

Selective Dihydrogen Addition to Iridium Ions in Polynuclear Complexes Derived from the Metallomacrocycles $M_2(CO)_2Cl_2\{(\mu-Ph_2PCH_2)_2AsPh\}_2$ ($M = Ir$ or Rh)

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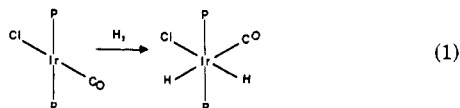
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Dihydrogen addition to $Ir_2(CO)_2Cl_2(\mu-dpma)_2$ (dpma is bis((diphenylphosphino)methyl)phenylarsine) yields $Ir_2(H)_4(CO)_2Cl_2(\mu-dpma)_2$ which, in turn, reacts with $[Cu(NCCH_3)_4][PF_6]$ to yield $[Ir_2(H)_4Cu(\mu-Cl)Cl(CO)_2(\mu-dpma)_2][PF_6]$. Yellow crystals of $[Ir_2(H)_4Cu(\mu-Cl)Cl(CO)_2(\mu-dpma)_2][PF_6] \cdot 3.5CH_2Cl_2$ belong to the monoclinic space group $P2_1/n$ with $a = 17.713$ (5) Å, $b = 18.906$ (6) Å, $c = 23.077$ (6) Å, $\beta = 92.26$ (2)°, and $Z = 4$ at 130 K. Least-squares refinement of 11 738 reflections with 759 parameters yielded $R = 0.062$. The structure consists of two $(H)_2Ir(CO)ClP_2$ units with trans phosphines and cis (CO) and Cl ligands and a central copper ion which is bonded to two arsenic atoms, a bridging chloride, and one iridium ($Cu-Ir = 2.822$ (1) Å). The fluxional cation undergoes caged turnstile motion in solution. Dihydrogen addition to the heterotrinnuclear complexes $Ir_2Ag(CO)_2Cl_3(\mu-dpma)_2$, $[Ir_2CuCl_2(CO)_2(\mu-dpma)_2]^+$, $[Ir_2Rh(CO)_3(\mu-Cl)Cl(\mu-dpma)_2]^+$, and $[Rh_2Ir(CO)_3(\mu-Cl)Cl(\mu-dpma)_2]^+$ results in oxidative addition to one iridium to give localized $(H)_2Ir(CO)ClP_2$ groups.

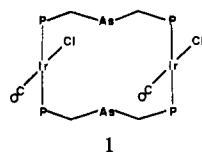
Introduction

Because of its relevance to catalytic hydrogenation, the oxidative addition of dihydrogen to iridium complexes has been extensively investigated since the discovery by Vaska of the reversible reaction shown in eq 1.¹ Kinetic and



mechanistic studies have indicated that the addition occurs in a concerted process to produce a cis dihydride adduct.² Complementary work by Eisenberg on the cis phosphine complexes $Ir(CO)Cl$ (chelating diphosphine) have shown that concerted cis addition occurs under kinetic control.³

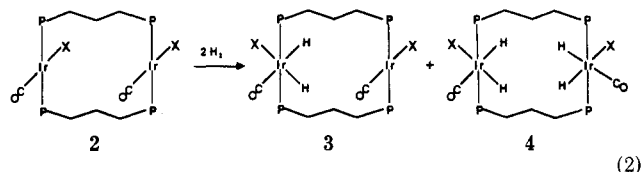
Recent work in this laboratory has produced the metallomacrocyclic 1, $Ir_2(CO)_2Cl_2(\mu-dpma)_2$, where dpma is



bis((diphenylphosphino)methyl)phenylarsine, which incorporates two Vaska-type $Ir(CO)ClP_2$ (1) units into a cyclic structure.⁴ The ability of 1 to complex a variety of both transition-metal ions^{4,5} and main-group metal ions⁶

through bonding to the arsenic, iridium, chloride, and/or carbon monoxide portions of 1 has been demonstrated. Here we describe some of the reactions of 1 and its transition-metal complexes with dihydrogen. Since the metal-metal interactions in phosphine-bridged aggregates of this sort are more labile than generally encountered in the traditional-metal carbonyl clusters, a greater variety of metal-metal and metal-hydride interactions may be anticipated.

Several studies closely related to the work described here have appeared. Addition of dihydrogen to the metallomacrocyclic 2 has been carried out (eq 2). For $X = Cl$ a



mixture, both the di- and tetrahydride 3 and 4, is present under 1 atm of dihydrogen⁷ while with $X = Br$ or I the tetrahydride 4 is exclusively formed.⁸ Complexes 3 and 4 and the dihydrogen adducts of 1 should be able to bind another metal ion via hydride bridging. This behavior has been demonstrated by Caulton for reactions of other iridium hydrides with Cu^+ .⁹

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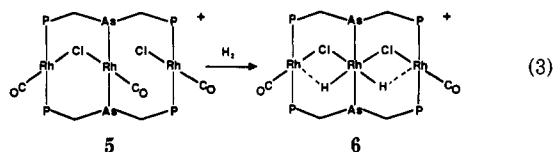
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Table I. NMR Spectral Data in Dichloromethane Solution

compd	¹ H NMR						³¹ P NMR δ, ppm
	hydride			methylene			
	δ, ppm	J(H,H), Hz	J(P,H), Hz	δ, ppm	J(H,H), Hz	J(H,P), Hz	
Ir ₂ (H) ₄ (CO) ₂ Cl ₂ (μ-dpma) ₂	-18.08 -7.91	4.6	12.6 18.3	4.04 2.96	11.9		3.4
[Ir ₂ (H) ₄ Cu(CO) ₂ Cl ₂ (μ-dpma) ₂][PF ₆]	-18.18 -7.29	5.4	11.8 14.1	3.30 3.10	12.3	3.5	3.1
[Ir ₂ (H) ₂ Cu(CO) ₂ Cl ₂ (μ-dpma) ₂][PF ₆]	-18.36 -8.62	2.2 1.8	12.6 13.5	{ 3.56 } { 3.26 } { 3.10 } { 2.51 }	12.8	4.2	18.8 1.1
[Ir ₂ (H) ₂ Ag(CO) ₂ Cl ₃ (μ-dpma) ₂]	-18.53 -6.77	4.7 4.0	13.3 14.2	{ 3.71 } { 3.39 } { 2.98 } { 2.80 }	11.3	5.4	21.9 -4.0
[Ir ₂ (H) ₂ Rh(CO) ₃ Cl ₂ (μ-dpma) ₂][BPh ₄] (A)	-17.89 -8.81		12.0 12.9 ^c				5.5 -8.3
[Ir ₂ (H) ₂ Rh(CO) ₃ Cl ₂ (μ-dpma) ₂][BPh ₄] (B)	-18.42 -7.91		13.5 11.7 ^d				5.6 3.9
[Rh ₂ Ir(H) ₂ (CO) ₃ Cl ₂ (μ-dpma) ₂][BPh ₄]	-13.48 -7.59		8.7 14.1				25.8 (120.7) ^b 22.4 (111.4) ^b

^a Braces indicate pair of protons on a single methylene group as verified by decoupling experiment. ^b ¹J(Rh,P). ^c Apparent J(Rh,H) also 12.9 Hz. ^d Apparent J(Rh,H) also 11.7 Hz.

