ration and that the (tripod)₂Cr₂Hₙ species is instrumental in transfer of tripod. A second explanation is based on the possibility that the first reaction of CrCl₃(tripod) with LiHBEt₃ is reduction to Cr(II), as in "CrCl₂(tripod)". The work of the Jones group,[8] taken together with the kinetic lability of Cr(II) and the highly unsaturated character of "CrCl₂(tripod)", allows the conclusion that tripod transfer may occur at this stage of the reaction, yielding the known compound CrCl₂(η^2-tripod)₂. From this point, a single Cl⁻/H⁻ exchange, followed by Cl⁻ displacement by one pendant arm of tripod, could yield HCr(tripod)₂⁺. The production of a cationic hydride from LiHBEt₃ thus might follow from the kinetic lability of Cr(II) halides.

The structure of HCr(tripod)₂⁺ demands comparison to that of its conjugate base, Cr(tripod)₂.[8] Intraligand P–Cr–P angles are unchanged on protonation. The degrees of freedom exercised upon protonation are (1) a systematic lengthening of Cr–P distances by (on average) 0.068 Å, consistent with protonation being *oxidative* addition, and (2) a twisting away from the precisely staggered form in Cr(tripod)₂ *toward* (but stopping far short of) a trigonal-prismatic form. This latter motion creates three nearly equally attractive edges of the former octahedron (trigonal antiprism) for the proton, with two consequences. The first is a nuisance consequence, in that it leads to disorder in the crystalline solid. The second consequence is that the three nearly equienergetic edges are attractive sites for a hydrogen migration process (eq 4), which alone is sufficient to account for the hydrogen fluxionality required by both the ambient-temperature ¹H and ³¹P NMR spectra.

While intramolecular migration of hydrogen in HCr(tripod)₂⁺ is facile, our observations of the ³¹P NMR of a mixture of the
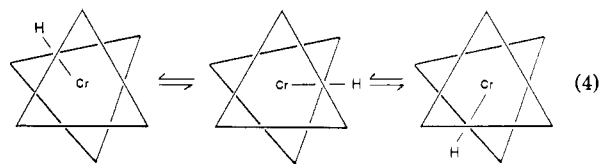
conjugate acid/base pair HCr(tripod)₂⁺/Cr(tripod)₂ show neither coalescence of the two resonances nor even line broadening of these resonances. The rate of intermolecular proton transfer is thus less than approximately 10 s⁻¹, if it occurs at all. Since the structural study reported here reveals only modest changes in CrP₆ skeletal geometry upon proton transfer, the slow proton transfer must be attributed to the steric bulk of the acid and base (Figure 3, supplementary materials). Previous work[12] has raised this point for HMo(CO)₂(Ph₂PC₂H₄PPh₂)⁺ and has demonstrated catalysis of proton transfer by small anionic bases.

(12) Hanckel, J. M.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1983**, *105*, 6979.

1,3-Bis(diphenylphosphino)propane-Bridged Complexes. X-ray Crystal and Molecular Structure of Ir₂(CO)₂Cl₂{μ-Ph₂P(CH₂)₃PPh₂}₂, Its Reactions with H₂ and O₂, and the Structure of Ir₂(CO)₂Cl₂(O₂){μ-Ph₂P(CH₂)₃PPh₂}₂

Hsien-Hau Wang,[1a] Louis H. Pignolet,*[1a] Philip E. Reedy, Jr.,[1b] Marilyn M. Olmstead,[1b] and Alan L. Balch*[1b]

Yellow Ir₂(CO)₂Cl₂(μ-dppp)₂·3CH₂Cl₂ (1) [dppp is 1,3-bis(diphenylphosphino)propane] crystallized in the monoclinic space group *C*2/*c* (No. 15), with *a* = 19.626 (3) Å, *b* = 22.051 (3) Å, *c* = 15.135 (8) Å, *β* = 90.36 (3)°, *V* = 6550 (5) Å³, and *Z* = 4 at 298 K. Refinement yielded *R* = 0.061 and *R*_w = 0.072 for 3462 reflections with $F_o^2 \geq 2.5\sigma(F_o^2)$. The molecule consists of a 12-membered ring with *trans*-IrP₂(CO)Cl units connected through the bridging dppp ligands. The planar Ir units are noninteracting, with the closest intramolecular approach being a 4.179 (4) Å Cl⋯Cl contact. Reaction of 1 with dioxygen at 1 atm with CH₂Cl₂ as solvent produced Ir₂(CO)₂Cl₂(O₂)(μ-dppp)₂ (2), while under 3 atm, Ir₂(CO)₂Cl₂(O₂)₂(μ-dppp)₂ was formed. Yellow Ir₂(CO)₂Cl₂(O₂)(μ-dppp)₂ crystallized in the monoclinic space group *P*2₁/*c* (No. 14), with *a* = 13.070 (2) Å, *b* = 20.474 (7) Å, *c* = 17.223 (3) Å, *β* = 90.75 (1)°, *V* = 5762 (2), and *Z* = 4 at 130 K. Refinement yielded *R* = 0.049 and *R*_w = 0.052 for 5853 reflections with *I* > 2σ(*I*). The complex consists of one planar IrP₂(CO)Cl unit connected to a IrP₂(CO)Cl(O₂) unit through two dppp bridges. The closest approach of the two coordination spheres of the iridium involves an intramolecular Cl⋯O contact of 3.91 (2) Å. Reaction of 1 with dihydrogen at 1 atm with CH₂Cl₂ as solvent produced a mixture of Ir₂(CO)₂Cl₂(H)₂(μ-dppp)₂ and Ir₂(CO)₂Cl₂(H)₄(μ-dppp)₂. In both of these complexes the hydrogen ligands are positioned in the region of space between the iridium atoms.

Introduction

There has been considerable exploration of the properties of binuclear transition-metal complexes with diphosphines as bridging ligands.[2,3] Most of these have concentrated on the use of small-bite ligands like bis(diphenylphosphino)methane,[3] which place the metal ions involved in close proximity and make direct metal⋯metal interactions and metal–metal bonding into major features of these compounds. Much less attention has been paid

to the structural characterization and chemical behavior of complexes that provide for larger separations between the metal ions.[4]

(1) (a) University of Minnesota. (b) University of California.
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(3) Puddephatt, R. *J. Chem. Soc. Rev.* **1983**, *12*, 99.

(4) (a) March, F. C.; Mason, R.; Thomas, K. M.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, 584. (b) Pryde, A.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1976**, 322. (c) Sanger, A. R. *J. Chem. Soc., Dalton, Trans.* **1977**, 120. (d) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971. (e) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59. (f) Faraone, F.; Bruno, G.; Tresoldi, G.; Faraone, G.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1981**, 1651. (g) Eisenberg, R.; Fisher, B. J. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 67. (h) Fisher, B. J.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 3216. (i) Brown, J. M.; Canning, L. R. *J. Chem. Soc., Chem. Commun.* **1983**, 460. (j) Alcock, N. W.; Judd, L.; Pringle, P. G. *Inorg. Chim. Acta* **1986**, *113*, L13.

