strength of the medium with sodium nitrate decreases the rate. (6) The reaction is markedly inhibited by allyl acetate. The reaction induces polymerization of acrylonitrile. This indicates the formation of radical intermediates during the reaction. (7) The presence of HSO_4^- changes the kinetic pattern of the oxidation of Mn(IV) to Mn(VII).

The foregoing kinetic results suggest that under the experimental conditions $H_3P_2O_8^-$ forms a 1:1 complex with Ag^+ ion which then decomposes in a rate-determining step to give reactive intermediates. These reactive intermediates then attack Mn(IV) to give Mn(VII) in a series of fast steps:

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^-$$

$$H_3P_2O_8^- + Ag^+ \overset{K_2}{\rightleftharpoons} \text{complex}$$

$$\text{complex} \xrightarrow[k_0]{\text{slow}} \text{intermediates}$$

$$\text{Mn(IV)} + \text{intermediates} \xrightarrow{\text{fast}} \text{products}$$

On the basis of this mechanism the rate law can be derived as

$$k_0' = \frac{k_0'K_1K_2[Ag^+][H_2P_2O_8^{2-}][H^+]}{1 + K_1[H^+] + K_1K_2[H_2P_2O_8^{2-}][H^+]}$$

From the slopes and intercepts of the plots between $1/k_0'$ vs. 1/[PDP] and $1/k_0'$ vs. $1/[H^+]$, the values of K_1, K_2, and k_0 can be calculated. The values of K_1 and K_2 are found to be K_1 = 4.0 (30 °C) and 4.8 (35 °C) L mol^{-1} and K_2 = 109 (30 °C) and 155 (35 °C) L mol^{-1}.

Edwards et al.[3] have reported the first, second, third, and fourth dissociation constants of $H_4P_2O_8$ to be $\simeq 2.0$, $\simeq 3 \times 10^{-1}$, $(6.6 \pm 0.3) \times 10^{-6}$, and $(2.1 \pm 0.1) \times 10^{-8}$ M, respectively. Because of the very low magnitude of the third and fourth dissociation constants, $P_2O_8^{4-}$ exists as $H_2P_2O_8^{2-}$ under the acid conditions employed in this investigation. The value of K_1 in the above mechanism corresponds to the inverse of the second dissociation constant reported by Edwards et al., and the agreement here is good. The values of k_0 at 25, 30, and 35 °C were found to be $(1.20 \pm 0.10) \times 10^{-4}$, $(1.85 \pm 0.10) \times 10^{-4}$, and $(2.33 \pm 0.14) \times 10^{-4}$ s^{-1}, respectively. From the estimated parameters k_0, K_1, and K_2 and the rate laws, the rates were calculated and compared with observed rates. These were shown in different tables.

Activation Parameters. The energy of activation and entropy of activation for the oxidation of Mn(IV) to Mn(VII) were computed from the rate constants (k_0) of the rate-determining step at three temperatures where the Arrhenius plot was linear. The energy of activation was found to be 47 ± 4 kJ mol^{-1}, and the entropy of activation was found to be −130 ± 10 J K^{-1} mol^{-1}.

On interesting observation is that under the same experimental conditions peroxodisulfate is not capable of oxidizing Mn(II) to Mn(VII) without precipitation of hydrated manganese dioxide due to its inability to stabilize Mn(III) and Mn(IV) formed as intermediates, whereas in the present investigation PDP itself is capable of stabilizing both Mn(III) and Mn(IV) for some time. If this is the case, in the presence of added phosphate, peroxodisulfate should oxidize Mn(II) to Mn(VII) with Mn(III) and Mn(IV) as the stable intermediates. The results of our preliminary investigation confirm this.

Acknowledgment. K.J.M.R. and A.S.P.V. are grateful to the CSIR and UGC, New Delhi, for the award of a Junior Research fellowship and a teacher fellowship, respectively. Our special thanks are due to Dr. Frank Caropreso of FMC Corp. for a generous gift of PDP.

Registry No. $P_2O_8^{4-}$, 15538-83-7; Mn, 7439-96-5; Ag, 7440-22-4.

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Mono- and Binuclear Iridium Carbonyl Hydrides Containing Bis(tertiary phosphine) Ligands

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New mono- and binuclear iridium(I) carbonyl halide complexes containing the bis(tertiary phosphine) ligands $Ph_2P(CH_2)_nPPh_2$ (n = 2, dppe; n = 3, dppp) have been prepared, and the formation of iridium(III) hydrides by H_2 oxidative addition has been studied. The binuclear complexes $[IrX(CO)(dppp)]_2$ (X = Br, I) possess trans phosphine donors, with the dppp ligands bridging the Ir(I) centers. Addition of H_2 yields the tetrahydride species $[IrH_2X(CO)(dppp)]_2$ in which the trans phosphine arrangement at each iridium is maintained. However, upon heating, cleavage of the dimers is noted, leading to the mononuclear species $IrH_2X(CO)(dppp)$. For X = I, mononuclear dppp complexes are also prepared starting with the reaction of $IrI_2(CO)_2^-$ + dppp under CO to yield $IrI(CO)_2(dppp)$. All of the dppe complexes are mononuclear, with dppe acting as a chelate. The necessarily cis disposition of phosphine donors in the mononuclear chelates is readily evidenced by ^1H NMR spectroscopy of the hydride complexes. Reversible addition of CO to IrX(CO)(dppe) (X = Br, I) is also observed.

Introduction

Metal hydrides play an important role in many metal-catalyzed reactions such as hydrogenation, hydroformylation, the water-gas shift reaction, and CO reduction chemistry.[1] For this reason, the preparation and reaction chemistry of transition-metal hydride complexes have been studied extensively. The oxidative addition of H_2 to a metal complex is one of the most important methods of hydride preparation, and one of the most relevant in the context of catalytic properties, since this reaction represents a principal mode for the activation of H_2. Since Vaska's initial report in 1962,[2] it has been known that d^8 iridium(I) phosphine complexes are particularly active with regard to H_2 oxidative addition.[1c] This reaction invariably proceeds with cis stereochemistry at the metal center and, in the case of *trans*-$IrCl(CO)(PPh_3)_2$ and its analogues,

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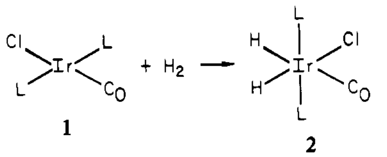
(1) For general reviews, see: (a) Muetterties, E. L., Ed. "Transition-Metal Hydrides"; Marcel Dekker; New York, 1971. (b) Bau, R., Ed. *Adv. Chem. Ser.* **1978**, *No. 167*. (c) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 60 ff.

(2) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679.

