricarbonyl complexes in Figure 3, the lowest energy, proximity-shifted absorption band can be assigned to the idealized, symmetry allowed $a_{1g} \rightarrow a_{2u}$ transition in Figure 4. Because the d to p band gap narrows as metal atoms are added to the chain, the transitions in $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ (532 nm) and in $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ (534 nm)[3] occur at lower energy than do the corresponding absorptions in binuclear complexes $Rh_2(\mu\text{-dpm})_2(CO)_2Cl_2$ (450 nm)[18] or $[Rh_2(\mu\text{-dpm})_2(\mu\text{-Cl})(CO)_2]^+$ (442 nm)[23] both of which have similar Rh···Rh separations.

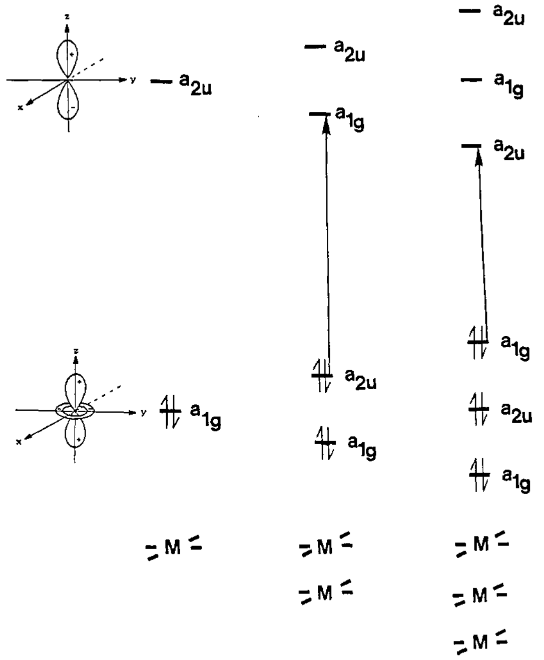

Figure 4. Relative energies of d_{z^2} and p_z orbitals for monomeric, dimeric, and trimeric ML_4 units in D_{4h} symmetry.

Experimental Section

Preparation of Compounds. Dpma,[9] $Ir(CO)_2Cl(p\text{-toluidine})$,[11] $Ir(Ph_3As)_2(CO)Cl$,[24] $Rh(SbPh_3)_2(CO)Cl$,[13] and $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$[12] were prepared by previously published procedures. Deoxygenated solvents and inert atmosphere conditions were used in the preparation of all of the complexes reported here. The pure complexes all exhibit good stability toward air and can be handled without special precautions to exclude dioxygen or moisture.

$Rh_2(\mu\text{-dpma})_2(CO)_2Cl_2$. A solution of 88.3 mg (0.227 mmol) of $Rh_2(CO)_4(\mu\text{-Cl})_2$ in 7 mL of toluene was added slowly (10 min) with stirring to a solution of 250 mg (0.455 mmol) of dpma in 8 mL of toluene. The reaction mixture turned yellow immediately and became red by the end of the addition. After the mixture was stirred for an additional 5 min, a red precipitate of $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]Cl$ formed. This precipitate was removed by filtration. Addition of 25 mL of diethyl ether to the yellow filtrate, followed by cooling at −20 °C for several hours, caused the yellow crystalline product to precipitate. The product was collected by filtration and washed successively with diethyl ether and acetone; yield 0.25 g, 77%. Anal. Calcd for $C_{66}H_{58}As_2Cl_2O_2P_4Rh_2$: C, 55.29; H, 4.08. Found: C, 54.71; H, 4.01.

$Ir_2(\mu\text{-dpma})_2(CO)_2Cl_2$. A solution of 282 mg (0.722 mmol) of $Ir(CO)_2Cl(p\text{-toluidine})$ in 40 mL of toluene was added slowly (1 h) with stirring to a solution of 400 mg (0.727 mmol) of dpma in 12 mL of toluene. The reaction mixture turned yellow immediately and became light orange by the end of the addition. After the orange solution was stirred for 1 h, the volume was reduced under vacuum to approximately 5 mL. Addition of diethyl ether precipitated the pale yellow crystalline product. The product was collected by filtration and washed with diethyl ether; yield 0.45 g, 78%. Anal. Calcd for $C_{66}H_{58}As_2Cl_2Ir_2O_2P_4{\cdot}CH_4Cl_2$: C, 47.42; H, 3.56; Cl, 8.36. Found: C, 48.21; H, 3.58; Cl, 8.39.