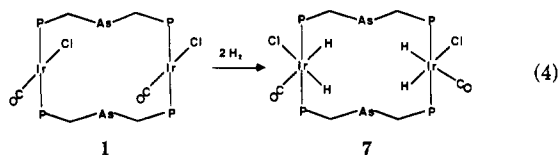
Although Rh(CO)Cl(PPh₃)₂ does not add dihydrogen, the trinuclear complex **5** does react with dihydrogen according to eq 3 to yield the cation **6** with loss of carbon



monoxide.¹⁰ The hydride ligands in **6** are best considered as semibridging hydrides. The Rh-H distances to the central rhodium are normal (1.55, 1.48 Å) for terminal hydrides, while the Rh...H distances, which involve the end rhodiums, are longer (2.02 Å). Nevertheless, the ¹H NMR spectrum of **6** shows substantial coupling to both the central rhodium (¹J(Rh,H) = 24.7 Hz) and to the terminal rhodium atoms (¹J(Rh,H) = 10.9 Hz).¹⁰ Since work on **1** and its rhodium analogue has made available the series of complexes [Ir₃(CO)₃Cl(μ-Cl)(μ-dpma)₂]⁺, [Ir₂Rh(CO)₃Cl(μ-Cl)(μ-dpma)₂]⁺, [Rh₂Ir(CO)₃Cl(μ-Cl)(μ-dpma)₂]⁺, and [Rh₃(CO)₃Cl(μ-Cl)(μ-dpma)₂]⁺,^{5c} we can explore the effect of metal ion location within these nearly linear chains on the site of dihydrogen addition.

Results

Dihydrogen Addition to Ir₂(CO)₂Cl₂(μ-dpma)₂. Storage of Ir₂(CO)₂Cl₂(μ-dpma)₂ in dichloromethane under 1 atm of dihydrogen for 16 h results in its conversion into the tetrahydride **7** as shown in eq 4. The product has been



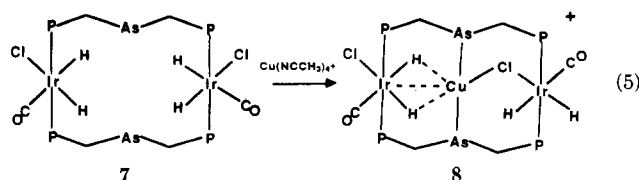
isolated as a colorless solid which is stable toward loss of dihydrogen. Solutions of **7** are also stable. Purging a dichloromethane solution with dinitrogen does not result in loss of dihydrogen. This stability contrasts markedly

with the behavior of the corresponding macrocycle Ir₂(CO)₂Cl₂(dppp)₂ (eq 2). A pressure of at least 3 atm of dihydrogen was required to discharge the yellow color of unreacted Ir(CO)ClP₂ groups, but upon release of H₂ pressure, the tetrahydride lost dihydrogen.

¹H and ³¹P NMR spectra that confirm the formation of the tetrahydride, and other new compounds, are collected in Table I. As with other Ir(H)₂(CO)Cl(PR₃)₂ complexes with trans phosphines, two hydride resonances are observed at ca. -8 and -18 ppm. These are due to the hydrides trans to carbon monoxide and trans to chloride, respectively. Each of these resonances is split into a 1:2:1 triplet by coupling to the two cis phosphine ligands and is split further by smaller coupling between the two hydride ligands. The methylene region of the spectrum consists of an AB quartet with H,H coupling of 11.9 Hz due to the fundamental inequivalence of the two methylene protons. In accord with the symmetrical nature of the tetrahydride, all four methylene groups are equivalent. Coupling of these protons to phosphorus was not resolved. The ³¹P NMR spectrum of **7** in dichloromethane consisted of a single resonance at 3.4 ppm. In contrast, the ³¹P chemical shift for the parent Ir₂(CO)₂Cl₂(μ-dpma)₂ (**1**) is 18.6 ppm. Throughout this work a consistent upfield shift of the ³¹P resonance of an individual P₂Ir(CO)Cl group of ca. 15–20 ppm is found upon dihydrogen addition to that unit.

The infrared spectrum of **7** shows bands at 2214, 2092, and 2080 cm⁻¹ due to Ir-H stretching and 1990 and 1979 cm⁻¹ due to carbon monoxide stretching vibrations.

Insertion of [Cu(NCCH₃)₄]⁺ into Ir₂(H)₄(CO)₂Cl₂(μ-dpma)₂. Addition of [Cu(NCCH₃)₄][PF₆] to **7** proceeds smoothly in dichloromethane according to eq 5 to yield the



pale yellow salt **8**[PF₆], which crystallized after the addition of ethyl ether. The product redissolves in dichloromethane and has an electrical conductivity in that solvent appropriate for a 1:1 electrolyte.

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}_2(\text{H})_4\text{CuCl}_2(\text{CO})_2(\text{dpma})_2]\text{PF}_6 \cdot 3.5\text{CH}_2\text{Cl}_2$