0020-1669/84/1323-3216$01.50/0

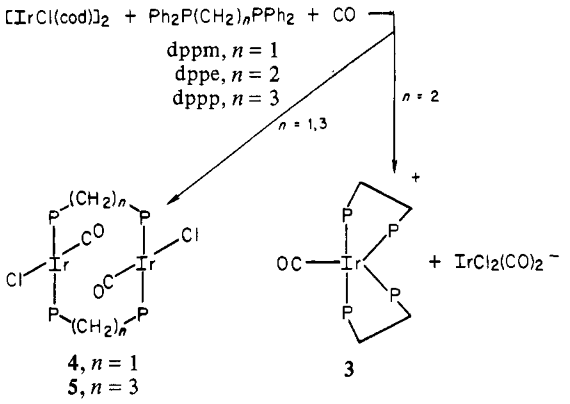
results in products in which the phosphine ligands maintain their trans disposition as shown in eq 1.



(1)

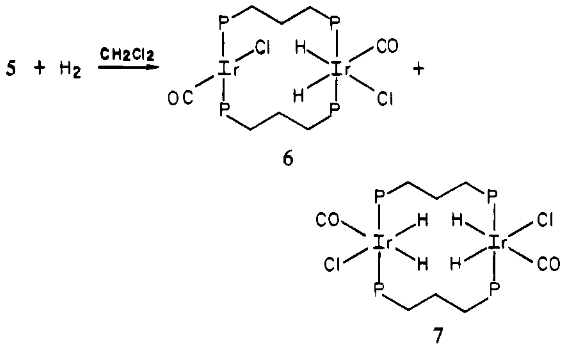
In this paper, we describe our studies on the synthesis, characterization, and H_2 oxidative-addition chemistry of new iridium complexes containing bis(tertiary phosphine) ligands. These ligand systems may either chelate a single metal center or bridge two Ir ions. The former leads to a cis stereochemistry of phosphine donors different from that observed in most adducts of Vaska's complex and its analogues, while the latter produces two metal centers in close proximity for the binding and activation of substrates.

The relative tendency of the bis(tertiary phosphine) ligand system $Ph_2P(CH_2)_nPPh_2$ to bridge or chelate is shown in eq 2 as reported by Sanger. In this reaction, only a monomer is synthesized when $n = 2$, whereas dimers form when $n = 1$ and 3.[3] Compound **3**, which was first reported by Vaska, forms because of the favorable driving force of five-membered chelate-ring formation.[4] Complexes **4** and **5**, on the other hand, maintain what seems to be the electronically favorable disposition of trans P donors, with the creation of face-to-face dimers of Ir(I) having ligand sets similar to that found in Vaska's complex.



(2)

Our interest in dimeric compounds of this type was stimulated by the notion of two metal centers in close proximity for the activation of two substrates simultaneously or for the activation of a single substrate using both metal centers and their attendant four electrons (two $d^8 \rightarrow d^6$ oxidative additions on a single substrate). Use of dppm as a bridging ligand has been explored extensively in face-to-face dimers and in A-frame complexes and yields a relatively rigid binuclear structure in which metal···metal distances vary between 2.7 and 3.5 Å.[5] The dppp ligand, on the other hand, allows a more flexible binuclear structure with metal···metal distances ranging up to 6 Å.[6] The chemistry of these systems has only begun to be explored. Pignolet and Wang have found that **5** oxidatively adds H_2 to form a mixture of the dihydride $Ir_2H_2(CO)_2Cl_2(dppp)_2$ (**6**) and the tetrahydride $Ir_2H_4(CO)_2Cl_2(dppp)_2$ (**7**) in eq 3.[6] The structural assignment of **6** and **7** are supported by crystallographic evidence. Loss of H_2 from **7** appears facile, and the increased steric bulk at one Ir center after the first oxidative addition appears to inhibit reactivity at the second metal center.



(3)

The studies described in this paper use the work of Sanger and Pignolet as a starting point. Because the bromo and iodo analogues of Vaska's complex were known to be more reactive than the parent chloro system, $IrCl(CO)(PPh_3)_2$,[7] we commenced studies on the bromo and iodo analogues of **5**. The context in which our studies were undertaken was the development of H_2 reduction catalysts for CO_2, a goal that still remains to be reached. On the basis of Herskovitz' work, it was known that electron-rich Ir(I) centers are capable of reacting with CO_2 to form metallocarboxylate species.[8] We envisioned that the presence of nearby hydrides on a second metal center would facilitate the desired reduction of bound CO_2.

The investigations that we outline here include studies of binuclear dppp complexes and the hydrides that they form, the unexpected cleavage of these dimers into mononuclear species, and the formation and reaction chemistry of previously unknown mononuclear complexes containing only a single bis(tertiary phosphine) ligand. These mononuclear complexes represent cis phosphine analogues of the well-studied $IrX(CO)L_2$ system.

Experimental Section

Physical Measurements. Microanalyses were performed by Galbraith Laboratories. Infrared spectra were recorded on a Perkin-Elmer 467 grating infrared spectrophotometer. ^1H NMR spectra were recorded with a Bruker WH-400 400-MHz spectrometer. ^{31}P NMR spectra were recorded with a JEOL FT 100 spectrometer at 41.25 MHz or a Bruker WH-400 spectrometer at 162 MHz. Gas chromatography was done on a Hewlett-Packard 5700A gas chromatograph interfaced with a Hewlett-Packard 3380A automatic integrator. Carbon monoxide was detected on either a 12-ft column of Poropak Q or a 2-ft column of 5A molecular sieves. Molecular H_2 was detected on the molecular sieves column. In all GC detection, $^1/_4$-in. columns were used at 42 °C with He as the carrier gas and thermal conductivity detectors. The flow rate of He was 35–48 mL/min, and retention times of 1.05 and 1.35 min were observed for H_2 and CO, respectively, on the Poropak Q column, and 0.31 and 4.1 min, respectively, on the molecular sieves column.

Reagents. All operations were performed under N_2, CO, or H_2 by using modified Schlenk techniques. Tetrahydrofuran and benzene were dried over Na and distilled under N_2 before use. Bis(diphenylphosphino)ethane (dppe) and bis(diphenylphopshino)propane (dppp) were purchased from Strem Chemical and recrystallized from boiling ethanol. Bio beads were purchased from Bio-Rad. Tetramethylene sulfone (sulfolane) was purchased from Aldrich and distilled twice (first time from P_2O_5) immediately prior to use. All other reagent grade chemicals were purchased commercially and used without further purification. Throughout, TBA = tetra-*n*-butylammonium.