Table I. Positional Parameters and Their Estimated Standard Deviations for **1**

atom	x	y	z	$B,^a$ Å^2
Ir	−0.10857 (3)	0.17719 (3)	0.12808 (4)	3.74 (1)
Cl	−0.0813 (3)	0.0764 (2)	0.1602 (3)	7.5 (1)
C	−0.1367 (9)	0.2507 (8)	0.096 (1)	10.2 (5)
O	−0.1583 (9)	0.2920 (7)	0.067 (1)	13.1 (5)
P(1)	−0.1805 (2)	0.1732 (2)	0.2491 (2)	4.01 (8)
C(1A)	−0.2069 (7)	0.2439 (8)	0.303 (1)	5.1 (4)
C(2A)	−0.166 (1)	0.2971 (8)	0.293 (1)	7.2 (5)
C(3A)	−0.185 (1)	0.3469 (9)	0.348 (1)	8.2 (6)
C(4A)	−0.240 (1)	0.346 (1)	0.400 (2)	9.3 (6)
C(5A)	−0.279 (1)	0.295 (1)	0.408 (1)	9.1 (6)
C(6A)	−0.2646 (9)	0.2420 (9)	0.357 (1)	6.7 (5)
C(1B)	−0.2601 (7)	0.1364 (7)	0.2233 (9)	4.3 (4)
C(2B)	−0.3040 (8)	0.1653 (8)	0.161 (1)	6.1 (5)
C(3B)	−0.3661 (8)	0.1377 (9)	0.136 (1)	6.4 (5)
C(4B)	−0.384 (1)	0.082 (1)	0.170 (1)	8.5 (6)
C(5B)	−0.340 (1)	0.0521 (9)	0.230 (1)	7.8 (5)
C(6B)	−0.2775 (9)	0.0789 (8)	0.257 (1)	6.8 (5)
P(2)	−0.0310 (2)	0.1703 (2)	0.0132 (2)	3.86 (8)
C(1C)	−0.0644 (8)	0.1303 (7)	−0.081 (1)	4.6 (4)
C(2C)	−0.0394 (8)	0.0742 (8)	−0.109 (1)	5.9 (4)
C(3C)	−0.0697 (9)	0.0440 (9)	−0.181 (1)	7.6 (5)
C(4C)	−0.125 (1)	0.0706 (9)	−0.226 (1)	7.6 (5)
C(5C)	−0.148 (1)	0.126 (1)	−0.199 (1)	9.7 (6)
C(6C)	−0.122 (1)	0.1572 (9)	−0.124 (1)	8.3 (6)
C(1D)	0.0029 (7)	0.2395 (7)	−0.035 (1)	4.6 (4)
C(2D)	0.0258 (8)	0.2388 (9)	−0.123 (1)	6.5 (5)
C(3D)	0.0563 (9)	0.293 (1)	−0.154 (1)	9.1 (6)
C(4D)	0.066 (1)	0.3421 (9)	−0.103 (2)	8.8 (6)
C(5D)	0.043 (1)	0.3425 (9)	−0.017 (2)	8.7 (6)
C(6D)	0.0098 (9)	0.2903 (8)	0.020 (1)	6.0 (5)
C(10)	−0.1446 (7)	0.1313 (7)	0.3444 (9)	4.6 (4)
C(20)	0.0484 (7)	0.1298 (7)	0.0457 (9)	4.4 (4)
C(21)	0.0797 (8)	0.1646 (7)	0.126 (1)	5.2 (4)
C(1)	0.230 (2)	−0.051 (2)	−0.003 (2)	16 (1)*
Cl(1)	0.1840 (7)	0.0132 (6)	−0.0082 (9)	21.7 (4)*
Cl(2)	0.302 (1)	−0.0300 (9)	0.044 (1)	22.4 (9)*
C(2)	0.000	0.405 (2)	0.250	17 (2)*
Cl(3)	−0.032 (2)	0.445 (1)	0.153 (2)	25 (2)*

^{a} Values marked with an asterisk denote isotropically refined atoms. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

While diphosphines with two methylene groups connecting the phosphorus generally form chelate rings rather than acting as binuclear bridging groups,[5] diphosphines with three or four methylene groups between the phosphorus atoms can form binuclear complexes in which the metal ions are close enough to allow interactions among ligands but in which direct metal–metal interactions are less likely.

Here we report on the structural characterization of one such complex, $Ir_2(CO)_2Cl_2(\mu\text{-dppp})_2$ (**1**)[4d] [dppp is 1,3-bis(diphenylphosphino)propane], and on some of its chemical reactions. This yellow complex contains two $Ir(CO)ClP_2$ units, which are highly reactive toward addition reactions[6] and which are linked in a noninteracting fashion. In molecules of this sort, it is expected that reaction of one center may affect the reactivity at the other in an indirect way. Some evidence for such behavior has been reported for $Rh_2(CO)_2Cl_2(\mu\text{-dppp})_2$, which shows evidence for the binding of 1, but not 2, equiv of sulfur dioxide or tetracyanoethylene.[7]

Results and Discussion

X-ray Crystal and Molecular Structure of $Ir_2(CO)_2Cl_2(\mu\text{-dppp})_2\cdot3CH_2Cl_2$ (1). Atomic coordinates are given in Table I. Selected bond distances and angles are given in Table IV. The structure consists of cyclic **1** and dichloromethane molecules with no unusually short intermolecular contacts. A drawing of **1** is
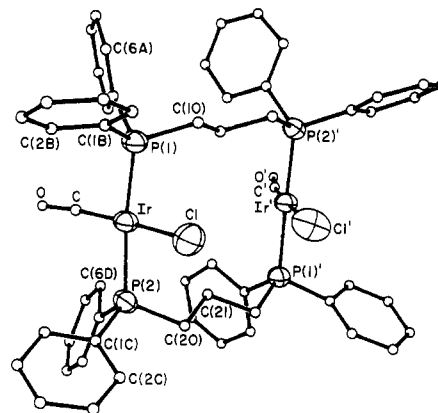
(5) Sanger, A. R. *J. Chem. Soc., Chem. Commun.* **1975**, 893.
(6) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335.
(7) Balch, A. L.; Tulyathan, B. *Inorg. Chem.* **1977**, *16*, 2840.

Figure 1. Perspective drawing of $Ir_2(CO)_2Cl_2(\mu\text{-dppp})_2$ (**1**), where primed and unprimed atoms are related by a crystallographic 2-fold axis. For anisotropically refined atoms 50% probability contours are shown; for carbon and oxygen arbitrarily sized, uniform circles are used.
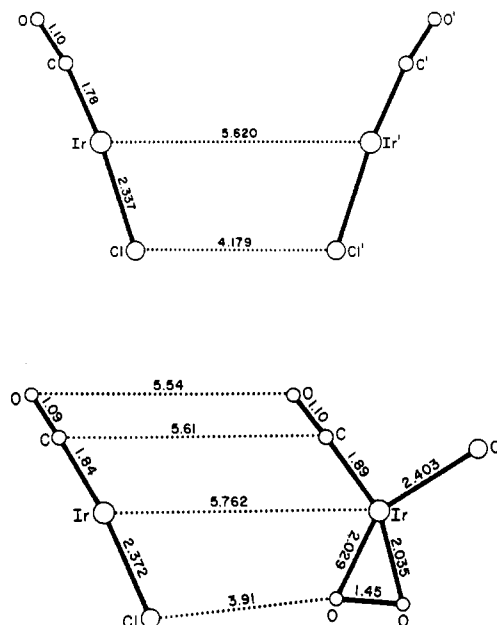

Figure 2. Cross section of $Ir_2(CO)_2Cl_2(\mu\text{-dppp})_2$ (**1**) (top) and $Ir_2(CO)_2Cl_2(O_2)(\mu\text{-dppp})_2$ (**2**) (bottom) showing some of the intramolecular contacts.

shown in Figure 1, and Figure 2 shows the nearly planar $Ir_2(CO)_2Cl_2$ section and indicates some of the intramolecular contacts. Complex **1** contains a crystallographic C_2 axis, which relates the primed to unprimed atoms in Figure 1.

The molecular structure of **1** consists of two planar $IrP_2(CO)Cl$ units bridged by the dppp ligands to form a 12-membered ring. Bond distances in **1** fall within normal ranges.[4a,8,9] The intramolecular Ir···Ir separation is 5.620 (1) Å, which is far beyond bonding distance. The closest intramolecular contact involves the two chloride ligands. Thus, the two $IrP_2(CO)Cl$ units are not parallel. Complex **1** is similar to the 12-membered macrocycle $Rh_2(CO)_2Cl_2\{\mu\text{-}(Ph_2PCH_2)_2AsPh\}_2$, which has a cis arrangement of $Rh(CO)Cl$ groups and a 5.428 (2) Å separation between the nonbonded rhodium centers.[10]

For dimers like **1**, both cis (C) and trans (T) isomers are possible. As seen in Figures 1 and 2, the $Ir(CO)Cl$ units have a cis relationship. In contrast, the face-to-face dimers $Rh_2(CO)_2Cl_2(\mu\text{-dpm})_2$[11] and $Rh_2(CO)_2Cl_2(\mu\text{-dam})_2$[12,13] [dpm is bis-

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(11) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.

