

Diphenylphosphido-Bridged Dirhodium Complexes Containing Combinations of 1,5-Cyclooctadiene, Chelating Diphosphines, and Monodentate Phosphine Ligands¹

PAUL E. KRETER and DEVON W. MEEK*²

Received January 26, 1982

The syntheses, characterization, and phosphorus-31 NMR spectra of 17 new diphenylphosphido-bridged dirhodium complexes of bidentate and monodentate phosphines are presented. Treatment of $[\text{RhCl}(\text{COD})]_2$ and $[\text{IrCl}(\text{COD})]_2$ with lithium diphenylphosphide in THF at room temperature produces the corresponding diphenylphosphido-bridged complexes $[\text{M}(\mu\text{-PPh}_2)(\text{COD})]_2$ in excellent yields. The 1,5-cyclooctadiene (COD) ligands of $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ are replaced stepwise by chelating diphosphines, LL (e.g., $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 1-4$) to produce complexes of the types $[(\text{LL})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ and $[\text{Rh}(\mu\text{-PPh}_2)(\text{LL})]_2$. In contrast, reactions with the monodentate phosphines PPh_3 , PMePh_2 , PEt_3 , and PCy_3 yield only "mixed" phosphine-COD complexes of the types $(\text{R}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$ and $(\text{Cy}_3\text{P})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$. These unusual complexes possess a rhodium-rhodium bond, two dissymmetrically bridging diphenylphosphido groups, and two different stereochemistries around the rhodium atoms. One rhodium is tetrahedral and surrounded by four phosphorus atoms, and the other rhodium (bonded to COD) is nearly planar. In the $(\text{R}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$ complexes, the phosphorus resonance of the $\mu\text{-PPh}_2$ group is shifted downfield approximately 300 ppm compared to the position for analogous complexes of the chelating diphosphines; the large shift is attributed to the formation of the rhodium-rhodium bond.

Introduction

A large number of metal clusters have been studied in which halide, hydroxide, or mercaptide anions serve as bridges between the metal ions.³ In contrast, until very recently only a relative few bi-, tri-, and tetrametallic compounds with bridging organophosphorus groups (e.g., R_2P^-) were known.^{4,5} However, during the past 3 years the number of bimetallic and cluster compounds that contain bridging organophosphido ligands has grown at a prodigious rate.⁶ Also during this time period, several rational substitution and photochemical methods have been reported for syntheses of phosphido complexes, in contrast to the earlier thermal degradations of triphenylphosphine complexes. Several of these preparative routes have been summarized recently.⁷

Although Hayter⁴ and Chatt⁵ first prepared diphenylphosphido complexes 20 years ago, the recent awakening of interest in the use of the organophosphido groups can be attributed to (1) the tremendous recent interest in catalysis by transition-metal clusters, (2) the realization that organophosphido groups form stable bridges between two metals similar to the case for the mercaptide ligands, and (3) the increasing use of ³¹P NMR spectra for characterization and structure elucidation of the resulting products. Our interest in phosphido ligands emanates from a desire to study the systematic synthesis of homo- and heterometal bi-, tri-, and tetrametallic complexes that would be useful for both catalysis and NMR studies. Thus, our initial studies have concentrated

on metals with magnetic nuclei (e.g., Rh and Pt) with R_2P^- and $\text{R}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}^-$ ligands.^{1,8}

At the beginning of this study (1976), only one reference had been reported on the ³¹P NMR spectrum of a phosphido-bridged complex.⁹ To acquire an understanding of the ³¹P NMR spectral parameters for phosphido-bridged compounds, we initially studied the ³¹P NMR spectra of a few complexes of the type $[\text{MCl}(\mu\text{-PPh}_2)(\text{L})]_2$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{L} = \text{HPPH}_2$, PEt_3 , PBu_3 , AsBu_3).¹ Subsequently, other investigators have published ³¹P NMR data on these same and similar complexes.^{10,11} Since our spectral data and interpretations agree with the published data, we are omitting the palladium and platinum complexes. We report herein the syntheses, ³¹P NMR, and structural results obtained on several diphenylphosphido-bridged dirhodium and two diridium complexes of 1,5-cyclooctadiene, chelating diphosphines and monodentate phosphines.