[TBA][Ir(CO)$_2$Br$_2$]. Cleare and Griffith's procedure for preparing the analogous Rh compound was followed.[9] Typically $IrCl_3{\cdot}(H_2O)_3$ (1 g) and KBr (1 g) were refluxed in a 1:1 (v/v, 20 mL) mixture of

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(3) Sanger, A. S. *J. Chem. Soc., Dalton Trans.* **1977**, 1971.

(4) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324.

(5) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 6129; *Ibid.* **1980**, *19*, 2726. Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733; *Ibid.* **1982**, *21*, 2119.

(6) Pignolet, L.; Wang, H. H. "Abstracts of Papers", 180th National Meeting of the American Chemical Society, Las Vegas, NV, 1980; American Chemical Society: Washington, DC, 1980; Abstract No. 168. Wang, H. H. Ph.D. Thesis, University of Minnesota, 1981.

(7) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

(8) Herskovitz, T., Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

(9) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1970**, 2788.

formic acid and HBr. The system was open only to a mineral oil bubbler, allowing the CO_2 generated during the reduction to escape. After 12–24 h, the solution had turned pale yellow. (If the solution had not turned pale yellow in 24 h, an additional 1–2 mL of formic acid was added, and the refluxing continued until a pale yellow solution was obtained.) After the mixture was cooled under a moderate stream of N_2, tetrabutylammonium bromide (1 g in 5 mL of H_2O) was added. The product precipitated as a yellow powder. An additional 10–20 mL of water was added and the solution cooled on an ice bath to ensure an almost quantitative yield. The product was washed with cold water, ethanol, and ether. The product was recrystallized from boiling isopropyl alcohol.

[TBA][Ir(CO)$_2$I$_2$]. Forster's procedure was followed.[10] Typically $IrCl_3\cdot(H_2O)_3$ (1 g) and NaI (5 g) were refluxed in 30 mL of 5% H_2O in 2-methoxyethanol under an extremely slow flow of CO, ca. 5 mL/min. After about 12 h, the solution had turned pale yellow. The solution was cooled under a stream of CO to room temperature, and tetrabutylammonium iodide (1 g in 30 mL of H_2O) was added. The product precipitated as a yellow powder. The product was washed with cold water, cold isopropyl alcohol, and pentane and was recrystallized from boiling isopropyl alcohol. The product is air sensitive and should be prepared immediately before use or stored under vacuum.

Ir$_2$Cl$_2$(CO)$_2$(dppp)$_2$ (5). This complex was prepared by Sanger's method;[3] yield ca. 80%.

Ir$_2$Br$_2$(CO)$_2$(dppp)$_2$ (8). A solution of 0.54 g (0.83 mmol of $[TBA][IrBr_2(CO)_2]$) and 0.3 g (0.83 mmol) of dppp was stirred in acetone (15 mL) for 24 h. The yellow solution initially evolved CO. A pale precipitate formed after about 15 min; the solution cleared after an additional 15–30 min. The desired product began to precipitate after 1 h, but the solution was allowed to stir for an additional 8 h. The yellow precipitate was washed with cold acetone and Et_2O. The isolated powder was analytically pure; yield 0.49 g (84%). Anal. Calcd for $Ir_2C_{56}H_{52}O_2P_4Br_2$: C, 47.1; H, 3.7; P, 8.7. Found: C, 46.5; H, 3.8; P. 8.5. The remainder of the product can be isolated by the addition of H_2O (0.5 mL) to the filtrate and stirring overnight. Samples of **8** were prepared for NMR spectral analysis by recrystallization from CH_2Cl_2/acetone under N_2 at 0 °C.

Ir$_2$I$_2$(CO)$_2$(dppp)$_2$ (9). Wang and Pignolet's method[6] was modified as follows. LiI (2 g) in EtOH (ca. 30 mL) was added to a slurry of 0.15 g of $Ir_2Cl_2(CO)_2(dppp)_2$ in benzene (ca. 20 mL). The solution was heated at 60 °C, and formation of the yellow precipitate was monitored by IR spectroscopy. After 6 h, the metathesis of I^- for Cl^- was complete as shown by a shift of ν_{CO} in the IR spectrum (KBr): $\nu_{CO} = 1950$ cm^{-1} for **9**, $\nu_{CO} = 1940$ cm^{-1} for $Ir_2Cl_2(CO)_2(dppp)_2$. The precipitate was filtered, and washed with EtOH and Et_2O.

Ir$_2$H$_4$Br$_2$(CO)$_2$(dppp)$_2$ (10). A 0.5-g (0.35 mmol) sample of **8** was dissolved in 100 mL of CH_2Cl_2. The solution was pumped and flushed with H_2 several times and then stirred vigorously under ca. 1 atm of H_2. After 24 h, the solution had lost its yellow color. The product precipitated as a colorless powder after the addition of 20 mL of 99% EtOH, followed by removal of ca. 20 mL of CH_2Cl_2; yield 0.42 g (84%). Anal. Calcd for $Ir_2C_{56}H_{56}O_2P_4Br_2$: C, 47.1; H, 3.9; P, 8.7; Br, 11.2. Found: C, 47.0; H, 4.0; P, 8.5; Br, 11.4.

Ir$_2$H$_4$I$_2$(CO)$_2$(dppp)$_2$ (11). A 0.2-g (0.13 mmol) sample of **9** was dissolved in 10 mL of THF, and the resultant mixture was placed under an atmosphere of H_2. The solution rapidly lost its yellow color (ca. 0.5 h) but was allowed to stir at room temperature for 8 h. Ethanol (20 mL) was added, and THF was removed until the product precipitated as a colorless powder. The product can be recrystallized from hot CH_2Cl_2 under H_2.

Ir$_2$H$_2$Br$_2$(CO)$_2$(dppp)$_2$ (12). A 0.1-g (0.07 mmol) sample of **8** was dissolved in 15 mL of CH_2Cl_2 and the resultant solution diluted with 15 mL THF. The solution was thoroughly degassed and placed under N_2. One equivalent (1.7 mL, 0.07 mmol) of H_2 at 1 atm was added wtih a Pressure-Lok gas-tight syringe. The solution was vigorously stirred for 24 h. Ethanol (15 mL) was added and the CH_2Cl_2/THF mixture removed until the product precipitated as a yellow powder; yield 0.8 g (80%).

IrI(CO)$_2$(dppp) (13). A 0.14-g sample of dppp in 10 mL of THF was added to 0.26 g of $[TBA][IrI_2(CO)_2]$ under CO. The solution was stirred at room temperature under CO overnight, during which time crystalline [TBA]I precipitated. Ethanol (ca. 5 mL) was added, resulting in the dissolution of the [TBA]I and the precipitation of a colorless material. (This colorless precipitate has one $\nu_{CO} = 1930$ cm^{-1} and was identified as $Ir(dppp)_2(CO)I$ by analogy to the known $Ir(dppe)_2(CO)Cl$, which is colorless and has one $\nu_{CO} = 1933$ cm^{-1}.[3,4] The yellow solution was filtered away from the precipitate and the THF removed by rotary evaporation until the desired product precipitated as a bright yellow powder; yield 0.15 g (57%). Anal. Calcd for $IrC_{29}H_{26}O_2P_2I$: C, 44.2; H, 3.3; P, 7.9. Found: C, 44.27; H, 3.54; P, 8.09.