C   T
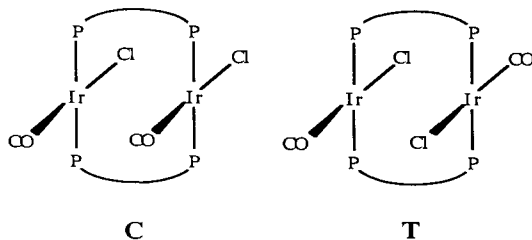
(diphenylphosphino)methane and dam is bis(diphenylarsino)methane] as well as the 26-membered ring compound Rh_2-$(CO)_2Cl_2\{\mu\text{-}t\text{-}Bu_2P(CH_2)_{16}P\text{-}t\text{-}PBu_2\}_2$[4a] have the $M(CO)Cl$ units in the trans geometry. For the dimers with short M···M separations, steric effects and dipole–dipole interaction should favor the trans geometry T with a parallel disposition of the coordination planes. For larger M···M separations the $M(CO)Cl$ units would appear to be free to adopt orientations dictated by packing and local environmental effects. Rotation about the P–M–P axis would be expected to be constrained mostly by interaction of the M-$(CO)Cl$ unit with the phosphorus substituents. However, for **1** the rotation necessary to convert the cis into the trans isomer is inhibited because the Ir···Ir separation [5.620 (1) Å] is too short to accommodate passage of the CO or Cl ligands through the central cavity. Interestingly, solutions of **1** show only a single ^{31}P NMR resonance.[14] Either the complex exists as a single, cis isomer in solution, or else the resolution of the ^{31}P NMR spectrum is not sufficient to distinguish between the two isomeric forms. In the solid state **1** shows only a single CO stretch.

There has been some confusion in the literature concerning the geometry of **1** and its bromide and iodide analogues. Sanger[4d] and Eisenberg[4h] independently concluded that **1** has the trans geometry T in the solid state because only one carbonyl stretching frequency was observed. In contrast, the bromide analogue had two distinct carbonyl stretches (1915 and 1944 cm^{-1}) in the solid state and was therefore assigned the cis geometry C.[4h] Since the X-ray analysis showed **1** to be cis and only one carbonyl stretch was observed, a question must be raised about the geometry of the bromide analogue. Interestingly, the iodide analogue shows only one carbonyl stretch in the solid state,[4h] and all three compounds (chloride, bromide, and iodide) show one singlet in the ^{31}P NMR in solution.[4d,4h] Moreover, $Rh_2(CO)_2Cl_2\{\mu\text{-}(Ph_2PCH_2)_2AsPh\}_2$ with cis geometry shows two carbonyl stretches in the solid (1995, 1985 cm^{-1}), where the two $Rh(CO)ClP_2$ groups are crystallographically distinct,[10] but only a single carbonyl stretch (1978 cm^{-1}) in toluene solution.[10] Perhaps the bromide analogue has two solid forms or two crystallographically distinct $Ir(CO)BrP_2$ groups. In any case, the iridium centers are sufficiently far apart that coupling between the two CO groups would be minimal, and therefore two vibrations for the cis geometry are not necessarily expected.

Reaction of 1 with O₂. Treatment of solutions of **1** with dioxygen at 1 atm resulted in the gradual formation of the mono-(dioxygen) adduct $Ir_2(CO)_2Cl_2(O_2)(\mu\text{-dppp})_2$ (**2**), which has been isolated as yellow crystals. Infrared spectra showed two carbonyl stretching vibrations, one at 2012 cm^{-1} for the $Ir(CO)ClP_2(O_2)$[6] unit and one at 1950 cm^{-1} for the $IrP_2(CO)Cl$ unit, and an O–O stretch at 843 cm^{-1}. The ^{31}P NMR spectrum consisted of two, equally intense singlets at 21.3 and –5.3 ppm. Hence, exchange of the dioxygen between the two iridium centers is slow, if it occurs at all.

Treatment of **1** with 3 atm of dioxygen resulted in the formation of $Ir_2(CO)_2Cl_2(O_2)_2(\mu\text{-dppp})_2$ (**3**). This substance showed a single ^{31}P NMR resonance at –4.2 ppm and a single carbon monoxide stretching band at 2006 cm^{-1} (2055 sh).

In contrast to $Ir(Ph_3P)_2(CO)Cl(O_2)$[6] neither **2** nor **3** lost dioxygen upon purging of solutions with dinitrogen or upon gentle

warming (38 °C). Even more surprisingly the related macrocycle $Ir_2(CO)_2Cl_2\{\mu\text{-}(Ph_2PCH_2)_2AsPh\}_2$[10] showed no tendency to add dioxygen (at atmosphere).

X-ray Crystal and Molecular Structure of $Ir_2(CO)_2Cl_2(O_2)(\mu\text{-dppm})_2\cdot2CH_2Cl_2$ (2). Atomic coordinates are given in Table II, and selected interatomic distances and angles are given in Table IV. A drawing of the macrocylic complex is shown in Figure 3, while the bottom of Figure 2 shows the nearly planar $Ir_2(CO)_2Cl_2(O_2)$ section and gives some of the intramolecular contacts. There is no crystallographically imposed symmetry.

The complex consists of a planar $IrP_2(CO)Cl$ unit and a $IrP_2(CO)Cl(O_2)$ unit bridged by dppp ligands that are trans to one another. The P–Ir–P angles at each iridium are nearly linear. The environment of Ir(1) is planar and the bond distances and angles around Ir(1) are similar to those in **1**. The coordination of Ir(2) involves a side-on bound dioxygen ligand with nearly equal Ir–O distances. In order to accommodate the dioxygen ligand, the CO and Cl ligands are bent together so that they occupy cis coordination sites. The surroundings of Ir(2) are similar to those of $trans\text{-}Ir(Ph_2EtP)_2(CO)Cl(O_2)$.[15] The O–O bond length [1.461 (14) Å] and Ir–O bond lengths [2.036 (9), 2.084 (9) Å] in this mononuclear complex[15] are quite similar to those in **2**.

The central cavity within **2** is relatively empty as the dioxygen ligand is set off to one side of the Ir–Ir midline. There are no unusually close contacts between the ligands on the two iridium atoms. The separation between iridium centers is only slightly longer in **2** than in **1**. The closest approach of the ligands on Ir(1) and Ir(2) involves Cl(1) and O(3). The 3.91 Å separation involved is considerably greater than the sum (3.2 Å)[16] of the van der Waals radii for these atoms.

On the basis of the Ir···Ir separations in **1** and **2** and the coordination environment of Ir(2) in **2**, it is possible to construct models of the bis(dioxygen) adduct **3** in which the in-plane ligands are all accommodated without contacts that violate the van der Waals radii of these ligands. In fact, there are a number of orientations into which these ligands can be placed. Thus, while **3** is necessarily more crowded than **2**, it is not exceptionally congested.