	x	y	z	U^a		x	y	z	U^a
Ir(1)	4562 (1)	7661 (1)	2126 (1)	15 (1)*	C(37)	2072 (8)	6344 (7)	1592 (5)	32 (4)*
Ir(2)	7559 (1)	7689 (1)	823 (1)	16 (1)*	C(38)	1640 (6)	6530 (6)	1116 (5)	27 (3)*
Cu	5842 (1)	8039 (1)	1505 (1)	22 (1)*	C(39)	1954 (6)	6909 (6)	674 (4)	22 (3)*
As(1)	6555 (1)	8708 (1)	2168 (1)	15 (1)*	C(40)	2710 (6)	7101 (6)	721 (4)	21 (3)*
As(2)	5399 (1)	7882 (1)	564 (1)	16 (1)*	C(41)	4583 (6)	6214 (5)	1160 (4)	18 (3)*
P(1)	5167 (2)	8263 (1)	2897 (1)	15 (1)*	C(42)	4251 (7)	5779 (5)	714 (4)	21 (3)*
P(2)	8082 (2)	8421 (1)	1542 (1)	16 (1)*	C(43)	4533 (7)	5106 (6)	628 (5)	31 (4)*
P(3)	4168 (2)	7085 (1)	1269 (1)	16 (1)*	C(44)	5159 (8)	4855 (7)	976 (6)	38 (4)*
P(4)	6870 (2)	7155 (1)	64 (1)	18 (1)*	C(45)	5476 (7)	5288 (6)	1389 (5)	28 (4)*
Cl(2)	6758 (2)	7069 (1)	1525 (1)	19 (1)*	C(46)	5185 (7)	5971 (5)	1504 (5)	23 (3)*
Cl(1)	4438 (2)	6590 (2)	2733 (1)	33 (1)*	C(47)	4335 (6)	7569 (5)	597 (4)	22 (3)*
O(1)	2965 (5)	8109 (5)	2420 (4)	40 (3)*	C(48)	5389 (6)	8593 (5)	-37 (4)	20 (2)
O(2)	8838 (5)	6600 (5)	851 (4)	38 (3)*	C(49)	5092 (7)	8482 (6)	-600 (5)	27 (2)
C(1)	3545 (7)	7963 (6)	2312 (5)	28 (4)*	C(50)	5143 (8)	8991 (6)	-1024 (6)	35 (3)
C(2)	8353 (6)	6994 (6)	849 (5)	24 (3)*	C(51)	5500 (8)	9622 (7)	-876 (6)	36 (3)
C(3)	4948 (6)	9201 (5)	2943 (4)	16 (3)*	C(52)	5819 (7)	9744 (7)	-320 (5)	32 (3)
C(4)	5269 (7)	9605 (6)	3404 (6)	33 (4)*	C(53)	5756 (7)	9220 (6)	97 (5)	25 (2)
C(5)	5156 (8)	10325 (7)	3408 (6)	40 (4)*	C(54)	5834 (6)	7074 (5)	173 (4)	21 (2)
C(6)	4737 (8)	10648 (7)	2984 (6)	37 (4)*	C(55)	6911 (7)	7579 (6)	-647 (5)	30 (3)
C(7)	4384 (8)	10279 (7)	2535 (6)	41 (5)*	C(56)	6593 (8)	7251 (7)	-1130 (6)	37 (3)
C(8)	4489 (7)	9541 (6)	2520 (5)	28 (4)*	C(57)	6675 (9)	7557 (8)	-1688 (7)	51 (4)
C(9)	5003 (7)	7942 (6)	3626 (5)	24 (3)*	C(58)	7037 (9)	8177 (8)	-1744 (7)	48 (4)
C(10)	5550 (7)	7602 (6)	3966 (5)	27 (3)*	C(59)	7308 (9)	8542 (8)	-1256 (7)	49 (4)
C(11)	5366 (7)	7370 (7)	4515 (5)	31 (4)*	C(60)	7256 (8)	8220 (7)	-708 (6)	35 (3)
C(12)	4667 (8)	7432 (7)	4715 (5)	36 (4)*	C(61)	7142 (7)	6233 (6)	-58 (5)	28 (3)
C(13)	4121 (8)	7751 (7)	4372 (5)	34 (4)*	C(62)	6987 (8)	5760 (7)	387 (6)	37 (3)
C(14)	4266 (7)	8007 (7)	3836 (5)	36 (4)*	C(63)	7208 (8)	5055 (7)	365 (6)	40 (3)
C(15)	6196 (6)	8277 (6)	2884 (4)	21 (3)*	C(64)	7573 (10)	4821 (9)	-123 (7)	53 (4)
C(16)	6659 (6)	9691 (5)	2363 (5)	22 (3)*	C(65)	7725 (10)	5268 (9)	-569 (7)	57 (4)
C(17)	6400 (6)	10212 (5)	1983 (5)	21 (3)*	C(66)	7528 (9)	5977 (8)	-530 (7)	47 (4)
C(18)	6510 (7)	10923 (6)	2102 (5)	31 (4)*	Cl(3)	1793 (3)	8797 (2)	450 (2)	55 (1)*
C(19)	6874 (7)	11124 (6)	2606 (6)	34 (4)*	Cl(4)	3064 (3)	9173 (3)	1213 (2)	69 (2)*
C(20)	7146 (7)	10611 (6)	3008 (5)	29 (4)*	Cl(5)	4264 (3)	4149 (2)	2278 (2)	76 (2)*
C(21)	7060 (7)	9896 (6)	2884 (5)	23 (3)*	Cl(6)	2799 (3)	4824 (3)	2417 (3)	94 (2)*
C(22)	7609 (6)	8395 (5)	2228 (4)	16 (3)*	Cl(7)	527 (3)	-16 (2)	1315 (2)	63 (2)*
C(23)	9051 (6)	8177 (5)	1737 (4)	17 (3)*	Cl(8)	954 (3)	625 (2)	222 (2)	74 (2)*
C(24)	9593 (6)	8267 (6)	1322 (5)	25 (3)*	Cl(9)	9634 (3)	4306 (2)	8 (2)	64 (2)*
C(25)	10331 (7)	8003 (7)	1419 (5)	32 (4)*	C(67)	2156 (8)	8810 (8)	1177 (6)	44 (3)
C(26)	10516 (7)	7660 (6)	1938 (5)	29 (4)*	C(68)	3728 (9)	4898 (8)	2139 (7)	54 (4)
C(27)	9981 (7)	7588 (6)	2348 (5)	27 (3)*	C(69)	413 (10)	697 (9)	840 (7)	58 (4)
C(28)	9252 (6)	7843 (5)	2253 (4)	18 (3)*	C(70)	10439 (18)	4748 (16)	111 (13)	47 (7)
C(29)	8139 (6)	9352 (5)	1388 (5)	21 (3)*	P(5)	6801 (2)	2947 (2)	1041 (1)	28 (1)*
C(30)	7713 (7)	9659 (6)	921 (5)	27 (4)*	F(1)	6816 (5)	2257 (4)	646 (3)	47 (3)*
C(31)	7694 (8)	10385 (6)	844 (5)	37 (4)*	F(2)	7547 (5)	3218 (5)	772 (4)	65 (4)*
C(32)	8115 (10)	10813 (7)	1220 (6)	48 (5)*	F(3)	6776 (5)	3646 (4)	1433 (3)	50 (3)*
C(33)	8563 (8)	10520 (6)	1677 (6)	41 (5)*	F(4)	6047 (5)	2675 (5)	1317 (4)	61 (3)*
C(34)	8561 (8)	9803 (6)	1750 (6)	36 (4)*	F(5)	7277 (5)	2547 (4)	1546 (4)	50 (3)*
C(35)	3137 (6)	6906 (5)	1193 (4)	20 (3)*	F(6)	6328 (6)	3352 (4)	538 (3)	56 (3)*
C(36)	2825 (7)	6518 (6)	1650 (5)	26 (3)*					

^a Parameters with an asterisk are equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

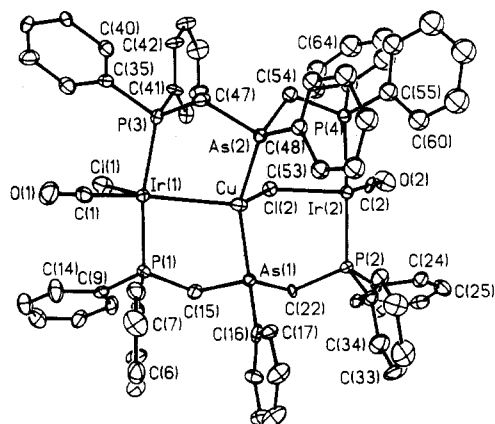


Figure 1. A perspective view of the $[\text{Ir}_2(\text{H})_4\text{Cu}(\mu\text{-Cl})\text{Cl}(\text{CO})_2(\mu\text{-dpma})_2]^+$ showing 50% thermal ellipsoids for heavy atoms and uniform, arbitrarily sized circles for carbon atoms.

Crystals of $[\text{Ir}_2(\text{H})_4\text{Cu}(\text{CO})_2(\mu\text{-Cl})\text{Cl}(\mu\text{-dpma})_2][\text{PF}_6] \cdot 3.5\text{CH}_2\text{Cl}_2$ that were suitable for X-ray crystallography

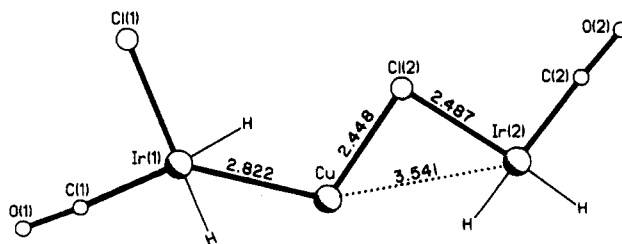


Figure 2. A view of the plane of $[\text{Ir}_2(\text{H})_4\text{Cu}(\mu\text{-Cl})\text{Cl}(\text{CO})_2(\mu\text{-dpma})_2]^+$ that contains the three metals and the mono- and diatomic ligands.

were obtained. The asymmetric unit contains one cation, one entirely normal hexafluorophosphate, and three and one half molecules of dichloromethane. All contacts between these entities are normal. A drawing of the cation is presented in Figure 1. Atomic positional parameters are given in Table II. Table III contains selected interatomic distances and angles.