IrH$_2$I(CO)(dppp) (14). A sample of **13** was dissolved in EtOH/THF (ca. 1:4, v/v) under H_2, and H_2 was slowly bubbled through the solution (ca. 5 mL/min). After 12 h the solution was colorless, and the product had started to precipitate. Vigorous bubbling of H_2 through the solution resulted in the precipitation of the rest of the product as a colorless powder. The product was filtered in air, washed with pentane, and recrystallized from hot CH_2Cl_2 under H_2; yield >90%.

IrH$_2$Br(CO)(dppp) (15). A 0.1-g (0.07 mmol) sample of **10** was dissolved in 10 mL of CH_2Cl_2 and the resultant mixture diluted with 20 mL of THF. Triethylamine (1 mL) was added and the solution placed under ca. 1 atm of H_2. The solution was stirred at 65 °C for 12–24 h. The solvent (including triethylamine) was removed under vacuum. The solids were dissolved in a minimum volume of acetone, and water was added until the product began to precipitate, usually as a cream-colored powder. The product can be recrystallized from hot CH_2Cl_2 under H_2. Complex **14** can be prepared by this method from complex **11**, but at least 24 h of heating is required.

IrBr(CO)(dppe) (16). Under CO, a 0.1-g (0.25 mmol) sample of dppe dissolved in ca. 7 mL of THF was added to 0.16 g (0.25 mmol) of $[TBA][IrBr_2(CO)_2]$ dissolved in 5 mL of THF cooled to −70 °C. The solution was allowed to warm to room temperature over 30 min. Ethanol (10 mL) was added to the reaction solution, which was briefly heated to 80 °C (3 min) and then reduced in volume by using a rotary evaporator until the product crystallized as bright orange microcrystals, yield 0.13 g (75%).

IrI(CO)(dppe) (17). A 0.1-g (0.25 mmol) sample of dppe dissolved in ca. 7 mL of THF was added to 0.2 g (0.26 mM) of $[TBA][IrI_2(CO)_2]$ dissolved in ca. 5 mL of THF. The mixture was heated to 60 °C for 15–20 min before cooling to room temperature. After this time, the yellow solution turned bright orange. Ethanol (10 mL) was then added to the orange solution and solvent removed until the product precipitated as an orange powder. The product is recrystallized from hot benzene/EtOH; yield 0.1 g (50%). Anal. Calcd for $IrC_{27}H_{24}OP_2I$: C, 43.5; H, 3.2; P, 8.3. Found: C, 43.7; H, 3.5; P, 8.38.

IrH$_2$X(CO)(dppe) (X = Br (18), I (19)). A sample of **16** or **17** was dissolved in benzene under a H_2 atmosphere and stirred until the solution lost its orange color (≤3 min). After the addition of EtOH, bubbling of H_2 through the reaction solution was continued for several hours until the product precipitated as a colorless powder, yield >90%. This procedure results in isolation of the thermodynamic isomer of **18** or **19**, which is described in the Results and Discussion.

IrX(CO)$_2$(dppe) (X = Br (20), X = I (21)). An orange benzene solution of **16** or **17** was placed under CO. The solution turned yellow immediately, with a corresponding change in the solution spectra. The CO adducts are difficult to isolate as solids because of CO loss; solution yield 100%, based on ^1H and ^{31}P NMR spectra.

Molecular Weight Determination by BioBeads Filtration. BioBeads SX-4 (ca. 30 mL) were placed in boiling CH_2Cl_2 and allowed to percolate in the refluxing solvent for 15 min, after which the mixture was allowed to cool. A 50-mL buret was packed with the beads using CH_2Cl_2 as the eluant. A calibration curve for molecular weight was made by using seven rhodium and iridium phosphine complexes in the following procedure. As much compound as possible was dissolved in 0.5 mL of CH_2Cl_2, loaded onto the column, and eluted with CH_2Cl_2 (dispensed from an addition funnel). The time for elution of each complex was measured and plotted against log (molecular weight) to give a straight line. The new complex, $Ir_2Br_2(CO)_2(dppp)_2$, was measured and found to be a dimer, as formulated. Formulation as a monomer results in a point significantly off the calibration curve.

Molecular Weight Determination by Freezing Point Depression.[11] Sulfolane was used as the cryoscopy solvent due to its large molal

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(10) Forster, D. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 433.

(11) For standard procedure, see: (a) Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I. "Experiments in Physical Chemistry", 3rd ed.; McGraw-Hill: New York, 1974; pp 179 ff. (b) Mikulak, R.; Runquist, O. *J. Chem. Educ.* **1961**, *38*, 557.

Table I. Infrared and ^{31}P NMR Spectral Data for Iridium dppp and dppe Complexes

compd	IR, cm^{-1}		^{31}P NMR, ppm
	ν_{CO}	ν_{Ir-H}	
$Ir_2Br_2(CO)_2(dppp)_2$ (**8**)	1915, 1944		18.93[c] (20% acetone-d_6 in CH_2Cl_2)
$Ir_2I_2(CO)_2(dppp)_2$ (**9**)	1950		14.0 (s)[e]
$Ir_2H_4Br_2(CO)_2(dppp)_2$ (**10**)	1945, 1980	2100, 2190	
$Ir_2D_4Br_2(CO)_2(dppp)_2$ (**10**-D_4)	2016	*b*	...
$Ir_2H_4I_2(CO)_2(dppp)_2$ (**11**)	1980	2090, 2160	
$Ir_2H_2Br_2(CO)_2(dppp)_2$ (**12**)	1945, 1980	2100, 2190	
$IrI(CO)_2(dppp)$ (**13**)	1955, 2040		−28.49 (s)[d] (acetone-d_6)
$IrH_2I(CO)(dppp)$ (**14**)	2042	2105	21.9 (d), 29.9 (d)[d] (J_{P-P} = 30.52 Hz; acetone-d_6)
$IrH_2Br(CO)(dppp)$ (**15**)	2043	2220	
$IrBr(CO)(dppe)$ (**16**)	1980		43.7 (d), 47.9 (d)[c] (J_{P-P} = 14 Hz; C_6D_6)
$IrI(CO)(dppe)$ (**17**)	1980		64.3 (d), 62.21 (d)[c] (J_{P-P} = 9.5 Hz; acetone-d_6)
$IrH_2Br(CO)(dppe)$ (**18**)	2030	2195	33.8 (d), 26.6 (d)[c,f] (C_6D_6)
$IrH_2I(CO)(dppe)$ (**19**)	2040	2160	28.06 (d), 20.62 (d)[d] (J_{P-P} = 7 Hz; acetone-d_6)
$IrBr(CO)_2(dppe)$ (**20**)	1940, 2040		53.51 (s)[c] (C_6D_6)
$IrI(CO)_2(dppe)$ (**21**)	1950, 2040		32.0 (s)[c] (C_6D_6)