Reaction of 1 with H₂. Treatment of a CH_2Cl_2 solution of **1** with dihydrogen at 1 atm resulted in the formation of a mixture of the tetra- and dihydrido compounds $Ir_2(CO)_2Cl_2(H)_4(\mu\text{-dppp})_2$ (**4**) and $Ir_2(CO)_2Cl_2(H)_2(\mu\text{-dppp})_2$ (**5**). Both of these compounds were always present in solid and solution phases, which indicates that the reaction to form the tetrahydride is incomplete. Complete irreversible conversion to **4** with use of up to 3 atm of H_2 pressure
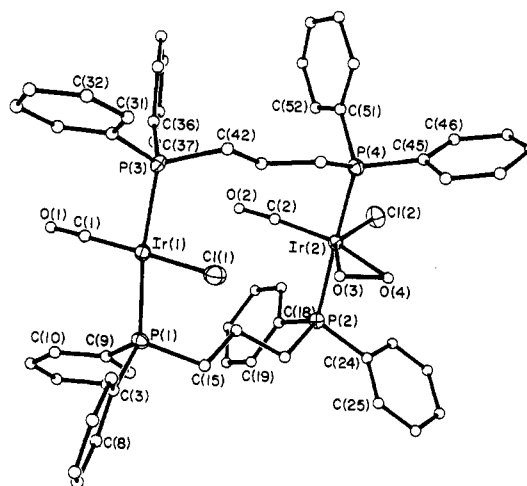

Figure 3. Perspective drawing of $Ir_2(CO)_2Cl_2(O_2)(\mu\text{-dppp})_2$ (**2**). For anisotropically refined atoms 50% probability contours are shown; for carbon and oxygen arbitrarily sized, uniform circles are used.

(12) Mague, J. T. *Inorg. Chem.* **1969**, *8*, 1975.
(13) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1981**, *20*, 1534.
(14) A previous report[4d] gave the ^{31}P NMR chemical shift for **1** as –4.6 ppm while both the Minnesota and Davis groups agree on the value of 20.4 ppm.

(15) Weininger, M. S.; Taylor, I. F., Jr.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1971**, 1172.
(16) Pauling, L. *The Nature of the Chemical Bond* Cornell University Press: Ithaca, NY, 1960; p 260.
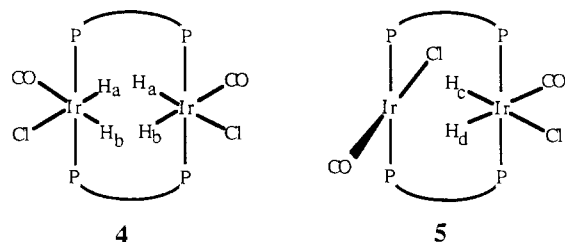
was not achieved although a nearly colorless solution was obtained. Upon release of the H$_2$ pressure, the pale yellow color of the mixture returned, which suggests that these two compounds are in rapid equilibrium. A single-crystal X-ray analysis of a pale yellow crystal isolated from the reaction mixture upon the addition of diethyl ether gave a disordered structure which consisted of a cocrystallized solid mixture of both **4** and **5**.[17] The X-ray analysis confirmed the presence of **4** and **5**, which have the structures shown in the drawings and, for **4**, the structure given as supplementary material. The hydride ligands were not located in the X-ray analysis but are obviously positioned trans to the CO and Cl ligands in the region of space between the Ir atoms. The bromide analogues of **4** and **5** and the iodide analogue of **4** have been reported by Eisenberg[4h] and their solid and solution spectral features are very similar to those of **4** and **5**.

The IR (KBr) spectrum of the **4**, **5** mixture showed ν(CO) bands at 1985 (s) and 1950 (m) cm^{-1} and ν(Ir–H) bands at 2080 (s) and 2195 (m) cm^{-1}. These values compare closely with those of the bromide analogues[4h] [ν(CO) = 1980 and 1945 cm^{-1}, ν(Ir–H) = 2100 and 2190 cm^{-1}]. The ν(CO) band at 1980 cm^{-1} has been assigned to the Ir(III) centers, (H)$_2$P$_2$Ir(CO)Br, and the 1945-cm^{-1} band to the nonhydrogenated Ir(I) center in the bromide analogue of **5**.[4h] Consistent with this assignment the iodide analogue of **4** showed a ν(CO) band at 1980 cm^{-1} and ν(Ir–H) bands at 2090 and 2160 cm^{-1}.[4h]

The 300-MHz ^{1}H NMR spectrum of the hydrogenated product of **1** provides direct evidence for the presence of both compounds. Figure 4 shows the hydride region of the spectrum recorded with use of CD$_2$Cl$_2$ and acetone-d_6 as solvents. The CD$_2$Cl$_2$ spectrum showed two pairs of doublets of triplets centered at δ −19.44, −19.08 and −8.22, −8.10. The relative intensities of the doublet of triplets patterns clearly show that the δ −19.44 and −8.10 resonances are due to one compound while the δ −19.08 and −8.22 resonances result from another. The acetone-d_6 spectrum confirms this assignment because one pair of doublet of triplets resonances is significantly decreased relative to the other due to a solvent effect on the relative stability of the two compounds. The bromide analogue of **4** shows two doublet of triplets resonances (CDCl$_3$, δ −18.7, −8.6),[4h] which correspond to one pair of resonances in the **4**, **5** mixture. The bromide analogue of **5**, which was made by the addition of 1 equiv of H$_2$ to the bromide analogue of **1**, shows two pairs of doublet of triplets resonances.[4h] Apparently this compound exists in two isomeric forms while **5** exhibits only one. The doublet of triplets patterns in all of these complexes have coupling constants within the range J(PH$_{cis}$) = 13–18 Hz and J(HH) = 3–5 Hz and are consistent with the structures shown for **4** and **5**. The assignment of the resonances shown in Figure
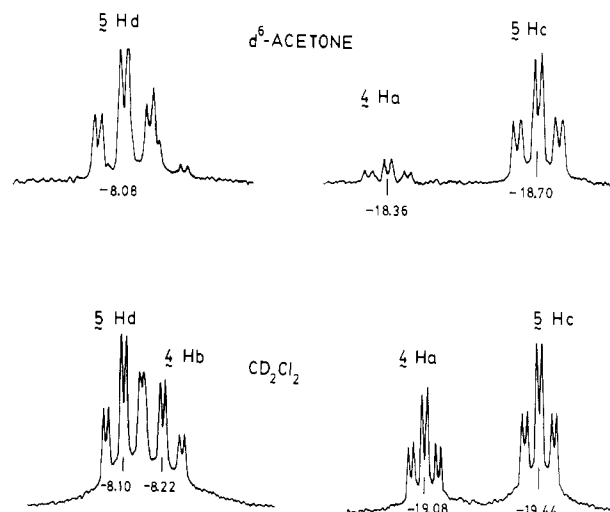

Figure 4. ^{1}H NMR spectrum of the product of the reaction of **1** with H$_2$ recorded with use of CD$_2$Cl$_2$ and acetone-d_6 solvents. See text for details of assignment: **4** = Ir$_2$(CO)$_2$Cl$_2$(H)$_4$(μ-dppp)$_2$ and **5** = Ir$_2$(CO)$_2$Cl$_2$(H)$_2$(μ-dppp)$_2$.

4 to H$_a$, H$_b$, H$_c$, and H$_d$ of compounds **4** and **5** are based on the assignments made by Eisenberg for the bromide and iodide analogues.[4h] Briefly, **4** is expected to be the minor compound in acetone solution, and the hydrides trans to the halide and carbon monoxide ligands resonate in the −18 to −19 and −8 to −9 ppm regions, respectively. Detailed support for these assignments has been presented by Eisenberg.[4h]

The similarity of the chloride, bromide, and iodide analogues of **4** and **5** clearly establishes the close relationship of the oxidative-addition chemistry of the halide analogues of **1** with H$_2$. The primary difference is that the chloride complex reacts less completely. In the case of the iodide analogue of **1**, the addition of H$_2$ is complete within 1 h, giving only the tetrahydride **4** and thus establishing the reactivity order Cl < Br < I.[4h]

It is interesting to compare the H$_2$ reaction chemistry of *trans*-[IrCl(CO)(μ-dpm)]$_2$ to that of **1**. The dpm-bridged compound reacts with H$_2$, yielding Ir$_2$(H)$_2$Cl$_2$(CO)$_2$(μ-dpm)$_2$ in which the hydrido ligands are mutually cis on adjacent metals.[18] Since the μ-dpm ligands hold the Ir atoms in close proximity, there is not sufficient space for a cis addition on one metal as observed in the reaction of H$_2$ with **1**. The cis addition of H$_2$ on adjacent metals in the μ-dpm compound is accompanied by the formation of an Ir–Ir bond.