$[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$. A solution of 24.2 mg (0.062 mmol) of $Ir(CO)_2Cl(p\text{-toluidine})$ in 2 mL of di-

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(21) Brady, R.; Flynn, B. R.; Geoffroy, G. R.; Gray, H. B.; Peone, J., Jr.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485.

(22) Fordyce, W. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 985.

(23) Olmstead, M. M.; Lindsay, C. H.; Benner, L. S.; Balch, A. L. *J. Organomet. Chem.* **1979**, *179*, 289.

(24) Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 725.

chloromethane was added slowly (10 min) with stirring to a solution of 100 mg (0.062 mmol) of $\mathrm{Ir_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ and 50 mg (0.15 mmol) of sodium tetraphenylborate in 4 mL of dichloromethane and 2 mL of methanol. The reaction mixture turned dark green immediately, and after 10 min orange crystals of $\mathrm{[Ir_3(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]}$ began to precipitate. After the solution was stirred for 1 h, 8 mL of methanol was added slowly. After the mixture was left standing for 30 min, the orange crystalline 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. The crystalline product was collected by filtration and washed with diethyl ether; yield 0.075 g, 56%. Anal. Calcd for $\mathrm{C_{92}H_{78}As_2BCl_2Ir_3O_4P_4}$: C, 50.70; H, 3.61; Cl, 3.25. Found: C, 50.79; H, 3.51; Cl, 3.50.

$\mathrm{[Ir_2Rh(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]}$. A solution of 12 mg (0.031 mmol) of $\mathrm{Rh_2(CO)_4(\mu\text{-}Cl)_2}$ in 2 mL of dichloromethane was added slowly (10 min) with stirring to a cold (−20 °C) solution of 100 mg (0.062 mmol) of $\mathrm{Ir_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ and 80 mg (0.24 mmol) of sodium tetraphenylborate in 4 mL of dichloromethane and 1 mL of methanol. The solution turned dark red immediately, and after 10 min red crystals began to precipitate. An additional 8 mL of methanol was added slowly and the solution allowed to stand for 30 min. The red crystalline 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 0.085 g, 66%. Anal. Calcd for $\mathrm{C_{92}H_{78}As_2BCl_2Ir_2O_4P_4Rh}$: C, 52.86; H, 3.76; Cl, 3.39. Found: C, 52.99; H, 3.70; Cl, 3.42.

$\mathrm{[Ir_2Rh(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]}$. A solution of 27 mg (0.031 mmol) of $\mathrm{Rh(SbPh_3)_2(CO)Cl}$ in 1 mL of dichloromethane was added slowly (10 min) with stirring to a solution of 50 mg (0.031 mmol) of $\mathrm{Ir_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ in 2 mL of dichloromethane and 1 mL of methanol. The solution rapidly turned dark blue. After 1 h a solution of 50 mg (0.15 mmol) of sodium tetraphenylborate in 1 mL of methanol was added, and dark blue crystals precipitated. An additional 3 mL of methanol was added slowly, and the mixture was allowed to stand for 1 h. The blue, crystalline 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 0.035 g, 55%. Anal. Calcd for $\mathrm{C_{91}H_{78}As_2BCl_2Ir_2O_3P_4Rh}$: C, 53.00; H, 3.81; Cl, 3.44. Found: C, 53.26; H, 3.75; Cl, 3.61.

$\mathrm{[Rh_2Ir(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]}$. A solution of 27.4 mg (0.07 mmol) of $\mathrm{Ir(CO)_2Cl}$(*p*-toluidine) in 4 mL of methanol was added slowly (30 min) with stirring to a cold (−20 °C) solution of 100 mg (0.07 mmol) of $\mathrm{Rh_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ in 4 mL of dichloromethane. The reaction mixture turned dark red-purple rapidly. After the addition was complete, a solution of 50 mg (0.15 mmol) of sodium tetraphenylborate in 2 mL of methanol was added slowly to the cold solution. Blue-purple crystals precipitated and were 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 0.085 g, 65%. Anal. Calcd for $\mathrm{C_{91}H_{78}As_2BCl_2IrO_3P_4Rh_2}$: C, 55.40; H, 3.99; Cl, 3.59. Found: C, 55.96; H, 3.87; Cl, 3.36.