[a] IR Spectra were recorded on a Perkin-Elmer 467 grating infrared spectrophotometer. All spectra were taken of KBr pellets except for those of **13**, **20**, and **21**, which were in benzene solution. [b] ν_{Ir-D} not observed. [c] Measured in 5-mm tubes on a Bruker WH-400 instrument at 162 MHz. Positive chemical shifts are downfield from H_3PO_4 (external). [d] Measured in 10-mm tubes on a JEOL PFT-100 spectrometer at 41.25 MHz. [e] Measured by Wang and Pignolet.[6] [f] J_{P-P} is less than 2 Hz in this compound.

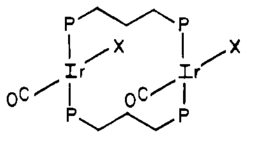
freezing point depression constant (66.2°/mol).[12] The standard procedure was used, employing a large test tube as the reaction vessel and a Beckman thermometer. The melting point of the solvent is 28.8 °C; thus, no artificial cooling is required.

The molecular weight of **13** was determined from two separate samples, measured two times each. Based on molecular weight determinations of several known complexes of similar type, the error involved in this measurement is estimated to be 15%.

Results and Discussion

The reaction of $[Ir(CO)_2Br_2]^-$ as its n-Bu_4N^+ salt with the bis(tertiary phosphine) ligands dppp and dppe serves as a convenient route to the formation of iridium(I) phosphine complexes. While both ligand systems react to form mononuclear species, only dppp is observed to form binuclear complexes as well.

Binuclear dppp Complexes. The room-temperature reaction of $[n\text{-}Bu_4N][Ir(CO)_2Br_2]$ with dppp in acetone under N_2 leads to the evolution of CO and the essentially quantitative production of the pale yellow complex $Ir_2Br_2(CO)_2(dppp)_2$ (**8**).

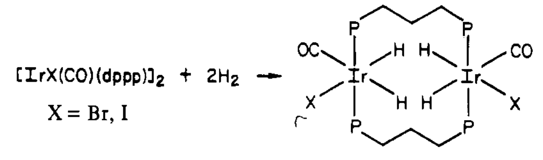


8, X = Br
9, X = I

This complex is air sensitive in solution but can be handled routinely as a solid in air. The dimeric structure of **8** is assigned on the basis of elemental analyses, the $^{31}P\{^1H\}$ NMR spectrum that shows only a singlet at 18.93 ppm indicative of trans P donors, the IR spectrum, and analogy with the chloro complex, **5**, first reported by Sanger.[3] An approximate molecular weight determination using Bio Bead filtration (see Experimental Section) indicates a molecular weight of ca. 1400 for **8**, consistent with its binuclear formulation. Conductivity measurements show **8** to be a nonelectrolyte in DMF solution. The CO ligands in **8** are shown in a cis orientation because two carbonyl stretches at 1944 and 1915 cm^{-1} are observed in its IR spectrum. Both ν_{CO}'s are indicative of terminal CO coordination to square-planar Ir(I). Additional support for the structural assignment of **8** derives from its reaction with H_2, which gives an essentially quantitative yield of a single, easily characterized binuclear product (vide infra). The infrared and ^{31}P NMR spectral data for **8** and all following compounds are presented in Table I.

The iodo complex **9** is prepared by metathesis of iodide for chloride in complex **5**. This method was first used by Wang and Pignolet, who found that **9** prepared by this route has only a single carbonyl stretching frequency in the IR spectrum (at 1950 cm^{-1}).[6] On the basis of the single ν_{CO}, **9** is assigned a structure with the CO ligands in the trans orientation as in the previously reported chloro complex **5**, but in contrast with the bromo analogue **8**. Wang and Pignolet have also found **9** to have a ^{31}P NMR spectrum containing only one sharp singlet at 14.0 ppm.[6] Like **8**, compound **9** is air sensitive in solution but can be handled in air as a solid.

The oxidative addition of H_2 to **8** and **9** yields binuclear hydride complexes as shown in eq 4. Under 1 atm of H_2 in CH_2Cl_2, **8** and **9** form the tetrahydride complexes **10** and **11**.

 (4)

10, X = Br
11, X = I

The formation of **11** in THF at 25 °C is essentially complete within 1 h compared with 24 h for the formation of **10** and only incomplete conversion of the chloro complex **5** to its tetrahydride **7** under the same conditions.[6] This observation is consistent with the notion of increased reactivity with halide ligand in the order Cl < Br < I. The same order of reactivity was found for the addition of H_2 to *trans*-$Ir(CO)X(PPh_3)_2$ (X = Cl, Br, I).[7]

The IR spectrum of **10** contains two ν_{CO}'s (1945, 1980 cm^{-1}) while that of **11** contains only one (1980 cm^{-1}). The two ν_{CO}'s of **10** change in relative intensity in solution, indicating that they belong to different species. Since **10** is known to lose H_2 readily, we propose the ν_{CO} at 1945 cm^{-1} to be due to iridium(I) carbonyl resulting from reductive elimination of H_2 at one of the iridium centers.

The ^{1}H NMR spectra of **10** and **11** provide key information about the structure of these complexes. The full ^{1}H NMR spectrum, from +10 to −20 ppm, of **10** is shown in Figure 1. There are three groups of resonances. The phenyl protons at ca. δ 7 are split into two groups—the ortho protons and the metal and para phenyl protons. The methylene protons of the

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[12] (a) Camiener, G. W.; Brown, G. M. *J. Am. Chem. Soc.* **1959**, *81*, 3799. (b) Monica, M. D.; Jannelli, L.; Lamanna, U. *J. Phys. Chem.* **1968**, *72*, 1068.