The cation has no crystallographically imposed symmetry. However, all of the carbonyl, hydride, and chloride

Table III. Selected Interatomic Distances (Å) and Angles (deg) for [Ir₂(H)₄Cu(CO)₂Cl₂(μ-dpma)₂][PF₆]₂·3.5CH₂Cl₂

Distances			
Ir(1)-Cu	2.822 (1)	Ir(2)···Cu	3.541 (1)
Ir(1)-P(1)	2.337 (3)	Ir(2)-P(2)	2.325 (3)
Ir(1)-P(3)	2.339 (3)	Ir(2)-P(4)	2.326 (3)
Ir(1)-Cl(1)	2.475 (3)	Ir(2)-Cl(2)	2.487 (3)
Ir(1)-C(1)	1.953 (13)	Ir(2)-C(2)	1.924 (11)
Cu-As(1)	2.321 (2)	Cu-As(2)	2.297 (2)
Cu-Cl(2)	2.448 (3)		
Angles			
P(1)-Ir(1)-P(3)	169.4 (1)	P(2)-Ir(2)-P(4)	168.2 (1)
P(1)-Ir(1)-Cl(1)	90.9 (1)	P(2)-Ir(2)-Cl(2)	92.1 (1)
P(1)-Ir(1)-C(1)	95.2 (3)	P(2)-Ir(2)-C(2)	96.53 (3)
P(3)-Ir(1)-Cl(1)	93.9 (1)	P(4)-Ir(2)-Cl(2)	89.4 (1)
P(3)-Ir(1)-C(1)	94.3 (3)	P(4)-Ir(2)-C(2)	95.0 (3)
Cl(1)-Ir(1)-C(1)	90.7 (3)	Cl(2)-Ir(2)-C(2)	95.3 (3)
Cu-Ir(1)-P(1)	84.8 (1)		
Cu-Ir(1)-P(3)	84.7 (1)		
Cu-Ir(1)-Cl(1)	125.8 (1)		
Cu-Ir(1)-C(1)	143.5 (3)		
Ir(1)-Cu-As(1)	103.3 (1)	Ir(1)-Cu-As(2)	101.3 (1)
As(1)-Cu-As(2)	148.2 (1)	Ir(1)-Cu-Cl(2)	110.2 (1)
As(1)-Cu-Cl(2)	93.0 (1)	As(2)-Cu-Cl(2)	97.1 (1)
Ir(1)-C(1)-O(1)	177.5 (11)	Ir(2)-C(2)-O(2)	177.3 (10)
Ir(2)-Cl(2)-Cu	91.7 (1)		

ligands as well as the metal atoms lie in a nearly planar array with the bridging dpma ligands placed above and below that plane. A view looking down upon that plane is given in Figure 2.

The basic metallocyclic structure of **1** is retained in **8**. The copper ion sits at the center. It is coordinated to each of the two arsenic atoms and Cl(2) which forms a bridge to Ir(2). The Cu-As distances (2.321 (2), 2.297 (2) Å) are comparable to those found in the hydride-free complexes [Ir₂CuI₂(CO)₂(μ-dpma)₂]⁺ and [Rh₂CuCl₂(CO)₂(μ-dpma)₂]⁺.^{5g} The Cu-Cl(2) distance (2.448 (3) Å) is within the range (2.3–2.5 Å) found for other Cu-Cl bonds.^{5g} The copper ion is 3.541 (1) Å from Ir(2) but much closer to Ir(1), 2.822 (1) Å.

Within the cation the two iridium environments are no longer equivalent. Each iridium is bound to two trans phosphines and a terminal carbonyl. Ir(1) is bound to a terminal chloride, while Ir(2) is bound to a bridging chloride. Hydride positions were not located directly but can be inferred to be trans to the chloride and carbonyl ligands on each iridium. Otherwise the carbonyl and chloride ligands would be mutually trans as seen in other derivatives of **1** and in the rhodium analogue of **1**. The angular distribution of ligands about the two iridium atoms appears fairly regular, although there is some bending of the P-Ir-P angles (169.4 (1)° at Ir(1) and 168.2 (1)° at Ir(2)). This is due to the stresses placed on the dpma bridges as they connect the three different metal ions.

The nature of the Ir(1)(H)₂/Cu interaction deserves attention. There is no need for any bond. In themselves, the Ir(P)₂(CO)Cl(H)₂ unit and the CuAs₂Cl unit are perfectly respectable coordination units. However, the Ir(1)···Cu separation (2.822 (1) Å) is significantly shorter than the Cu···Ir separations (2.938–3.086 Å) and Cu···Rh separations (3.084 Å) seen in [Ir₂CuI₂(CO)₂(μ-dpma)₂]⁺ and in [Rh₂CuCl₂(CO)₂(μ-dpma)₂]⁺.^{5g} Strong Ir(H)₂Cu bonding has been seen before, and Cu(NCCH₃)₄⁺ is known to add to other iridium hydrides.^{11,12} In both *fac*-(Me₂PhP)₃HIr(H)₂Cl₂Cu⁺ (Cu-Ir = 2.502 (4), 2.529 (4) Å)¹¹ and [*fac*-(Me₂PhP)₃Ir(H)₃]₂Cu³(NCCH₃)₃³⁺ (Cu-Ir =

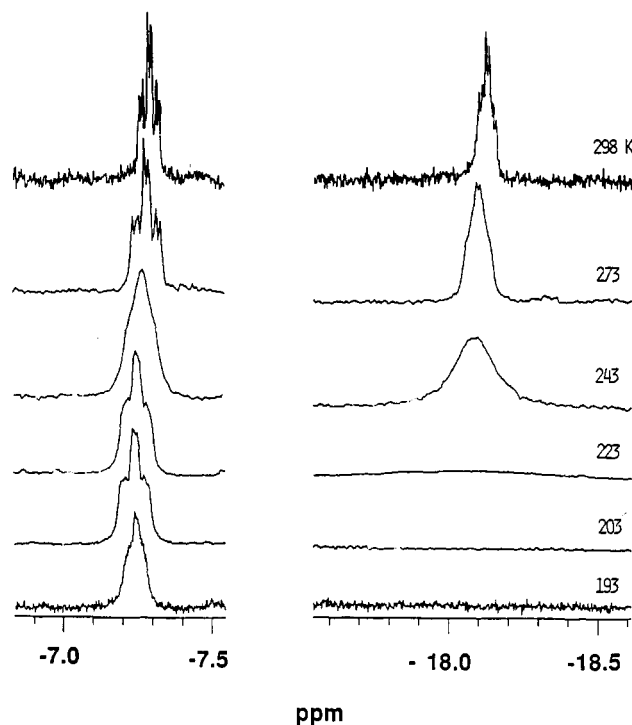


Figure 3. Variable-temperature 360-MHz ¹H NMR spectra (hydride region) of [Ir₂(H)₄Cu(μ-Cl)Cl(CO)₂(μ-dpma)₂][PF₆]₂ in dichloromethane-*d*₂.

2.793 (9) Å),¹² where IrH₂Cu and IrHCu units are present, respectively, the Ir-Cu distances are shorter than those seen in **8**. Moreover, the infrared spectra of *fac*-(Me₂PhP)₃HIr(H)₂Cl₂Cu⁺ and *fac*-(Me₂PhP)₃Ir(H)₃]₂Cu₃(NCCH₃)₃³⁺ both show bridging Ir-H-Cu absorptions in the infrared spectra in the 1886–1624 cm⁻¹ region. No corresponding absorptions are seen in the infrared spectrum of **8**. Consequently, we believe that in **8**, there is an attractive interaction between the copper ion and the Ir-H units. This may be ionic, similar to the copper-halide interactions seen in [Ir₂CuI₂(CO)₂(μ-dpma)₂]⁺, or it may be of the semibridging sort seen in **6**. This interaction is much weaker than those found in the *fac*-(R₃P)₃Ir₂H₃ complexes of Caulton where only the IrHCu bridges support the polynuclear complex.