Experimental Section

Physical Measurements. ^{1}H NMR spectra were recorded at 300 MHz with use of a Nicolet NT-300 spectrometer. Chemical shifts are referenced to the internal standard Me$_4$Si and are reported as δ values. Positive chemical shifts are downfield from Me$_4$Si. ^{31}P{^{1}H} NMR spectra were recorded at 40.5 MHz with use of a Varian XL-100 FT instrument or at 81 MHz on a Nicolet NT 200 spectrometer. Chemical shifts are referenced to external standard 85% H$_3$PO$_4$ as δ values with positive shifts downfield. Infrared spectra were recorded with use of a Beckman Model 4250 grating spectrometer.

Preparation of Compounds. Ir$_2$(CO)$_2$Cl$_2$(μ-dppp)$_2$ (1). 1 was first prepared by Sanger[4d] by the reaction of [Ir(COD)Cl]$_2$ with a stoichiometric amount of the diphosphine ligand under a CO atmosphere.[4d] Compound 1 can also be made by two different methods.

Method 1. Iridium trichloride hydrate (0.72 g, 2.0 mmol) and lithium chloride (0.22 g, 5.2 mmol) were added to 10 mL of a freshly distilled 2-methoxyethanol solution in a Kontes Griffin–Worden pressure tube. The mixture was freeze–thaw–degassed three times and placed under 40 psig carbon monoxide. When the pressure vessel was heated to 170 °C, the iridium trichloride and lithium chloride dissolved. The resulting solution of [Ir(CO)$_2$Cl$_2$]Li was passed through a frit after 20 min of reaction and was stored under nitrogen. A toluene solution of dppp (0.84 g, 2.0 mmol) was added to give a yellow solution. After the mixture was heated for ca. 30 min, a yellow crystalline product formed. Slow re-

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(17) Crystal parameters for **4**·2CH$_2$Cl$_2$: pale yellow crystal (0.15 × 0.20 × 0.25 mm^3) of Ir$_2$P$_4$Cl$_6$C$_{58}$O$_2$H$_{60}$, M_r 1510.13, monoclinic P2$_1$/n, 23 °C, a = 17.245 (4) Å, b = 20.474 (7) Å, c = 17.562 (7) Å, β = 96.04 (3)°, V = 6166 (6) Å^3, Z = 4, ρ = 1.627 g cm^{-3}. Refinement parameters: 8524 unique data in the 0–46° 2θ range, R = 0.071, R_w = 0.077 with 324 variables and 3758 observed reflections with $F_o^2 \geq 2.5\sigma(F_o^2)$. Data collection, solution, and refinement methods were the same as for **1**. The structure was disordered but clearly showed an ordered bis(μ-1,3-bis(diphenylphosphino)propane) framework with the CO and Cl ligands bent back away from the region between the Ir atoms. Superimposed on this tetrahydrido molecule was a dihydrido molecule with trans CO and Cl groups on one Ir (as in 1) and cis CO and Cl groups on the other exactly as in the tetrahydrido molecule. An ORTEP drawing of the tetrahydrido molecule with some distances and angles is included as supplementary material. Details of this structure determination are given in: Wang, H. H. Ph.D. Dissertation, University of Minnesota, 1981.

(18) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1801.

Table II. Atom Coordinates ($\times 10^4$) and Thermal Parameters ($\text{Å}^2 \times 10^3$) for $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\text{O}_2)(\mu\text{-dppp})_2$ (**2**)

atom	x	y	z	U^a	atom	x	y	z	U^a
Ir(1)	644 (1)	6753 (1)	5000 (1)	17 (1)*	C(26)	6942 (9)	4941 (4)	5989 (7)	21 (3)
Ir(2)	2920 (1)	5431 (1)	7109 (1)	16 (1)*	C(27)	7381 (10)	4830 (5)	6704 (7)	28 (3)
Cl(1)	865 (2)	5882 (1)	4564 (2)	30 (1)*	C(28)	6929 (10)	5010 (5)	7374 (8)	37 (3)
Cl(2)	3628 (3)	5300 (1)	8389 (2)	32 (1)*	C(29)	6024 (10)	5288 (5)	7319 (8)	31 (3)
P(1)	2155 (2)	6940 (1)	4368 (2)	19 (1)*	C(30)	-1963 (9)	6602 (5)	5232 (7)	23 (3)
P(2)	4418 (2)	5800 (1)	6582 (2)	17 (1)*	C(31)	-2543 (8)	6211 (4)	4893 (6)	17 (3)
P(3)	-744 (2)	6475 (1)	5723 (2)	18 (1)*	C(32)	-3419 (9)	6331 (5)	4470 (7)	24 (3)
P(4)	1362 (2)	5009 (1)	7413 (2)	20 (1)*	C(33)	-3737 (10)	6848 (5)	4414 (7)	26 (3)
O(1)	184 (7)	7848 (4)	5365 (5)	40 (2)	C(34)	-3178 (9)	7235 (5)	4747 (7)	28 (3)
O(2)	2137 (7)	6507 (4)	7425 (5)	39 (2)	C(35)	-2303 (9)	7118 (5)	5171 (7)	24 (3)
O(3)	2664 (6)	5141 (3)	6027 (5)	26 (2)	C(36)	-900 (9)	6753 (4)	6689 (7)	18 (3)
O(4)	3287 (6)	4785 (3)	6483 (5)	26 (2)	C(37)	-98 (9)	7011 (5)	7069 (7)	24 (3)
C(1)	361 (9)	7439 (5)	5241 (7)	25 (3)	C(38)	-162 (10)	7141 (5)	7843 (8)	33 (3)
C(2)	2402 (9)	6104 (5)	7328 (7)	20 (3)	C(39)	-1041 (9)	7019 (5)	8249 (8)	37 (3)
C(3)	2115 (9)	6953 (5)	3309 (7)	23 (3)	C(40)	-1875 (10)	6768 (5)	7886 (7)	27 (3)
C(4)	1336 (10)	6687 (5)	2909 (7)	29 (3)	C(41)	-1787 (10)	6626 (5)	7102 (7)	28 (3)
C(5)	1342 (11)	6669 (6)	2113 (8)	42 (4)	C(42)	-702 (9)	5773 (4)	5955 (7)	23 (3)
C(6)	2075 (11)	6910 (6)	1697 (9)	44 (4)	C(43)	207 (9)	5687 (5)	6492 (7)	28 (3)
C(7)	2866 (11)	7180 (6)	2075 (8)	43 (4)	C(44)	438 (9)	5098 (4)	6624 (7)	21 (3)
C(8)	2875 (9)	7198 (5)	2881 (7)	25 (3)	C(45)	1479 (9)	4303 (4)	7561 (7)	21 (3)
C(9)	2792 (9)	7555 (4)	4608 (7)	22 (3)	C(46)	1709 (12)	4112 (6)	8274 (10)	52 (4)
C(10)	2358 (9)	8020 (4)	4390 (7)	24 (3)	C(47)	1849 (13)	3570 (7)	8399 (10)	60 (5)
C(11)	2834 (11)	8496 (6)	4568 (8)	39 (4)	C(48)	1709 (11)	3236 (6)	7803 (8)	39 (4)
C(12)	3766 (10)	8504 (5)	4951 (8)	36 (3)	C(49)	1513 (11)	3433 (5)	7049 (8)	39 (4)
C(13)	4232 (10)	8032 (5)	5162 (8)	34 (3)	C(50)	1396 (9)	3963 (5)	6930 (7)	28 (3)
C(14)	3736 (9)	7576 (5)	4994 (7)	23 (3)	C(51)	655 (9)	5225 (5)	8252 (7)	23 (3)
C(15)	3130 (8)	6448 (4)	4575 (6)	18 (3)	C(52)	912 (14)	5639 (7)	8684 (10)	60 (5)
C(16)	3234 (8)	6293 (4)	5420 (6)	17 (3)	C(53)	280 (15)	5811 (8)	9299 (12)	78 (6)
C(17)	4170 (8)	5932 (4)	5559 (7)	19 (3)	C(54)	-562 (15)	5590 (7)	9426 (11)	72 (5)
C(18)	4863 (8)	6422 (4)	6982 (7)	17 (3)	C(55)	-881 (18)	5131 (9)	9042 (13)	98 (7)
C(19)	5424 (8)	6774 (4)	6524 (7)	20 (3)	C(56)	-247 (15)	4958 (8)	8408 (12)	84 (6)
C(20)	5783 (9)	7229 (5)	6837 (7)	24 (3)	C(57)	4388 (11)	4072 (6)	7581 (8)	46 (4)
C(21)	5637 (9)	7354 (5)	7614 (7)	29 (3)	C(58)	3963 (17)	4524 (8)	191 (8)	90 (7)
C(22)	5123 (9)	7009 (5)	8084 (7)	25 (3)	Cl(3)	5372 (3)	3862 (2)	6992 (3)	63 (2)*
C(23)	4741 (9)	6535 (5)	7771 (7)	22 (3)	Cl(4)	4457 (5)	3763 (2)	8486 (3)	83 (2)*
C(24)	5570 (9)	5401 (4)	6610 (7)	21 (3)	Cl(5)	3607 (4)	5082 (2)	565 (3)	77 (2)*
C(25)	6042 (8)	5227 (4)	5939 (7)	19 (3)	Cl(6)	3353 (4)	3951 (2)	492 (3)	82 (2)*