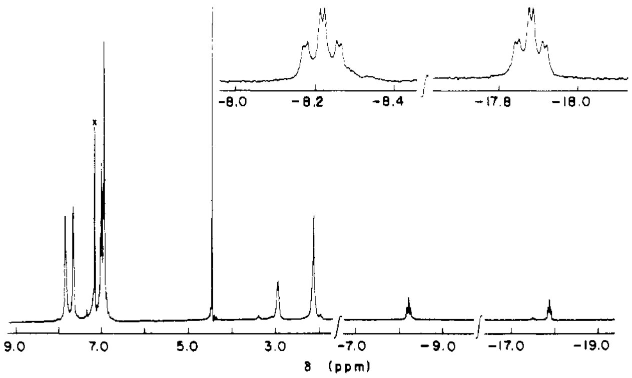
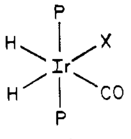


Figure 1. ^{1}H NMR spectrum of $Ir_2H_4Br_2(CO)_2(dppp)_2$ (**10**) in C_6D_6. The resonance labeled X is C_6D_5H. The resonance at 4.46 ppm is dissolved H_2. The inset is an expanded view of the hydride region.

dppp ligand are split into two broad, symmetrical resonances. Homonuclear decoupling indicates that the broadness is due to phosphorus coupling. Last, the pair of triplets of doublets in the hydride region, expanded in the Figure 1 inset, integrates as four protons compared to the 12 methylene protons, indicating a tetrahydride.

The pair of triplets of doublets, separated by ca. 9 ppm, indicate that the hydride ligands are trans to very different ligands. The doublet splitting of 3 Hz is due to hydride–hydride coupling, as shown by homonuclear decoupling experiments. When each triplet of doublets is irradiated, the other one collapses to a simple triplet. This indicates that the hydride ligands are cis to each other. The triplet splitting is 13 Hz and is due to the coupling of two equivalent P atoms to the hydride ligands. The P donors are therefore necessarily trans to each other and cis to the hydride ligands in **10** and **11**.

The ^{1}H NMR spectral data for **10** and **11** are consistent with structure A about each Ir center. For **10** the hydride ligand trans to CO gives rise to the resonance at −8.6 ppm, while the hydride trans to halide gives rise to the one at −18.7 ppm in the ^{1}H NMR spectrum. The assignment of the hydride resonances is by analogy to the known mononuclear dihydride complexes, $IrH_2X(CO)(PR_3)_2$ (X = Cl, Br, I), which possess geometry A and whose ^{1}H NMR spectra have hydride regions very similar to those of **7**, **10**, and **11**. For example, the hydride region in the ^{1}H NMR spectrum of $IrH_2Cl(CO)(P(CH_3)_2(Ph))_2$ contains two triplets of doublets at δ −7.58 and −18.36.[1a] For the complex $IrHCl_2(CO)(P(CH_3)_2(Ph))_2$, in which the hydride is known to be trans to the halide, the single triplet is found at −15.7 ppm.[1a] Thus, the hydride at −18.36 ppm in $IrH_2Cl(CO)(P(CH_3)_2(Ph))_2$ is assigned as trans to chloride. Many similar examples have been tabulated and suggest the generality that hydride ligands trans to halides appear at considerably higher fields than those trans to carbonyl groups.[1a] The ^{1}H NMR spectral data for $IrH_2Br(CO)(PPh_3)_2$, complexes **10** and **11**, and related complexes that remain to be discussed are tabulated in Table II.



A

While the preparative procedure for **10** was being optimized, it was found that oxidative addition of only a single molecule of H_2 to **8** can be accomplished to form the Ir(I)–Ir(III) dihydride, **12**, analogous to **6** reported by Pignolet and Wang.[6] In acetone, the reaction of **8** with H_2 yields a mixture of **10** and **12**, as evidenced by the ^{1}H NMR spectrum that contains three pairs of triplets of doublets. The pair at δ −8.6 and −18.7 is attributed to the tetrahydride, **10**. The four new triplets of doublets are found at −8.4, −8.8, −18.2, and −18.8 ppm. When a sample of this mixture is sealed in an NMR tube under vacuum and spectra are recorded at hourly intervals, these new resonances are observed to gain intensity at the expense of the resonances assigned to the tetrahydride, **10**. Homonuclear decoupling experiments relate the −8.4 ppm triplet to the −18.8 ppm triplet and the −8.8 ppm triplet to the −18.2 triplet, indicating the presence of two species in addition to **10**. These two species correspond to two geometric isomers of the Ir(I)–Ir(III) dihydride complex **12**. The addition of 1 equiv of H_2 to a CH_2Cl_2 solution of **8** under N_2 also results in the formation of the pale yellow dihydride **12**, and the ^{1}H NMR spectrum of a sample of **12** prepared this way contains the four new triplets of doublets described above.

Table II. ^{1}H NMR Spectral Data for Iridium dppp and dppe Hydride Complexes (Hydride Region Only)

compd	^{1}H NMR,[a] ppm
$IrH_2Br(CO)(PPh_3)_2$	−7.35 (t of d) ($J_{PH\text{-}cis}$ = 17.5 Hz, J_{HH} = 4.5 Hz), −16.53 (t of d) ($J_{PH\text{-}cis}$ = 13.7 Hz, J_{HH} = 4.5 Hz; $CDCl_3$
$Ir_2H_4Br_2(CO)_2(dppp)_2$ (**10**)	−8.6 (t of d), −18.7 (t of d) ($J_{PH\text{-}cis}$ = 13 Hz, J_{HH} = 3 Hz; $CDCl_3$)
$Ir_2H_4I_2(CO)_2(dppp)_2$ (**11**)	−9.74 (t of d), −16.84 (t of d) ($J_{PH\text{-}cis}$ = 13 Hz, J_{HH} = 3 Hz; $CDCl_3$)
$Ir_2H_2Br_2(CO)_2(dppp)_2$ (**12**)	−8.4, −8.8, −18.2, −18.8 (all t of d) ($J_{PH\text{-}cis}$ = 13 Hz, J_{HH} = 3 Hz; $CDCl_3$)
$IrH_2I(CO)(dppp)$ (**14**)	−9.27 (d of d) ($J_{PH\text{-}trans}$ = 120 Hz, $J_{PH\text{-}cis}$ = 16 Hz), −15.35 (m) (C_6D_6)
$IrH_2Br(CO)(dppp)$ (**15**)	−9.27 (d of d) ($J_{PH\text{-}trans}$ = 120 Hz, $J_{PH\text{-}cis}$ = 16 Hz), −17.99 (m) (C_6D_6)
$IrH_2Br(CO)(dppe)$ (**18**)	−9.05 (d of d of d) ($J_{PH\text{-}cis}$ = 17 Hz, $J_{PH\text{-}trans}$ = 130 Hz, J_{HH} = 4.5 Hz), −18.26 (m) ($CDCl_3$)
$IrH_2I(CO)(dppe)$ (**19**)	−9.92 (d of d of d) ($J_{PH\text{-}cis}$ = 17 Hz, $J_{PH\text{-}trans}$ = 128 Hz, J_{HH} = 4.5 Hz), −16.27 (m) (acetone-d_6)

[a] All proton NMR spectra are recorded on a Bruker WH-400 at 400.134 MHz. Positive chemical shifts are downfield from Me_4Si.