Experimental Section

A. Reagents and Chemicals. The chemicals were reagent grade and were used without further purification unless stated otherwise. The sources are listed after the chemical names: diphenylphosphine (Ph_2PH), bis(diphenylphosphino)methane (DPPM), 1,3-bis(diphenylphosphino)propane (DPPP), 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos), methyldiphenylphosphine (PMePh_2), and triethylphosphine (PEt_3) from Pressure Chemical Co.; triphenylphosphine from Aldrich; tricyclohexylphosphine (PCy_3) from Organometallics, Inc.; *cis*-1,2-bis(diphenylphosphino)ethene (*cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$) and 1,2-bis(diphenylphosphino)ethane (DPPE) from Strem Chemicals; 1-(diphenylphosphino)-3-(phenylphosphino)propane ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}$) and 1-(diphenylphosphino)-2-(ethylphenylphosphino)ethane ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhEt}$) from R. D. Waid (OSU) and Professor S. O. Grim (University of Maryland) respectively; *n*-butyllithium, as a 2.4 M hexane solution, from Alfa Products; rhodium trichloride trihydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) from Englehard Industries; iridium trichloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$) from Matthey Bishop Co. Tetrahydrofuran (THF) was distilled just before use from potassium-benzophenone under a nitrogen atmosphere. Olefins that were used in the hydrogenation experiments were purified according to literature methods.¹²

B. Instrumentation. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer from 4000 to 400

- (1) Condensed from: Kreter, P. E. Ph.D. Dissertation, The Ohio State University, Columbus, OH, Dec 1980. Presented at the 11th Regional Meeting of the American Chemical Society, Columbus, OH, May 1979, Abstract INOR 59. Dr. Kreter's present address is Arco Chemical Co., Newtown Square, PA.
- (2) John Simon Guggenheim Fellow, 1981-1982.
- (3) Johnson, B. F. G., Ed. "Transition Metal Clusters"; Wiley: Chichester, England, 1980.
- (4) (a) Hayter, R. G. *Prep. Inorg. React.* **1965**, *2*, 211-236 and references cited therein. (b) Hayter, R. G.; Humiec, F. S. *Inorg. Chem.* **1963**, *2*, 306. (c) Hayter, R. G. *Ibid.* **1963**, *2*, 1031. (d) Hayter, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 823.
- (5) (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1964**, 2433. (b) Chatt, J.; Thornton, D. A. *Ibid.* **1964**, 1005.
- (6) Recent papers that provide leading references on organophosphido bridging ligands are: Fischer, K.; Vahrenkamp, H. *Z. Anorg. Allg. Chem.* **1981**, *475*, 109-115. Schumann, H.; Neumann, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 708-712. Braunstein, P.; Matt, D.; Bars, O.; Louer, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79-107. Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *Ibid.* **1981**, *204*, C27-32. Iwasaki, F.; Mays, M. J.; Raithby, P. R.; Taylor, P. L.; Wheatley, P. J. *Ibid.* **1981**, *213*, 185-206. Haines, R. J.; Steen, N. D. C. T.; English, R. B. *Ibid.* **1981**, *209*, C34. Mays, M. J.; Raithby, P. R.; Taylor, P. L. *Ibid.* **1982**, *224*, C45-48.
- (7) Young, D. A. *Inorg. Chem.* **1981**, *20*, 2049.

- (8) Waid, R. D. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1982. Preliminary results were presented at the 11th Regional Meeting of the American Chemical Society, Columbus, OH, May 1979, Abstract INOR 59.
- (9) Coulson, D. R. *Chem. Commun.* **1968**, 1530.
- (10) Eaborn, C.; O'Dell, K. J.; Pidcock, A. *J. Organomet. Chem.* **1979**, *170*, 105.
- (11) Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188.
- (12) Riddick, J. A.; Bunger, W. B. "Organic Solvents"; Wiley-Interscience: New York, 1970.