The NMR spectral data obtained for **8** in dichloromethane solution indicate that the molecule must be fluxional. The [¹H]³¹P NMR spectrum consists of a single line at 25 °C and is unaffected on cooling to -60 °C. The chemical shift of this resonance is similar to, but the resonance is distinct from, that of its precursor, the tetrahydride **7**. At 25 °C the ¹H NMR spectrum shows two hydride resonances at -7.23 and -18.1 ppm due to the hydrides trans to carbon monoxide and chloride on each iridium. These can be seen in the top trace of Figure 3. The coupling of these resonances to one another and to the two adjacent phosphorus ligands is apparent. Thus there exists a mechanism that renders the different hydride environments on Ir(1) and Ir(2) equivalent. The methylene resonances of **8** at 25 °C show up as a single AB quartet. These data indicate that at 25 °C that two HIr(CO), the two trans HIrCl, the four phosphorus, and the four methylene environments become equivalent. A likely means for this involves a concerted rotation of the (H)₂-Ir(CO)Cl units about the trans P-Ir-P pivots as shown in Figure 4. In the process the Ir-H units pass through the space between the iridium and copper ions. Such inversion reactions of M-H-M units have been reported previously for related bis(diphenylphosphino)methane complexes.¹³

(11) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 6874.

(12) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 1759.

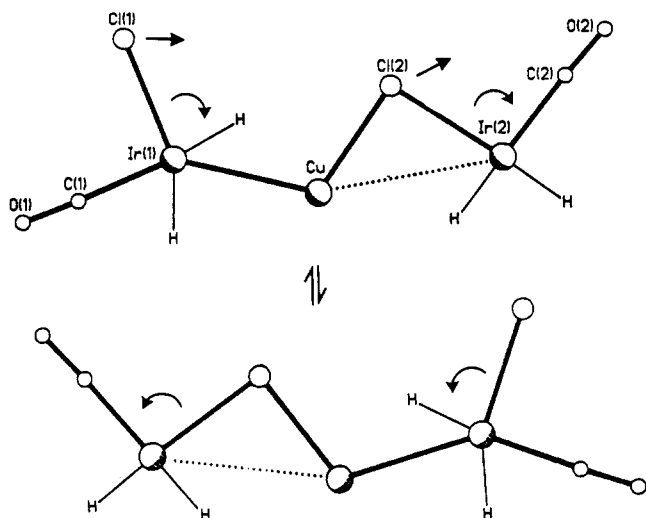
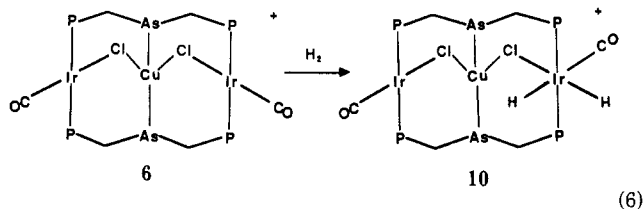


Figure 4. Proposed movement of in-plane ligands of $[\text{Ir}_2(\text{H})_4\text{Cu}(\mu\text{-Cl})\text{Cl}(\text{CO})_2(\mu\text{-dpma})_2]^+$ during fluxional process.

On cooling the ^1H NMR spectral data show changes consistent with the occurrence of a dynamic exchange process. Figure 3 shows the effect of cooling on the Ir-H resonances. The Ir-H resonances trans to the Ir-Cl bond undergoes selective broadening, which is explicable if the chemical shift difference for the two different trans Cl-Ir-H units is larger than the chemical shift difference for the two different trans OC-Ir-H units. Further cooling was not practical, but the changes observed were reversed on warming. On cooling, the methylene resonances broadened as expected for slowing of the dynamic process.

Dihydrogen Addition to $[\text{Ir}_2\text{CuCl}_2(\text{CO})_2(\mu\text{-dpma})_2]^+$ (9). Exposure of a solution of $[\text{Ir}_2\text{CuCl}_2(\text{CO})_2(\mu\text{-dpma})_2][\text{PF}_6]$ (9)^{5g,14} to 1 atm of dihydrogen leads to addition to only one of the two iridium ions as shown in eq 6. The product 10 has been isolated as a yellow powder,



but crystals suitable for X-ray crystallography could not be grown. Solutions of the adduct 10, which behaves as a 1:1 electrolyte, are stable and show no loss of dihydrogen or of the copper ion. The ^1H NMR spectrum shows two hydride resonances with coupling to one another and to two phosphines as expected for structure 10. The methylene region, however, shows four methylene resonances which are consistent with an asymmetric structure in which the two iridium environments differ. The ^{31}P NMR spectrum (shown in the top trace of Figure 5) with broad-band decoupling shows two equally intense resonances, one near the positions, 23.3–16.5 ppm, found for the parent 9 and the other near that found for the corresponding tetrahydrides 7 and 8. Thus, the spectrum is consistent with dihydrogen addition to only one iridium

(13) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Gressel, M. C. *J. Am. Chem. Soc.* 1983, 105, 5642.

(14) In solution this complex exists in two forms: a symmetrical one with all phosphorus nuclei equivalent (i.e. 9) and an unsymmetrical one with two types of phosphorus nuclei.^{5g} Only the symmetrical structure 9 is known definitively from X-ray studies. Both forms react with dihydrogen to yield a single hydride.

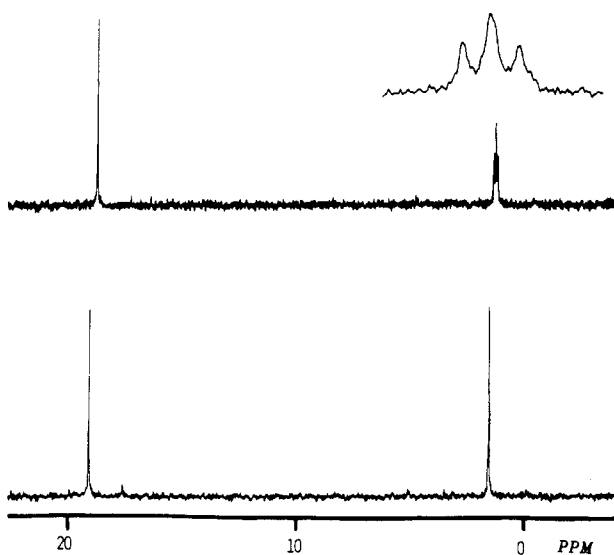


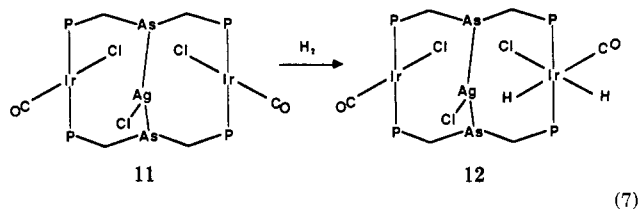
Figure 5. ^{31}P NMR spectra (121.5 MHz) of $[\text{Ir}_2(\text{H})_4\text{Cu}(\mu\text{-Cl})\text{Cl}(\text{CO})_2(\mu\text{-dpma})_2][\text{PF}_6]$ in dichloromethane/acetone (4:1 v/v). Top: selective decoupling of protons with chemical shifts 10–0 ppm range. Bottom: full broad-band proton decoupling.

ion. This is verified by observation of the ^{31}P spectrum under conditions in which the methylene protons were selectively decoupled but the hydride protons were not decoupled. The resulting spectrum is shown in the lower trace of Figure 5. The upfield resonance, the one we ascribe to the $\text{P}_2\text{Ir}(\text{H})_2(\text{CO})\text{Cl}$ unit in 10, appears as a 1:2:1 triplet while the low-field resonance remains as a singlet. The apparent P-H coupling constant observed in the ^{31}P NMR spectrum, 10.5 Hz, is in reasonable agreement with values of 12.6 and 13.5 Hz seen in the ^1H spectrum.