Mononuclear dppp Complexes. A mononuclear Ir(I) dppp complex can also be formed from the reaction of $Ir(CO)_2I_2^-$ with dppp. The room-temperature reaction of $Ir(CO)_2I_2^-$ with dppp leads to apparent evolution of CO and the isolation of an orange complex, **13**. This complex exhibits two carbonyl stretching frequencies (2040, 1955 cm^{-1}) in both solution- and solid-state IR spectra and shows only one singlet in the ^{31}P NMR spectrum. A molecular weight determination by freezing point depression yields a molecular weight of 715, indicating a mononuclear formulation for **13**. Compound **13** is not air sensitive during short periods of exposure (<15 min). The complex reacts with H_2 in benzene over 24 h to form a new hydride complex **14**, along with the evolution of CO.

This new hydride species **14** exhibits only one ν_{CO} in the IR spectrum (see Table I) and has a ^{1}H NMR spectrum very different from that observed for the dimeric hydrides **7**, **10**, and **11**. The ^{1}H NMR spectrum of **14** is shown in Figure 2. The main features of the hydride pattern are two groups of resonances separated by ~6 ppm, one of which is a broad doublet of doublets and the other a more complicated multiplet. The spectrum is consistent with chemically different P nuclei, and the magnitude of the larger doublet-of-doublets splitting ($J_{P\text{-}H}$ = 120 Hz) suggests that one of the hydrides is trans to a phosphine donor. The second hydride is located trans to

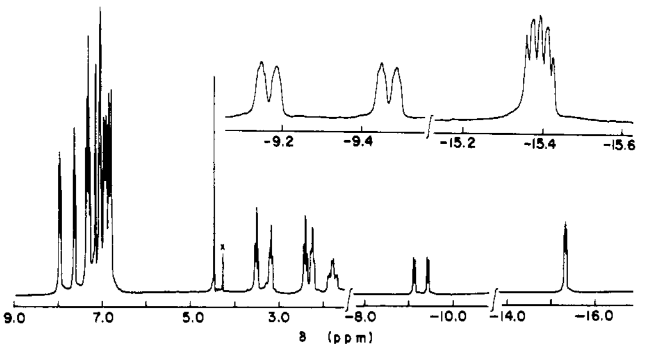
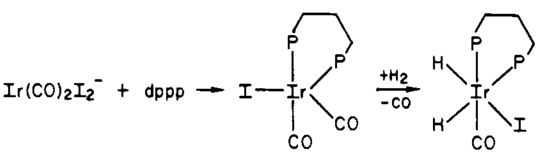


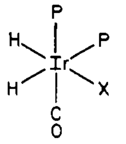
Figure 2. ^{1}H NMR spectrum of $IrH_2I(CO)(dppp)$ (**14**) in C_6D_6. The resonance labeled × is an impurity in the solvents. The resonance at 4.46 ppm is dissolved H_2. The inset is an expanded view of the hydride region.

iodide on the basis of its chemical shift. In addition, the ^{31}P NMR spectrum of **14** consists of two doublets with 30.5-Hz coupling, indicative of two chemically inequivalent cis P ligands.

The spectroscopic data provide the basis for a consistent interpretation of the reactions involving $Ir(CO)_2I_2^-$ + dppp and H_2 as shown in eq 5. The initial product having ν_{CO} of 2040 and 1955 cm^{-1} is mononuclear, unlike the other dppp complexes formed in analogous reactions. The two carbonyl stretches indicate a cis disposition of CO ligands in the complex. This complex, $IrI(CO)_2(dppp)$, is thus assigned structure **13** with a chelating bis(tertiary phosphine) ligand. The singlet in the ^{31}P NMR spectrum of **13** is proposed to be due to the stereochemical nonrigidity of this five-coordinate d^8 species. The reaction of **13** with H_2 leads to loss of CO, which is detected in the gas phase above the solution and helps confirm the formulation of **13** as a mononuclear dicarbonyl complex. The reaction with H_2 leads to the formation of **14**, which possesses structure B and gives rise to one ν_{CO} and one broad ν_{Ir-H} in its IR spectrum. An alternative binuclear formulation of **14** with bridging dppp ligands in cis positions of the coordination sphere is ruled out on the basis of highly unfavorable steric interactions between neighboring diphenylphosphino groups, the mononuclear nature of **13**, and parallel reaction chemistry observed using dppe that is discussed below.

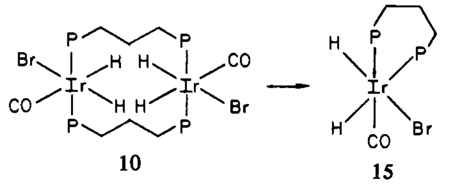


13 14 (5)



B

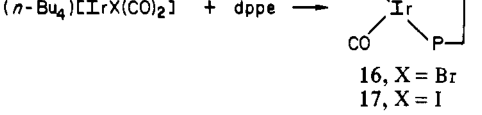
Cleavage of Binuclear dppp Hydrides. The mononuclear dppp dihydride **14**, and its bromo analogue, $IrH_2Br(CO)$(dppp) (**15**), can also be formed by cleaving the binuclear tetrahydrides **10** and **11**. When CH_2Cl_2 or THF solutions of **10** and **11** are heated for several hours in the presence of NEt_3, a striking change occurs in the hydride region of the ^{1}H NMR spectra. Specifically, the resonances characteristic of the trans P donors of **10** and **11** are replaced by those consistent with cis P donors. The change from trans to cis P donors occurs with a cleavage of the binuclear hydride system to the mononuclear structure as shown in eq 6. The cleavage of **10** can also be effected by heating of **10** under Ar or CO_2. When a similar experiment was carried out with **11**, the complex decomposed during the 24-h experiment.



10 15 (6)

The lack of integrity of **10** and **11** as binuclear species was surprising since Pignolet and Wang have employed **5** as a decarbonylation catalyst at 150 °C and have not observed dimer cleavage.[6] Moreover, reactions of similar complexes having dppm bridges under a variety of conditions have revealed no tendency of these dimers to break apart into monomeric species.[5] Our observation of dimer cleavage provides an important caveat to studies based on using bis- and poly(tertiary phosphine) ligands to hold two or more metal atoms together in systems having structural integrity.