Table I. Analysis Data for the Solid Bis(μ -diphenylphosphido)dirhodium Complexes

complex	formula		% C	% H	% P	% other
[Rh(μ -PPh ₂)(DPPM)] ₂	C ₇₄ H ₆₄ P ₆ Rh ₂	calcd	66.07	4.76	13.84	0 (Cl)
		found	65.74	4.92	14.18	0.5
[Rh(μ -PPh ₂)(DPPE)] ₂	C ₇₆ H ₆₈ P ₆ Rh ₂	calcd	66.47	4.96	13.56	
		found	66.25	5.22	13.34	
[Rh(μ -PPh ₂)(DPPP)] ₂	C ₇₈ H ₇₂ P ₆ Rh ₂	calcd	66.86	5.14	13.29	
		found	64.96	5.36	12.90	
[Rh(μ -PPh ₂)(Arphos)] ₂	C ₇₆ H ₆₈ As ₂ P ₄ Rh ₂	calcd	62.46	4.66	8.49	10.27 (As)
		found	62.42	4.92	8.52	10.19
(PEt ₃) ₂ Rh(μ -PPh ₂) ₂ Rh(COD)	C ₄₄ H ₆₂ P ₄ Rh ₂	calcd	57.39	6.74	13.48	
		found	57.52	7.00	13.50	
(PMePh ₂) ₂ Rh(μ -PPh ₂) ₂ Rh(COD)	C ₅₆ H ₅₀ P ₄ Rh ₂	calcd	64.21	5.35	11.44	0 (Cl)
		found	66.17	5.17	10.51	0.4

cm⁻¹ with the samples as pressed KBr pellets or as Nujol mulls between KBr plates. Polystyrene film was used for calibration of the spectra.

Proton magnetic resonance spectra, as well as phosphorus-31 NMR spectra, were collected on a Bruker HX-90 spectrometer operating at 90.00 and 36.43 MHz, respectively, in the Fourier transform mode. Phosphorus-31 NMR spectra were proton noise decoupled, except when the ³¹P-H coupling constants were to be determined. The proton NMR spectra were run in deuterated solvents and standardized by assignment of the proton resonance of the residual nondeuterated solvent molecules that are present in the deuterated solvents. The phosphorus-31 NMR spectra were run in 10-mm tubes as solutions generally with nondeuterated solvents. The spectra were calibrated through the use of coaxial insert tubes that contained the secondary standard, trimethyl phosphate ($\delta = 1.595$ relative to 85% H₃PO₄ at 0.00), and deuterated acetone or deuterated toluene for the lock signal. The insert tube was placed in the sample tube throughout the data collection period. The resolution of the ³¹P NMR coupling constant data is ± 0.6 Hz, while the accuracy in the chemical shift data is ± 0.2 ppm, with variations in the latter due mainly to solvent and concentration effects. Elemental analyses were performed either by M-H-W Laboratories, Phoenix, Az, or by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

The hydrogenation experiments were performed at ~ 750 torr pressure with an automatic gas-measuring instrument that was designed and constructed by J. R. Fagan of the OSU Chemistry Department. This instrument was coupled to a small vacuum line to ensure rigorous exclusion of oxygen and other contaminants from the reaction vessel. Volatile products from the hydrogenation reactions were identified with use of a Varian Aerograph Series 1200 gas chromatograph equipped with a flame ionization detector and a Chromosorb P column coated with 20% β, β' -oxydipropionitrile.

C. General Experimental Procedures. Standard techniques for the manipulation of air-sensitive compounds were used for all reactions unless specified otherwise.¹³ Schlenk equipment was used for most reactions of air-sensitive compounds, and solution transfers were performed with use of either a long stainless steel transfer needle or a nitrogen-flushed syringe. All reactions were carried out under an atmosphere of high-purity nitrogen. Solvents were purged with nitrogen for 30 min prior to use.