$\mathrm{[Rh_3(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]}$. In addition to the method described in ref 12, this complex can also be prepared by using the following procedure. A solution of 6.1 mg (0.016 mmol) of $\mathrm{Rh_2(CO)_4(\mu\text{-}Cl)_2}$ in 2 mL of methanol was added rapidly with stirring to a solution of 45 mg (0.032 mmol) of $\mathrm{Rh_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ in 2 mL of dichloromethane. The reaction mixture immediately turned red. Addition of a solution of 40 mg (0.12 mmol) of sodium tetraphenylborate in 2 mL of methanol caused rose-colored crystals to precipitate. The solution was allowed to stand for 30 min, and then the product was collected by filtration and washed successively with methanol and diethyl ether; yield 0.045 g, 76%. The product was identified as $\mathrm{[Rh_3(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]}$ by infrared and UV–visible spectroscopy.

$\mathrm{[Ir_3(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]}$. $\mathrm{Ir_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ (25 mg, 0.016 mmol) and $\mathrm{Ir(AsPh_3)_2(CO)Cl}$ (13.5 mg, 0.016 mmol) were dissolved in 4 mL of dichloromethane and 1 mL of methanol. The solution gradually became dark green in color over a period of several hours. After 30 min, the ^{31}P NMR spectrum contained five singlets. The largest singlet corresponded to unreacted $\mathrm{Ir_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ (area = 100). The second largest singlet (area = 40) is believed to be due to $\mathrm{[Ir_3(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl]^+}$. A pair of singlets of equal intensity (total area = 20) is believed to be due to a nonfluxional isomer of this complex in which a terminal chloride and terminal carbonyl group on an end iridium atom have exchanged positions.[25] The fifth singlet (area = 12) was due to a species identified as $\mathrm{[Ir_3(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+}$. After a reaction time of 6 h unreacted $\mathrm{Ir_2(\mu\text{-}dpma)_2(CO)_2Cl_2}$ was still present, although in a significantly lesser amount (area = 100). The singlet corresponding to $\mathrm{[Ir_3(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl]^+}$ increased in size (area = 115) as did the pair of singlets corresponding to its isomer (area = 30). The amount of $\mathrm{[Ir_3(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+}$ also increased (area = 70). At this point carbon monoxide was bubbled through the reaction mixture, and it turned from dark green to yellow in color. The ^{31}P NMR at this point showed only $\mathrm{[Ir_3(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl]^+}$ to be present.

$\mathrm{[Rh_2Ir(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]}$. This complex was prepared in solution by dissolving 30 mg (0.016 mmol) of $\mathrm{[Rh_2Ir(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]}$ in 4 mL of dichloromethane and bubbling carbon monoxide through the solution for 30 s. The color rapidly changed from blue to red. The product was characterized spectroscopically in solution under an atmosphere of carbon monoxide. Crystals suitable for X-ray diffraction study were obtained by slow diffusion of carbon monoxide saturated diethyl ether into the solution. $\mathrm{[Rh_2Ir\{\mu\text{-}(C_6H_5)_2PCH_2As(C_6H_5)CH_2P(C_6H_5)_2\}_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][B(C_6H_5)_4]\cdot}n\mathrm{CH_2Cl_2}$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 12.794 (3) Å, b = 16.972 (3) Å, c = 22.584 (4) Å, α = 85.07 (1)°, β = 79.62 (2)°, and γ = 77.12 (2)° at 140 K. The structure was solved, but when it was found to be essentially like that of $\mathrm{[Ir_3(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]}$,[14] including disorder in the bridging and terminal chloride positions, but with a RhIrRh central chain, refinement was stopped.

$\mathrm{[Rh_3(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh]}$. This complex was prepared and characterized in solution by using the procedure described above for $\mathrm{[Rh_2Ir(\mu\text{-}dpma)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]}$. The complex was not isolated due to the extreme ease with which it loses carbon monoxide.

Spectroscopic Measurements. The ^{31}P NMR spectra were recorded with proton decoupling on a Nicolet NT-200 Fourier transform spectrometer operating at 81 MHz or on a Nicolet NT-360 spectrometer at 145.8 MHz. The ^{1}H and ^{13}C NMR spectra were recorded at 360 and 90.5 MHz, respectively, on a Nicolet NT-360 FT spectrometer. The references were as follows: ^{31}P, external 85% phosphoric acid; ^{1}H, ^{13}C, internal tetramethylsilane. The high frequency positive convention, recommended by IUPAC, has been used in reporting all chemical shifts. Infrared spectra were recorded from mineral oil mulls by using a Perkin-Elmer 180 spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8450A spectrophotometer.