The infrared spectrum of 10 shows Ir-H stretching vibrations at 2214 and 2073 cm^{-1} and carbonyl absorption at 1951 cm^{-1} ; no indications of a Ir-H-Cu bridging band in the 1800–1650 cm^{-1} region were seen.

Addition of a second mole of dihydrogen to 10 should yield 8 (or an isomer thereof). However, we have not detected 8 under the hydrogenation conditions reported here. We expect that with higher dihydrogen pressure the rate of dihydrogen addition to 10 might be accelerated and 8 obtained, but we have not examined the reaction under higher dihydrogen pressures.

Dihydrogen Addition to $\text{Ir}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$ (11).^{5h} The reaction proceeds in accord with eq 7 to give



the yellow complex 12 which has been isolated in 60% yield. The infrared spectrum shows $\nu(\text{Ir-H})$ at 2157 and 2078 cm^{-1} and $\nu(\text{CO})$ at 1970 and 1954 cm^{-1} . No bands attributable to an Ir-H-Ag group were present.

The NMR data are in accord with the schematic structure 12. The fully proton decoupled ^{31}P NMR spectrum consists of two equally intense singlets at 21.9 (Ir(CO)CIP₂ group) and -4.0 ppm (Ir(H)₂(CO)CIP₂ group). When the decoupler is tuned so that the hydride protons are not decoupled, the upfield resonance appears as a 1:2:1 triplet much like that shown in the bottom trace in Figure 5. The apparent H-P coupling constant of 13 Hz is in good agreement with the values observed from the proton data.

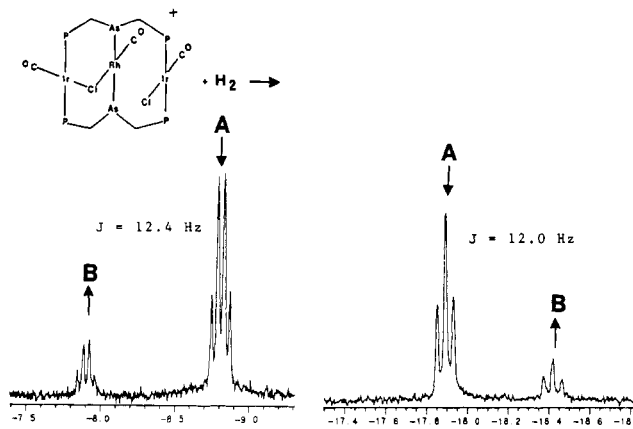
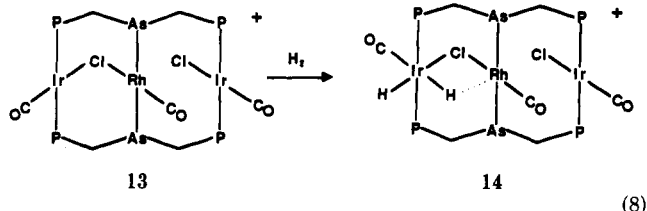


Figure 6. 360-MHz ¹H NMR spectra of the reaction of dihydrogen with dichloromethane-*d*₂ solutions of [Ir₂Rh(CO)₃(μ-Cl)Cl(μ-dpma)₂]⁺. The peaks with downward pointing arrows decay while those with upward pointing arrows grow in intensity overtime.

The ¹H NMR spectrum shows that the two hydride resonances are coupled to one another and to the two adjacent phosphorus atoms with coupling parameters consistent with our other observations. The methylene region indicates that four distinct methylene proton environments are present.

Dihydrogen Addition to [Ir₂Rh(CO)₃(μ-Cl)Cl(μ-dpma)₂]⁺ (13).^{5c} The reaction, which proceeds via eq 8,



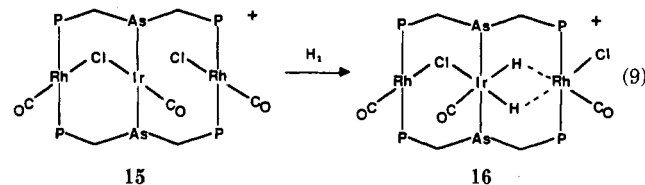
has been monitored spectroscopically, since it has not been possible to isolate the products in pure form. The reaction initially shows formation of a new hydride species, 14, within 5 min of exposure of the solution to dihydrogen. During that time the solution's color changes from bluish purple to red. On standing, however, the initial hydride resonances decay in intensity while a new, but quite similar, set replaces them. Figure 6 shows the hydride region at a point where both species are present. The resonances labeled A are due to the first formed species, while those labeled B are due to the second. The chemical shifts observed for both sets of resonances are consistent with the formation of a Ir(H)₂(CO)ClP₂ group within the molecule. The upfield resonance of each group consists of a 1:2:1 triplet with coupling appropriate for proton-phosphorus coupling to the cis phosphines. Coupling between the cis hydrides, however, must be too small to be resolved, for it was not observed. The downfield resonances in both compounds differ from all previous examples since they appear as 1:3:3:1 quartets with an apparent coupling constant of 12.9 Hz for species A and 11.7 Hz for species B. This pattern can readily be explained if the hydride involved is coupled to the usual two adjacent phosphines and to another spin 1/2 nucleus as well. The only reasonable candidate for that added spin 1/2 nucleus is the central rhodium. Consequently, we postulate that the hydrides trans to the carbon monoxide ligands in A and B are weakly coupled to the central rhodium. The observed Rh,H coupling constant is significantly smaller than those found for typical terminal rhodium hydrides where ¹J(Rh,H) is in the range 15–30 Hz. However, the

observed coupling is nearly identical with that seen for 6 where the semibridging hydride has a 24.7 Hz coupling to the directly bound rhodium and a 10.9 Hz coupling to the other rhodium.

Observation of the ³¹P NMR spectra during this reaction confirmed the interpretation based on the ¹H NMR data. Initially, two equally intense ³¹P NMR resonances are observed after hydrogenation. On standing, these decrease in intensity while a new pair grow into the spectrum.

On the basis of these observations, we suspect that species A and B are two isomeric forms of the cation. The differences between them must involve changes that produce only minor variation at the hydrogenated iridium since the basic spectral features at that site are unaltered. One likely possibility involves exchange of positions of the carbonyl and chloride ligands on the iridium that is remote from the site of hydrogenation. Another possibility might involve the changing nature of the halide bridging along the IrRhIr chain. The proposed structure for 14 has an analogue in binuclear chemistry. Addition of dihydrogen to [RhIr(μ-dpm)₂(μ-Cl)(CO)₂]⁺ yields [RhIr(H)₂(μ-dpm)₂(μ-Cl)(CO)₂]⁺.¹⁵ The latter has been characterized by X-ray crystallography and found to have a structure similar to the left side of 14 with both hydrides bound to iridium and one semibridging to rhodium. The ¹H NMR spectrum of this binuclear cation also shows evidence for semibridging hydride with coupling to rhodium of similar magnitude to that seen for 14.