D. Preparation of the Iridium Complexes. 1. [Ir(μ -PPh₂)(CO)(PPh₃)₂]. A solution of 0.07 mL of Ph₂PH (0.08 g, 0.41 mmol) in 5 mL of THF was treated with 0.18 mL of *n*-butyllithium (2.4 M, 0.43 mmol) under nitrogen. The resulting bright red solution was transferred via a stainless steel needle to a flask containing 0.316 g of IrCl(CO)(PPh₃)₂¹⁴ (0.41 mmol) in 10 mL of THF under nitrogen. The initially yellow IrCl(CO)(PPh₃)₂ solution turned dark red and slowly deposited a red precipitate. The mixture was filtered after 1 h, and the solid was washed with cold THF (2 \times 5 mL) and then dried under vacuum; yield 0.26 g (90%). The infrared carbonyl absorption of the solid, $\nu_{CO} = 1920$ cm⁻¹, was identical with the reported value.¹⁵

2. [Ir(μ -PPh₂)(COD)]₂. A solution of 0.18 mL of Ph₂PH (0.19 g, 1 mmol) in 10 mL of THF was treated with 0.44 mL of butyllithium (2.4 M, 1 mmol); the resultant lithium diphenylphosphide solution

was added via a transfer needle to a flask containing a THF solution of [Ir(μ -Cl)(COD)]₂¹⁶ (0.336 g, 0.5 mmol in 10 mL). The resulting solution was stirred for 2 h, during which time a red solid precipitated. The solid was collected on a filter, washed with cold THF (2 \times 5 mL) and then with water (2 \times 5 mL), and dried in vacuo; yield 0.15 g (60%). Anal. Calcd for C₄₀H₄₄Ir₂P₂: C, 49.46; H, 4.53; P, 6.39; Cl, 0. Found: C, 48.84; H, 4.60; P, 6.12; Cl, 0.2.

3. Attempted Reaction of [Ir(μ -PPh₂)(COD)]₂ with 1,3-Bis(diphenylphosphino)propane, DPPP. To a solution of [Ir(μ -PPh₂)(COD)]₂ (0.2 g, 0.2 mmol) in 5 mL of THF was added 0.35 g of DPPP (0.84 mmol). The solution was refluxed for 1 h under nitrogen and then cooled; a ³¹P NMR spectrum indicated that no reaction had occurred, showing only resonances at $\delta = 166$ and -18.6 due to the reagents [Ir(μ -PPh₂)(COD)]₂ and DPPP, respectively.

E. Preparation of the Rhodium Complexes. 1. [Rh(μ -PPh₂)(COD)]₂. To a solution of 0.37 mL of Ph₂PH (0.39 g, 2.0 mmol) in 20 mL of THF was added 0.84 mL of *n*-butyllithium (2.4 M in hexane; 2.0 mmol), producing a red solution with evolution of heat. This solution was transferred via a stainless steel needle to a flask containing 0.493 g of [RhCl(COD)]₂¹⁷ (1.0 mmol) in 30 mL of THF. The resulting dark green solution was stirred for 1 h, and then the solvent was evaporated under vacuum. The resulting dark brown residue was washed with cold acetone (3 \times 15 mL) and then water (3 \times 10 mL). The dark green solid that was left was dried under vacuum, dissolved in 15 mL of THF, and recrystallized by addition of 10 mL of acetone; yield 0.51 g (64%). The reaction gave the same results when carried out under a helium or argon atmosphere. Analytical results consistently showed small amounts of chloride, probably due to Rh₂(μ -Cl)(μ -PPh₂)(COD)₂ as an impurity. Anal. Calcd for C₄₀H₄₄P₂Rh₂: C, 59.30; H, 5.72; P, 7.65; Cl, 0. Found: C, 58.81; H, 5.67; P, 6.87; Cl, 0.60.

2. Reaction of [Rh(μ -PPh₂)(COD)]₂ with the Bidentate Ligands DPPM, DPPE, DPPP, *cis*-Ph₂PCH=CHPh₂, and Ph₂PCH₂CH₂AsPh₂. All these reactions were carried out with use of the same general method, which is described here. The elemental analyses are given in Table I. Solid [Rh(μ -PPh₂)(COD)]₂ was placed in a flask along with 1.0 equiv of the solid ligand. The flask was flushed with nitrogen, and then 5 mL of THF was added. After the solution was stirred for 30 min, a 2-mL aliquot was removed with a syringe and placed in a 10-mm NMR tube under nitrogen. The ³¹P NMR spectrum of the "mixed" complex (LL)Rh(μ -PPh₂)₂Rh(COD) was recorded, and then the aliquot was transferred back to the original solution with a syringe. Then another 1.0 equiv of the appropriate solid ligand was added to the solution under a stream of nitrogen. The resulting solution was stirred for 1 h, and then 5 mL of acetone was added, causing precipitation of the crystalline material. The mixture was allowed to stand overnight; then it was filtered, and the solid was washed with 2 \times 5 mL of acetone and dried under vacuum. The bis(diphosphine)-dirhodium complexes were isolated in 94-99% yields.