X-ray Data Collection, Solution, and Refinement for $\mathrm{[Rh_2Ir(\mu\text{-}dpma)_2(CO)_3(\mu\text{-}Cl)Cl][B(C_6H_5)_4]\cdot 2^1/_2CH_2Cl_2}$. Well-formed green-brown parallelepipeds were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. Crystal data, data collection procedures, and refinement of the structure are summarized in Table VI. The lattice was found to be triclinic by standard procedures using the software associated with the Syntex $\mathrm{P2_1}$ diffractometer. The data were collected at 140 K by using a locally modified LT-1 low-temperature apparatus on the Syntex $\mathrm{P2_1}$ diffractometer. The data were corrected for Lorentz and polarization effects.

The structure was solved by locating the two rhodium and iridium atoms using the Patterson method (FMAP 8 routine of SHELXTL, version 4, 1984, Nicolet Instrument Corporation, Madison, WI). Other atoms were located from successive difference Fourier maps. Final cycles of refinement were made with anisotropic thermal parameters for iridium, rhodium, arsenic, phosphorus, and the nondisordered chlorines, and isotropic

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[25] Precedent for such a structure has been established by the X-ray crystal structure of $\mathrm{[Rh_3\{\mu\text{-}(Me_2PCH_2)_2PMe\}_2(CO)_3(\mu\text{-}Cl)Cl]^+}$: Oram, D. E.; Balch, A. L., unpublished results.

Table VI. Crystal Data for $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][B(C_6H_5)_4]\bullet 2.5CH_2Cl_2$

formula	$C_{93.5}H_{79}As_2BCl_7IrO_3P_4Rh_2$
fw incl solvent	2181.41
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
cryst dimens, mm	0.20 × 0.45 × 0.62
color and habit	green-brown parallelepipeds
unit cell dimens (140 K)	
a, Å	12.618 (2)
b, Å	17.057 (5)
c, Å	22.545 (6)
α, deg	85.23 (2)
β, deg	79.73 (2)
γ, deg	77.38 (2)
V, Å^3	4654 (2)
ρ(calcd), g cm^{-3} (at 140 K)	1.56
Z	2
radiatn λ, Å (graphite monochromator)	Mo K$\bar{\alpha}$, 0.071069
μ(Mo Kα), cm^{-1}	29.6
range of absorption correctn factors	1.65–3.32
scan type, $2\theta_{max}$, deg	ω, 45
scan range, deg	1.2
octants	$+h,\pm k,\pm l$
scan speed, deg min^{-1}	60
check refl, interval no.	2 measured every 200 reflectns
no. of unique data	12174
no. of data $I > 3\sigma(I)$	7036
R	0.071
R_w	0.079
no. of parameters	526

thermal parameters for all remaining atoms. Hydrogen atoms were refined by using a riding model in which an idealized C–H vector of 0.96-Å length is recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[26] An absorption correction (XABS) was applied.[27] One molecule of dichloromethane was present at full occupancy and not disordered. The atoms of three disordered dichloromethane molecules were assigned equivalent isotropic U values of 0.05 and were allowed to refine with variable occupancy. The final occupancies were 0.367 (8) for Cl(5)···Cl (6), 0.330 (9) for Cl(7)···Cl (8), and 0.343 (8) for Cl (9)···Cl (10). Carbon atoms for the latter two dichloromethanes were not located due to the disorder. Two low angle reflections suffering from extinction were removed from the data set for the final cycles of refinement. A conventional R factor of 0.071 was obtained. The final difference map showed some residual electron density in the vicinity of the rhodium atoms and the dichloromethane molecules, but otherwise no significant features were present.

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Registry No. 1, 97551-38-7; 2, 97570-01-9; $Rh_2(CO)_4(\mu\text{-Cl})_2$, 14523-22-9; $Ir(CO)_2Cl$(p-toluidene), 14243-22-2; $[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$, 100700-75-2; $[Ir_2Rh(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$, 103190-53-0; $[Ir_2Rh(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$, 103148-39-6; $Rh(SbPh_3)_2(CO)Cl$, 17967-63-4; $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$, 103148-41-0; $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$, 100082-61-9; $[Ir_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$, 103148-43-2; $Ir(AsPh_3)_2(CO)Cl$, 15682-62-9; $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$, 103190-55-2; $[Rh_2Ir(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]\cdot nCH_2Cl_2$, 103190-56-3; $[Rh_2Ir(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]\cdot XCH_2Cl_2$, 103148-44-3; Ir, 7439-88-5; Rh, 7440-16-6.

Supplementary Material Available: Listings of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom positions (7 pages); a listing of structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

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(26) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(27) The method obtains an empirical absorption tensor from an expression relating F_o and F_c: Hope, H.; Moezzi, B. Department of Chemistry, University of California, Davis.

(28) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)