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

Table III. Summary of Crystal Data Collection for **1** and **2**

	$\text{Ir}_2(\text{CO})_2\text{Cl}_2$-$(\mu\text{-dppp})_2\cdot3\text{CH}_2\text{Cl}_2$ (**1**)	$\text{Ir}_2(\text{CO})_2\text{Cl}_2(\text{O}_2)$-$(\mu\text{-dppp})_2\cdot2\text{CH}_2\text{Cl}_2$ (**2**)
formula	$\text{Ir}_2\text{P}_4\text{Cl}_8\text{C}_{59}\text{O}_2\text{H}_{58}$	$\text{Ir}_2\text{P}_4\text{Cl}_6\text{C}_{58}\text{O}_4\text{H}_{56}$
fw	1591.03	1538.11
a, Å	19.626 (3)	13.070 (2)
b, Å	22.051 (3)	20.474 (7)
c, Å	15.135 (8)	17.223 (3)
β, deg	90.36 (3)	90.75 (1)
V, Å^3	6550 (5)	5762 (2)
Z	4	4
ρ(calcd), g cm^{-3}	1.613	1.77
space group	$C2/c$	$P2_1/c$
temp, K	298	130
radiation	Mo Kα (0.710 69 Å)^c	Mo Kα (0.710 69 Å)^c
μ, cm^{-1}	47.5	53.3
range of abs cor	1.01–1.60	1.48–2.15
octants colld	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of unique data collcd	5751	7535
2θ limits, deg	0–50	0–45
final no. of variables	317	358
no. of unique data used	3462 ($F_o^2 \geq 2.5\sigma(F_o^2)$)	5853 ($I \geq 2\sigma(I)$)
R^a	0.061	0.049
$R_w{}^a$	0.072	0.052
GOF^b	2.543	

^{a} The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$; $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/\sum w|F_o|^2]^{1/2}$. ^{b} The error in observation of unit weight (GOF) was $[\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively. ^{c} From a monochromator.

crystallization from dichloromethane/diethyl ether yielded crystals of pure $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dppp})_2\cdot3\text{CH}_2\text{Cl}_2$ in 68%. The bright yellow, rec-

tangular crystals slowly lost solvent upon removal from the mother liquor. IR (KBr): ν(CO) 1947 cm^{-1} (vs). Anal. Calcd for $\text{Ir}_2\text{P}_4\text{Cl}_2\text{O}_2\text{C}_{56}\text{H}_{52}\cdot1.2\text{CH}_2\text{Cl}_2$: C, 47.77; H, 3.81. Found: C, 47.97; H, 3.93. $^{31}\text{P}\{^1\text{H}\}$ NMR (35 °C and CH$_2$Cl$_2$) gave a broad singlet at δ 20.4. Upon concentrating the remaining solution from which **1** was isolated, a pale yellow compound precipitated out. Recrystallization from dichloromethane/diethyl ether yielded white crystals, which were characterized as [Ir(H)(CO)Cl$_2$(dppp)] by spectroscopic data. This side product was formed in ca. 15% yield. IR (KBr): ν(CO) 2052 cm^{-1} (vs); ν(Ir–H) 2215 cm^{-1} (s). ^1H NMR spectrum in the hydride region at ambient temperature (CD$_2$Cl$_2$) recorded at 80 MHz: δ -16.9, sharp triplet, $J_{\text{H-P(c)}} = 10$ Hz. $^{31}\text{P}\{^1\text{H}\}$ NMR at 35 °C (CH$_2$Cl$_2$): δ -14.6.

Method 2. A solution of $\text{Ir}(\text{CO})_2\text{Cl}(p\text{-toluidine})^{19}$ (142 mg, 0.36 mmol) in 20 mL of degassed toluene was added slowly (20 min) with stirring to a solution of dppp (150 mg, 0.36 mmol) in 10 mL of degassed toluene. A light brown flocculent precipitate formed immediately but dissolved after the mixture was stirred for 1 h to yield a yellow solution. This solution was filtered under nitrogen and the volume reduced to 10 mL, causing yellow crystals to precipitate. A 20-mL aliquot of degassed diethyl ether was added to insure complete precipitation. The product was collected by filtration and washed with diethyl ether; yield 200 mg, 82%. $^{31}\text{P}\{^1\text{H}\}$ NMR and Ir spectra were identical with those of the product obtained by method 1.

$\text{Ir}_2(\text{CO})_2\text{Cl}_2(\text{O}_2)(\mu\text{-dppp})_2$ (**2**). Dioxygen was bubbled through a bright yellow dichloromethane solution of **1** for several hours. Diethyl ether was added to the deep yellow solution to give a deep yellow precipitate of **2**. Slow oxidation of **1** in the solid state by air also leads to compound **2**. IR (KBr): ν(CO) 2012 (s), 1950 cm^{-1} (s); ν(0–0) 843 cm^{-1} (m). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (35 °C and CH$_2$Cl$_2$) gave two singlets of equal intensity, δ 21.3 and -5.3.

$\text{Ir}_2(\text{CO})_2\text{Cl}_2(\text{O}_2)_2(\mu\text{-dppp})_2$ (**3**). A solution of **1** (25 mg, 0.019 mmol) in 4 mL of CDCl$_3$ was placed in a Kontes Griffin–Worden pressure tube under a pressure of 3 atm of dioxygen. After 16 h, the initially yellow solution had become nearly colorless. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a large singlet at δ -4.2 ($\cong$90% by area), which we assign to the bis-

(19) Klabunde, U. *Inorg. Synth.* **1974**, *15*, 82.