Dihydrogen Addition to [Rh₂Ir(CO)₃(μ-Cl)Cl(μ-dpma)₂]⁺ (15). The addition proceeds as shown in eq 9.



After exposure to 1 atm of dihydrogen, the solution changes color from bluish purple to red. Observation of the ¹H NMR spectrum shows the growth of two equally intense hydride resonances at -7.59 and -13.48 ppm. These resonances appear at different chemical shifts than all other hydrides described here because they are bound to an IrAs₂(CO)Cl group rather than an IrP₂(CO)Cl group. Each resonance is a simple doublet. The coupling constants of 14.1 and 8.7 Hz are too small for terminal rhodium hydrides but are in the range reported for the semibridging hydrides in 6 and its analogues.¹⁰ The fact that the two couplings are unequal rules out the possibility that it results from H-H coupling between the two nonequivalent hydrides. The lack of the characteristic coupling to phosphorus, which has been seen in all other hydrides reported here, is consistent with dihydrogen addition to an iridium ion that is bound to arsenic (natural abundance 100%, spin 3/2). This reaction has also been monitored by ¹³C NMR spectroscopy. The essential point of this experiment was to determine whether the carbonyl group on the iridium atom was retained as shown in eq 9 or lost as it would be if the reaction proceeded (eq 3) as established for the trirhodium complexes [Rh₃(CO)₃Cl(μ-Cl)(μ-dpmp)₂]⁺ and [Rh₃(CO)₃Cl(μ-Cl)(μ-dpma)₂]⁺. The ¹³C NMR spectrum of ¹³CO-enriched 15 consists of a singlet at 168.8 ppm due to the iridium-bound carbon monoxide and a doublet of triplets at 188.9 ppm, with ¹J(Rh,C) = 76.1 Hz and ²J(Rh,P) = 14.5 Hz. Upon exposure to dihydrogen the resonances of 15 are lost and a new resonance

(15) Cowie, M., personal communication.

at 172.0 ppm as well as a complex multiplet in the 187–192 ppm region appears. The sharp singlet at 172.0 ppm indicates that the carbonyl group bound to iridium is retained. The complex multiplet at lower field results from the presence of two Rh–CO groups, each with coupling from carbon to both rhodium and phosphorus. Overlapping resonances and signal-to-noise considerations did not allow us to sort out the individual coupling constants.

Discussion

The results presented here show that dihydrogen addition to the group of complexes examined occurs at a single site, and that, despite the fluxional properties of many dpma-bridged trinuclear complexes⁵ (which can lead to mobility of carbon monoxide ligands, halide ligands, and metal–metal bonds), the hydrides remain localized at that single metal center. Moreover, when there are different metal centers that might react with dihydrogen, it is always the iridium centers that undergo the addition. This is probably a result of the fact that, of the metal centers involved, iridium forms the stronger metal–hydrogen bond. In related work, dihydrogen addition specifically to the iridium centers in (CO)(PPh₃)IrMo(CO)₃(η⁵-C₅H₄P-(C₆H₄-p-CH₃)) has been reported.¹⁶

In contrast to this behavior, several examples of reactions of dihydrogen resulting in addition across two metal centers have been reported.¹⁷ Although the trinuclear complexes studied here are well set up for multicentered additions and the ligands in general have a high degree of mobility, multicentered addition does not result. However, it has been suggested^{17a} and observed^{17e} that multicenter additions begin by addition to a single center and that a hydride ligand then migrates to the second center. Our results, which show addition to single centers in polynuclear species, are, in a sense, then consistent with these previous studies.

Experimental Section

Preparation of Compounds. Ir₂Cl₂(CO)₂(μ-dpma)₂ (1),⁴ Ir₂AgCl₃(CO)₂(μ-dpma)₂ (11),^{5b} [Ir₂CuCl₂(CO)₂(μ-dpma)₂][PF₆]₂ (9),^{5c} [Ir₂Rh(CO)₃Cl₂(μ-dpma)₂][BPh₄]₂ (13),^{5c} [Rh₂Ir(CO)₃Cl₂(μ-dpma)₂][BPh₄]₂ (15)^{5c} and [Cu(NCCH₃)₄][PF₆]₂¹⁸ were prepared by reported procedures.

Ir₂(H)₄(CO)₂Cl₂(μ-dpma)₂ (7). A solution of 150 mg (0.093 mmol) of Ir₂(CO)₂Cl₂(μ-dpma)₂ in 3 mL of deoxygenated dichloromethane was added by syringe into a 50-mL flask filled with hydrogen at 1 atm of pressure. Hydrogen was then bubbled through the yellow solution for several minutes. The solution was stirred for 16 h under a dihydrogen atmosphere. At this point the solution was colorless. The volume of the solution was reduced to 1 mL under a stream of hydrogen and diethyl ether added slowly to precipitate colorless crystals. The product was collected by filtration and washed with diethyl ether; yield 120 mg, 80%. IR (Nujol): five peaks due to Ir–H and CO stretches are observed at 2214, 2092, 2080, 1990, and 1979 cm⁻¹.

[Ir₂(H)₄Cu(CO)₂(μ-Cl)Cl(μ-dpma)₂][PF₆]₂ (8). A solution of 22 mg (0.056 mmol) of [Cu(NCCH₃)₄][PF₆]₂ in 2 mL of dichloromethane was added to a colorless solution of 90 mg (0.056 mmol) of Ir₂(H)₄(CO)₂Cl₂(μ-dpma)₂ in 3 mL of dichloromethane. After the pale yellow solution was stirred for 1 h, 25 mL of diethyl ether was added. The pale yellow product was collected by filtration, washed with diethyl ether, and vacuum dried; yield 91

Table IV. Crystal Data and Collection Parameters for [Ir₂(H)₄CuCl(μ-Cl)(CO)₂(μ-dpma)₂][PF₆]₂·3.5CH₂Cl₂

formula	C _{69.5} H ₆₉ As ₂ CuCl ₉ F ₆ Ir ₂ O ₂ P ₅
fw	1742.90
color and habit	yellow parallelepipeds
cryst system	monoclinic
space group	P2 ₁ /n
a, Å	17.713 (5)
b, Å	18.906 (6)
c, Å	23.077 (6)
β, deg	92.26 (2)
V, Å ³	7722 (4)
T, K	130
Z	4
cryst dimens, mm	0.15 × 0.20 × 0.37
d _{calc} , g cm ⁻³	1.50
radiatn (Å)	Mo Kα (λ = 0.710 69)
μ(Mo Kα), cm ⁻¹	52.4
range of transmissn factors	0.33–0.55
diffractometer	P2 ₁ , graphite monochromator
scan method	ω, 0.9° range, 0.9° offset for bkgnd
scan speed, deg min ⁻¹	8
2θ range, deg	0–55
octants collected	h, k, ±l
no of data collected	18 863
no. of unique data	17 214 [R(merge) = 0.005]
no. of data used in refinement	11 738 [I > 2σ(I)]
no. of parameters refined	759
R ^a	0.062
R _w ^a	0.066 [w = 1/σ ² (F _o)]

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

mg, 90%. Anal. Calcd for C₆₆H₆₂As₂Cl₂CuF₆Ir₂O₂P₅: C, 43.4; H, 3.4; Cl, 3.9. Found: C, 42.8; H, 3.4; Cl, 4.0. Conductivity (CH₂Cl₂ solution): λ_M = 58.1 Ω⁻¹ mol⁻¹ cm². IR (Nujol): ν(CO) + ν(Ir–H) 2211 m, 2097 vs, 2065 vs, 2002 m cm⁻¹.