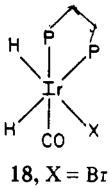
dppe Complexes. In order to provide additional support for the structural assignments of **13**–**15** as mononuclear species, the analogous complexes with dppe in place of dppp were synthesized and characterized. The ligand dppe shows a much greater tendency toward chelation than does dppp and only rarely forms a bridge between two metals.[13] The new mononuclear dppe complexes Ir(CO)X(dppe) (**16** (X = Br), **17** (X = I)) are prepared by reacting [n-Bu_4N][$Ir(CO)_2X_2$] with dppe in THF or benzene according to eq 7. Formation of $Ir(CO)(dppe)_2^+$ (**3**) cannot be avoided in this reaction, but the two different products can be easily separated because of their greatly different solubilities. Complexes **16** and **17**, which are modestly air sensitive in solution, have very similar spectroscopic properties (see Table I). The single ν_{CO} of 1980 cm^{-1} for **16** and 1980 cm^{-1} for **17** and the two doublets in the ^{31}P NMR spectrum of each complex provide good evidence that **16** and **17** are mononuclear dppe species. It is surprising that complexes **16** and **17** have not been reported previously since they are cis phosphine analogues of the well-studied systems *trans*-$IrX(CO)L_2$ where L is a tertiary phosphine.



(7)

16, X = Br
17, X = I

Solutions of the orange, square-planar Ir(I) complexes **16** and **17** in THF or CH_2Cl_2 react rapidly with H_2, and after several hours, result in formation of the mononuclear dihydride species **18** and **19**, respectively (see below). These complexes are readily isolated as colorless crystals by the addition of EtOH and removal of solvent under a stream of H_2. The Ir(III) dihydride complexes **18** and **19** as isolated are considerably less soluble than their Ir(I) precursors. Complexes **18** and **19** are spectroscopically similar to complexes **14** and



18, X = Br
19, X = I

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(13) (a) Haines, R. J.; DuPreez, A. L. *Inorg. Chem.* **1972**, *11*, 330. (b) Davies, S. G.; Hibberd, J.; Simpson, S. J. *J. Organomet. Chem.* **1982**, C7. (c) Davies, S. G.; Hibberd, J.; Simpson, S. J. *Ibid.* **1983**, *241*, C31. (d) Day, V.; Thompson, M.; Nelson, G. O.; Wright, M. *Organometallics* **1983**, *2*, 794.

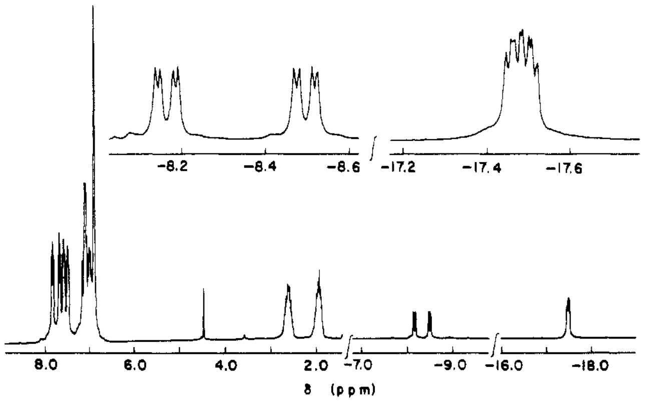

Figure 3. ^{1}H NMR spectrum of $IrH_2Br(CO)(dppe)$ (**18**) in C_6D_6. The resonance at 4.46 ppm is dissolved H_2. The inset is an expanded view of the hydride region.

15 (see Tables I and II). The ^{1}H NMR spectrum of **18** is shown in Figure 3, and an expanded view of the hydride region is shown in the inset. The "downfield" hydride resonance is a doublet of doublets of doublets ($J_{\text{H-P}_{\text{trans}}}$ = 130 Hz; $J_{\text{H-P}_{\text{cis}}}$ = 17 Hz; $J_{\text{H-H}}$ = 4.5 Hz) and is separated from the "upfield" hydride multiplet by 9 ppm. Irradiation of the upfield multiplet results in loss of the smallest doublet splitting in the downfield hydride resonances, leaving a doublet of doublets pattern. The observation of hydride–hydride coupling for **18** and **19** represents the only difference in their ^{1}H NMR spectra from those observed for the analogous dppp complexes, **14** and **15**.

An intriguing aspect of the H_2 oxidative addition to **16** and **17** is that it is not only extremely facile but also stereospecific. The initial product formed is an isomer of **18** or **19**, which contains one hydride trans to CO and the other trans to P. This material then isomerizes to the product as drawn above and shown in Figure 3. A detailed examination of this observation has been reported in a separate paper.[14]

Complexes **16** and **17** also react with CO to form dicarbonyl species **20** and **21** analogous to **13**. These complexes exhibit two ν_{CO}'s at 1940 and 2040 cm^{-1} for **20** and 1950 and 2040 cm^{-1} for **21**. The ^{31}P NMR spectrum of each complex exhibits only one sharp singlet at room temperature, in accord with that observed for the dppp complex **13**, suggesting that these five-coordinate d^8 species are stereochemically nonrigid at room temperature.

Both H_2 oxidative addition and CO addition to **16** and **17** are reversible. Refluxing THF or benzene solutions of these adducts under N_2 leads to loss of the addend molecule and regeneration of **16** or **17**. Because of the extreme facility with which **20** and **21** lose CO, attempts to isolate analytically pure samples of these compounds were unsuccessful. However, the dicarbonyl compounds were completely characterized by solution spectroscopic methods. It is interesting to note that Vaska's complex, *trans*-$IrCl(CO)(PPh_3)_2$, also reversibly binds CO to give a dicarbonyl complex,[15] but the forward reaction is not as rapid as that observed for **16** or **17**.

In summary, the synthesis and characterization of iridium hydrides having the bis(tertiary phosphine) ligands dppp and dppe as bridges and chelates have been examined. Binuclear dppp-bridged complexes of formula $[IrH_2X(CO)(dppp)]_2$ (X = Br, I) possess the phosphine donors in trans disposition as shown by ^{1}H NMR spectroscopy. Upon heating, these dimers cleave into monomeric species of the same stoichiometry in which dppp acts as a chelate. The dppe complexes are all mononuclear and contain a dppe-chelated ring. The hitherto unreported complexes IrX(CO)(dppe) (X = Br, I) have been described as has their reaction chemistry to form reversible adducts with H_2 and CO.

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Registry No. **8**, 89935-23-9; **9**, 91383-65-2; **10**, 89935-25-1; **11**, 89947-74-0; **12**, 89935-26-2; **13**, 89935-27-3; **14**, 89935-28-4; **15**, 89935-29-5; **16**, 29638-05-9; **17**, 85421-68-7; **18**, 88035-04-5; **19**, 88035-05-6; **20**, 89935-30-8; **21**, 85421-70-1; [TBA][$Ir(CO)_2Br_2$], 73190-78-0; [TBA][$Ir(CO)_2I_2$], 60255-19-8; H_2, 1333-74-0.

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