Table IV. Structural Parameters for **1** and **2**

	Ir₂(CO)₂Cl₂(μ-dppp)₂ (1)	Ir₂(CO)₂Cl₂(O₂)(μ-dppp)₂ (2) at Ir(1)		at Ir(2)	
Bond Lengths (Å)					
Ir–P(1)	2.320 (2)	Ir(1)–P(1)	2.319 (3)	Ir(2)–P(2)	2.366 (3)
Ir–P(2)	2.323 (2)	Ir(1)–P(3)	2.324 (3)	Ir(2)–P(4)	2.370 (3)
Ir–Cl	2.337 (3)	Ir(1)–Cl(1)	2.372 (3)	Ir(2)–Cl(2)	2.403 (3)
Ir–C	1.78 (2)	Ir(1)–C(1)	1.841 (12)	Ir(2)–C(2)	1.891 (12)
C–O	1.10 (2)	C(1)–O(1)	1.093 (15)	C(2)–O(2)	1.100 (15)
				Ir(2)–O(3)	2.029 (8)
				Ir(2)–O(4)	2.035 (8)
				O(3)–O(4)	1.477 (11)
Bond Angles (deg)					
P(1)–Ir–P(2)	173.10 (9)	P(1)–Ir(1)–P(3)	172.1 (1)	P(2)–Ir(2)–P(4)	170.0 (1)
P(1)–Ir–Cl	86.5 (1)	P(1)–Ir(1)–Cl(1)	86.4 (1)	P(2)–Ir(2)–Cl(2)	95.6 (1)
P(2)–Ir–C	93.6 (4)	P(1)–Ir(1)–Cl(1)	94.8 (4)	P(2)–Ir(2)–C(2)	90.7 (4)
				P(2)–Ir(2)–O(3)	85.5 (2)
				P(2)–Ir(2)–O(4)	85.4 (2)
				P(4)–Ir(2)–Cl(2)	93.1 (1)
				P(4)–Ir(2)–C(2)	93.5 (4)
				P(4)–Ir(2)–O(3)	84.5 (2)
				P(4)–Ir(2)–O(4)	87.5 (2)
Cl–Ir–C	173.5 (7)	Cl(1)–Ir(1)–C(1)	172.9 (4)	Cl(2)–Ir(2)–C(2)	94.6 (4)
				Cl(2)–Ir(2)–O(4)	106.4 (2)
				Cl(2)–Ir(2)–O(3)	148.0 (2)
				C(2)–Ir(2)–O(3)	117.5 (4)
				C(2)–Ir(2)–O(4)	159.0 (4)
				O(3)–Ir(2)–O(4)	41.7 (3)
Ir–C–O	170 (2)	Ir(1)–C(1)–O(1)	178.2 (10)	Ir(2)–C(2)–O(2)	176.1 (11)
				Ir(2)–O(3)–O(4)	69.4 (4)
				Ir(2)–O(4)–O(3)	68.9 (4)

(dioxygen) complex. A small peak ($\cong$10% by area) was also observed at δ −6.1 but was not characterized further. No unreacted **1** was present, and only a very small amount of the mono(dioxygen) adduct **2** was observed. An infrared spectrum of the solution exhibited absorbances for ν(CO) at 2006 cm⁻¹ and a shoulder at 2055 cm⁻¹. Purging the solution for 1 h with nitrogen caused no changes in the ³¹P{¹H} NMR, indicating that loss of O₂ from **3** was slow at best.

Ir₂(CO)₂Cl₂(H)₄(μ-dppp)₂ (4). A solution of **1** (0.30 g, 0.23 mmol) in 15 mL of CH₂Cl₂ was pumped and flushed with H₂ several times and was stirred for 15 h under 1 atm of H₂. The yellow solution slowly bleached to a colorless solution. Pale yellow crystals separated upon the addition of diethyl ether. X-ray analysis of one of these single crystals showed it to be a cocrystallized mixture of **4** and the dihydride Ir₂-(CO)₂Cl₂(H)₂(μ-dppp)₂ (**5**).[17] Spectral analysis is consistent with a mixture of **4** and **5** (see text). ³¹P{¹H} NMR with use of CH₂Cl₂ as solvent showed two singlets of different intensity, δ 3.0 (w) and 1.0 (s). IR (KBr): ν(CO) 1950 (m), 1985 cm⁻¹ (s); ν(Ir–H) 2195 (m), 2080 (s) cm⁻¹. ¹H NMR in hydride region (CD₂Cl₂, 300 MHz): δ −8.10, t of d, J(H–P) = 16.8 Hz, J(H–H) = 4.6 Hz; δ −8.22, t of d, J(H–P) = 18.2 Hz, J(H–H) = 4.8 Hz; δ −19.08, t of d, J(H–P) = 12.7 Hz, J(H–H) = 4.9 Hz; δ −19.44, t of d, J(H–P) = 13.9 Hz, J(H–H) = 4.7 Hz (see text and Figure 4).

X-ray Crystallographic Studies. Ir₂(CO)₂Cl₂(μ-dppp)₂·3CH₂Cl₂ (1). A crystal of **1** (thick plate, 0.05 × 0.25 × 0.20 mm) was sealed inside of a 0.2-mm capillary tube, which contained some CH₂Cl₂–O(C₂H₅)₂ solution and was found to belong to the *C*-centered monoclinic crystal class by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs and by a Delaunay reduction calculation.[20] The space group *C2/c* was chosen from systematic absences observed during data collection and was verified by successful solution and refinement. The data were collected with use of a CAD4 Nonius automatic diffractometer. Background counts were measured at both ends of the scan range with the use of an ω–2θ scan equal, at each side, to one-fourth of the scan range of the peak. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure time, and no decay with time was noted. The data were corrected for Lorentz, polarization, background, and absorption effects (ψ-scan data).[21] The structure was solved

by conventional heavy-atom techniques. The Ir atoms were located by Patterson synthesis, and full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining nonhydrogen atoms (Table III). The atomic scattering factors were taken from the usual tabulation,[22] and the effects of anomalous dispersion were included in F_c with use of Cromer and Ibers' value of $\Delta f'$ and $\Delta f''$.[23] All non-hydrogen atoms within the dimer were refined with anisotropic thermal parameters. The three CH₂Cl₂ solvate molecules showed signs of disorder and therefore were refined with isotropic thermal parameters. Hydrogen atoms were not included in any calculations. In the last cycle of refinement the mean shift/esd was 0.05. The largest feature on the final difference Fourier map was 0.9 e Å⁻³, located about 1 Å from the Ir atom. Crystal structure data, positional and thermal parameters, and observed and calculated structure factor amplitudes are shown in Tables I and III and are given as supplementary material.

Ir₂(CO)₂Cl₂(O₂)(μ-dppp)₂·2CH₂Cl₂ (2). X-ray data were collected with a Syntex P2₁ diffractometer equipped with a locally modified LT-1 device. Calculations were carried out on a Data General Eclipse computer using the SHELXTL version 4 program system. The atom form factors, including anomalous scattering, were from a standard source.[22] Yellow crystals were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **2**. A suitable needle (0.87 × 0.125 × 0.375 mm) was mounted in the low-temperature N₂ stream of the diffractometer. Lattice constants were determined by a least-squares fit of 16 centered reflections in the 2θ range 15–35°. Data were collected as summarized in Table III. Two check reflections were examined every 200 reflections and showed no alterations. The data were corrected for Lorentz, polarization, and absorption effects. Solution of the structure proceeded smoothly from location of the two iridium atoms in a Patterson map. Final refinement was carried out with anisotropic thermal param-

(20) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD4-SDP programs. This crystallographic computing package is described in the following references: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. *CAD4-SDP Users Manual*; Enraf-Nonius: Delft, Holland, 1978.

(21) The intensity data were processed as described in: *CAD4 and SDP Users Manual*; Enraf-Nonius: Delft, Holland, 1978. The net intensity I is given by $I = K/\text{NPI} (C - 2B)$ where $K = 20.1166$ × (attenuator factor), NPI = ratio of fastest possible scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/\text{NPI})^2[C + 4B + (pI)^2]$ where $p = 0.03$ and is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$ where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = \frac{1}{2}(\sigma(I)/I)F_o$.

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

(23) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

eters for Ir, P, and Cl, and isotropic thermal parameters were used 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. In the last cycle of refinement the mean shift/esd was 0.008. The largest feature on the final difference map was 1.35 e Å^{-3}, located near the center of one phenyl ring.