[Ir₂(H)₂Cu(CO)₂Cl₂(μ-dpma)₂][PF₆]₂ (10). A stream of dihydrogen was bubbled through a solution of 90 mg of [Ir₂Cu(CO)₂Cl₂(μ-dpma)₂][PF₆]₂ in 10 mL of dichloromethane. During this time the color lightened from orange to bright yellow. Diethyl ether (10 mL) was added slowly to give a light yellow precipitate. This was collected by filtration, washed with diethyl ether and vacuum dried; yield 59 mg, 65%. Anal. Calcd for C₆₆H₆₀As₂Cl₂CuF₆Ir₂O₂P₅: C, 43.5; H, 3.3; Cl, 3.9. Found: C, 42.2; H, 3.3; Cl, 3.8. Conductivity (dichloromethane): λ_M = 58.5 Ω⁻¹ M⁻¹ cm². IR (Nujol): ν(CO) + ν(Ir–H) 2214 w, 2073 m, 1951 s cm⁻¹; ν(PF): 833 s, br cm⁻¹.

Ir₂(H)₂Ag(CO)₂Cl₃(μ-dpma)₂ (12). A stream of dihydrogen was passed through a solution of 75 mg (0.043 mmol) of Ir₂Ag(CO)₂Cl₃(μ-dpma)₂ in 15 mL of dichloromethane for 1 h. The solution was then stirred under 1 atm of dihydrogen for 3 days. The volume of the yellow solution was reduced to 5 mL, and 10 mL of diethyl ether was added. The yellow precipitate was collected by filtration, washed with diethyl ether, and vacuum dried; yield 60 mg, 73%. Anal. Calcd for C₆₆H₆₀AgAs₂Cl₃Ir₂O₂P₄: C, 45.1; H, 3.4; Cl, 6.1. Found: C, 44.3; H, 3.5; Cl, 6.3. IR (Nujol): ν(CO) + ν(Ir–H) 2157 m, 2078 s, 1970 s, 1954 s cm⁻¹.

X-ray Structure Determination and Refinement. Crystals of [Ir₂(H)₄Cu(CO)₂(μ-Cl)Cl(μ-dpma)₂][PF₆]₂·3.5CH₂Cl₂ were grown by diffusion of ethyl ether into a dichloromethane solution of the complex. A suitable crystal was mounted on a glass fiber using silicone grease and positioned in the cold stream of the X-ray diffractometer. Only random fluctuations (<2%) in the intensities of two standard reflections was observed during the course of data collection. Crystal data 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 5, installed on a Data General Eclipse computer. Scattering factors and corrections for anomalous dispersion were from ref 19.

The structure was solved by Patterson methods. An absorption correction was applied.²⁰ Final refinement was carried out with

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anisotropic thermal parameters for all except 23 non-hydrogen atoms, due to the limitations of SHELXTL. The 23 atoms left as isotropic were normal carbon atoms. Hydrogen atoms were included at calculated positions by using a riding model, with C-H of 0.96 Å and $U_H = 1.2U^*_C$. The largest shift in the final cycle of refinement was 0.005 for y of C(57). There are no exceptionally short intermolecular contacts in the structure.

The final difference map has 50 peaks with heights between 1.0 and 2.7 $e \text{ \AA}^{-3}$. Four of the largest fifteen appear to be hydride ligands. These were not well-behaved upon refinement, but contour maps drawn through and parallel to the $\text{Ir}_2\text{CuCl}_2(\text{CO})_2$

plane reveal that these electron densities have radial symmetry and central maxima. Their presence can also be inferred from the vacant coordination sites at Ir.

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Supplementary Material Available: Complete tables of bond distances and angles, hydrogen atom positions, and anisotropic thermal parameters (7 pages); a listing of structure factor amplitudes (70 pages). Ordering information is given on any current masthead page.

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Transformation of a Trialkynylphosphine Oxide to a 2-Alkylidene-1,2-dihydro-3-phosphete *P*-Oxide Ligand by Pt-H Addition and Rearrangement Reactions. Activation of Molecular Hydrogen by a Platinum(II) Complex

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Addition of the Pt-H bond of $[\text{trans-Pt}(\text{H})(\text{PEt}_3)_2(\text{THF})]^+$ to the C≡C triple bond of the alkynyl substituent of $\text{O}=\text{PPh}_2(\text{C}\equiv\text{CPh})$ occurs regioselectively to give a Pt,P μ -alkenylidene complex. Similar addition of a Pt-H bond to the trialkynylphosphine oxide $\text{O}=\text{P}(\text{C}\equiv\text{CCMe}_3)_3$ presumably occurs also, but a facile insertion rearrangement takes place to form a novel 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand. Complexes containing this heterocyclic alkenyl ligand react with molecular hydrogen at -78°C and at atmospheric pressure to give neutral monohydride complexes. The X-ray structure of one such complex has been determined: $\{\text{trans-Pt}[\text{C}=\text{C}(\text{CMe}_3)\text{P}(\text{OBF}_3)(\text{C}\equiv\text{CCMe}_3)\text{C}=\text{C}(\text{CMe}_3)(\text{H})][\text{P}(n\text{-Pr})_3]_2(\text{H})\}$; monoclinic; $P2_1/c$; $Z = 4$; $a = 11.006(4) \text{ \AA}$, $b = 21.435(5) \text{ \AA}$, $c = 19.518(5) \text{ \AA}$; $\beta = 100.72(3)^\circ$. Other reaction chemistry and a discussion of proposed mechanisms for the formation of these unusual complexes are reported.

Introduction

We have reported previously that the Pt-H or Pt-R bond of the reagents $[\text{trans-Pt}(\text{R})(\text{PEt}_3)_2(\text{acetone})]^+$ adds regioselectively across the C≡C triple bond of terminal alkynyl ligands of mononuclear organometallic compounds to give homo- or heterodinuclear complexes containing μ -alkenylidene ligands.^{2a,b} These platinum reagents also add Pt-H or Pt-R bonds regioselectively across M≡C triple bonds of terminal alkylidyne ligands of mononuclear organometallic compounds to afford heterodinuclear complexes containing μ -alkylidene ligands.^{2c-e} The regiochemistry observed for these Pt-H addition reactions is precisely that expected for having initial coordination of

the C-C or M-C multiple bond to the coordinatively unsaturated complex $[\text{HPt}(\text{PEt}_3)_2]^+$ followed by 1,2-addition of the Pt-H bond across the unsaturated bond such that the H ligand adds to the site normally preferred by electrophilic reagents. This mechanism is proposed by analogy to the mechanism deduced by Clark and co-workers for the addition of this platinum hydride species to alkynes.³

We have undertaken a study of the addition of Pt-H reagents to *main-group* alkynyl compounds to obtain new heterocyclic compounds containing bridging alkenylidene functional groups. We now report our initial results of Pt-H additions to phosphine oxides that contain one or more alkynyl substituents. The cationic Pt-H reagent $[\text{trans-Pt}(\text{H})(\text{PEt}_3)_2(\text{THF})]^+$ adds regioselectively to the C≡C triple bond of the alkynyl substituent of $\text{O}=\text{PPh}_2(\text{C}\equiv\text{CPh})$ to give a Pt,P μ -alkenylidene compound where

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