Supplementary Material Available: ORTEP drawing of **4** and listings of anisotropic thermal parameters, hydrogen atom positions, and additional bond lengths and bond angles (11 pages); listings of structure factor amplitudes (50 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164

Synthesis and Chemistry of [Cp₂Zr(CH₃CN)₃][BPh₄]₂: A Five-Coordinate, Dicationic Zirconocene Complex
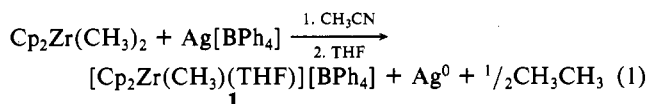
Richard F. Jordan* and Scott F. Echols

The five-coordinate, dicationic complex [Cp₂Zr(CH₃CN)₃][BPh₄]₂ (**2**) is formed by reaction of Cp₂ZrI₂ and 2 equiv of Ag[BPh₄] in CH₃CN. A stable derivative of complex **2**, [Cp₂Zr(4,4′-dimethylbipyridine)(CH₃CN)][BPh₄]₂ (**11**), has been synthesized and fully characterized. Reaction of complex **2** with PMe₃ produces a complex mixture of Cp₂Zr^{IV}–PMe₃ products. Complex **2** reacts rapidly with Cp₂Zr(CH₃)₂ to form [Cp₂Zr(CH₃)(CH₃CN)₂][BPh₄] (**10**) but reacts only slowly with Cp₂Zr(CH₂Ph)₂ to form [Cp₂Zr(η^n-CH₂Ph)(CH₃CN)][BPh₄] (**3**). The relevance of these results to the synthesis of Cp₂Zr(R)(L)$_n^+$ complexes is discussed. Halide complexes Cp₂ZrX₂ react with complex **2** to form the monohalide cations Cp₂Zr(X)(L)$_n^+$, which are unstable with respect to disproportionation to Cp₂ZrX₂ and **2** in CH₃CN.
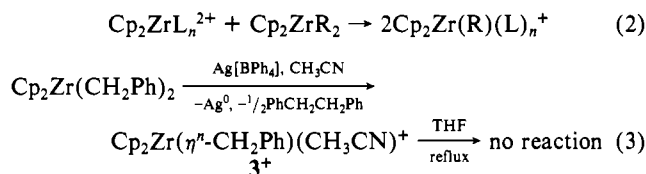
Introduction

Cationic Cp₂Zr^{IV} alkyl complexes Cp₂Zr(R)(L)$_n^+$ (L = THF, CH₃CN) are highly reactive as a result of the charge at the metal center and the lability of the ligand L.[1] We recently reported the synthesis and structure of [Cp₂Zr(CH₃)(THF)][BPh₄] (**1**) formed by reaction of Ag[BPh₄] and Cp₂Zr(CH₃)₂ (eq 1).

$$\text{Cp}_2\text{Zr(CH}_3)_2 + \text{Ag[BPh}_4] \xrightarrow[\text{2. THF}]{\text{1. CH}_3\text{CN}}$$
$$\underset{\textbf{1}}{[\text{Cp}_2\text{Zr(CH}_3)(\text{THF})][\text{BPh}_4]} + \text{Ag}^0 + {}^1/_2\text{CH}_3\text{CH}_3 \quad (1)$$

Complex **1** polymerizes ethylene in CH₂Cl₂ solution and alkylates polar substrates, including ketones and nitriles.[1,2] Tetraphenylborate, BPh₄⁻, is the anion of choice for these cationic complexes as it is apparently nonreactive and noncoordinating.

We were interested in the related dicationic species [Cp₂Zr(CH₃CN)₃][BPh₄]₂ (**2**) and its THF analogue Cp₂Zr(THF)$_n^{2+}$ for use as synthetic intermediates and mechanistic probes[3] in support of this work. Reaction of Cp₂ZrL$_n^{2+}$ complexes with Cp₂ZrR₂ provides a potential route to Cp₂Zr(R)(L)$_n^+$ complexes

(eq 2) which may be useful in certain cases. For example, the

$$\text{Cp}_2\text{ZrL}_n^{2+} + \text{Cp}_2\text{ZrR}_2 \rightarrow 2\text{Cp}_2\text{Zr(R)(L)}_n^+ \quad (2)$$

$$\text{Cp}_2\text{Zr(CH}_2\text{Ph)}_2 \xrightarrow[-\text{Ag}^0, -^1/_2\text{PhCH}_2\text{CH}_2\text{Ph}]{\text{Ag[BPh}_4], \text{ CH}_3\text{CN}}$$
$$\underset{\textbf{3}^+}{\text{Cp}_2\text{Zr(}\eta^n\text{-CH}_2\text{Ph)(CH}_3\text{CN)}^+} \xrightarrow[\text{reflux}]{\text{THF}} \text{no reaction} \quad (3)$$
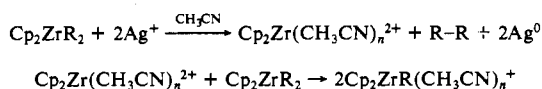
cationic benzyl complex [Cp₂Zr(η^n-CH₂Ph)(CH₃CN)][BPh₄] (**3**)[4] has been synthesized with use of Ag[BPh₄] as shown in eq 3; however, attempts to replace the CH₃CN with THF by a simple ligand-exchange reaction have proven unsuccessful. We reasoned that it might be possible to synthesize Cp₂Zr(η^n-CH₂Ph)(THF)$_n^+$ via comproportionation of Cp₂Zr(THF)$_n^{2+}$ and Cp₂Zr(CH₂Ph)₂ in THF. Also, reaction of the dication of **2** with Cp₂ZrX₂ provides a potential route to the monohalide cations Cp₂Zr(X)(L)$_n^+$, which were previously reported but not well characterized.[5]

The best characterized examples of dicationic Cp₂M^{IV} (M = Ti, Zr) complexes are [Cp₂Ti(H₂O)₂][ClO₄]₂ (**4**) and [Cp₂Zr(H₂O)₃][CF₃SO₃]₂·THF (**5**), for which X-ray structures have been reported by Thewalt.[6] However, ligands such as H₂O are incompatible with many organometallic applications. The dicationic Ti species [Cp₂Ti(CH₃CN)₂][PF₆] (**6**) has been partially characterized by ¹H NMR and IR spectroscopy though its reactivity has not been explored.[7] The chloro cations [(Cp₂ZrCl)₂(μ-

(1) (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410.
(2) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Scott, B.; Rheingold, A. L. *Organometallics*, in press.
(3) One possible mechanism for the formation of the cationic complexes **1** and **3** in eq 1 and 3 involves a Cp₂Zr(CH₃CN)$_n^{2+}$ intermediate formed from Cp₂ZrR₂ and 2 equiv of Ag⁺ (e.g. via oxidatively induced R–R elimination). Comproportionation of this intermediate and Cp₂ZrR₂ would produce the Cp₂Zr(R)(L)$_n^+$ product.

$$\text{Cp}_2\text{ZrR}_2 + 2\text{Ag}^+ \xrightarrow{\text{CH}_3\text{CN}} \text{Cp}_2\text{Zr(CH}_3\text{CN)}_n^{2+} + \text{R–R} + 2\text{Ag}^0$$
$$\text{Cp}_2\text{Zr(CH}_3\text{CN)}_n^{2+} + \text{Cp}_2\text{ZrR}_2 \rightarrow 2\text{Cp}_2\text{ZrR(CH}_3\text{CN)}_n^+$$

(4) Compound **3** has been fully characterized by spectroscopy and X-ray diffraction: Jordan, R. F.; Willett, R., manuscript in preparation.
(5) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *293*, 61.
(6) (a) Thewalt, U.; Klein, H. P. *J. Organomet. Chem.* **1980**, *194*, 297. (b) Thewalt, U.; Lasser, W. *J. Organomet. Chem.* **1984**, *276*, 341. (c) Related complexes include Cp₂Zr(THF)(CF₃SO₃)₂ (Thewalt, U.; Klein, H. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*(11), 1501) and [{Cp₂Ti(H₂O)}₂O][ClO₄]₂·2H₂O (Thewalt, U.; Kebbel, B. *J. Organomet. Chem.* **1978**, *150*, 59).