3. Reaction of [Rh(μ -PPh₂)(COD)]₂ with Ph₂PCH₂CH₂PPhEt and Ph₂PCH₂CH₂CH₂PPhH. Since these ligands are liquids, the above synthetic method was modified as described below. The solid sample of [Rh(μ -PPh₂)(COD)]₂ was dissolved in 5 mL of THF under nitrogen, and then the liquid ligand was added via a syringe. The volume of solution was reduced to ~ 2 mL under a stream of nitrogen, the solution was transferred to a 10-mm NMR tube, and the ³¹P NMR

(13) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

(14) Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1958**, *11*, 101.

(15) (a) Mason, R.; Sztöfte, I.; Robinson, S. D.; Uttley, M. F. *J. Organomet. Chem.* **1972**, *46*, C61. (b) Bellon, P. L.; Benedicenti, C.; Caglio, G.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1973**, 946.

(16) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

(17) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.

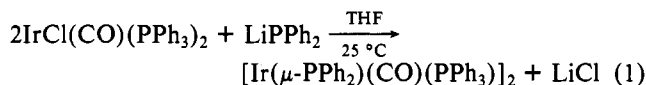
spectrum was recorded. Attempts to isolate solid complexes from these liquid ligands resulted in air-sensitive red oils that could not be characterized adequately.

4. $[(L)_2Rh(\mu-PPh_2)Rh(COD)]$: $L = PPh_3, PMePh_2, PEt_3$. A sample of $[Rh(\mu-PPh_2)(COD)]_2$ was dissolved in 10 mL of THF, and 2.0 equiv of the desired ligand was added to the solution. The solution was stirred for 2 h, and then the volume was reduced to ~ 5 mL; then acetone (5 mL) was added. The resulting crystalline precipitate was collected by filtration, washed with cold acetone (2×5 mL), and dried in vacuo. The three complexes were isolated in 68, 95, and 75% yield, respectively.

Results and Discussion

As recently as 1 year ago, rhodium and iridium organo-phosphido-bridged complexes had been studied very little; existing references were concerned with structure determinations of compounds in which the phosphido group had been produced accidentally by heating triphenylphosphine complexes vigorously.^{15,18,19} This paucity of rhodium and iridium phosphido complexes is somewhat surprising in view of the rich catalysis and oxidative-addition chemistry that rhodium and iridium complexes display. Certainly, we can expect to see the number of studies on Rh and Ir phosphido-bridged complexes increase in the future.

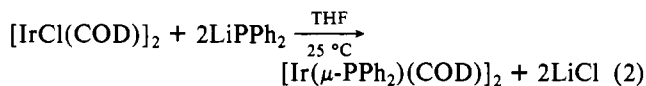
In an effort to correlate our first ^{31}P NMR results with a known structure, the compound $[Ir(\mu-PPh_2)(CO)(PPh_3)]_2$ was prepared in 90% yield according to eq 1; the high yield should



be contrasted with the low yield that had been obtained previously from the thermal degradation of $IrH(CO)(PPh_3)_2$.¹⁵ The diiridium compound is insoluble in most organic solvents; however, it is sufficiently soluble in THF to permit collection of its $^{31}P\{^1H\}$ FT NMR spectrum, which consists of two first-order triplets at $\delta = 86$ and 221. Magnetic equivalence of the two phosphines, and of the two phosphido groups, suggests that the center of symmetry of the diiridium complex and the pseudotetrahedral geometry around each iridium atom (found in the crystal structure¹⁵) are maintained in solution. The observed phosphino-phosphido coupling constant, $^2J_{PP}$, is 36 Hz.

The resonance position of the phosphido phosphorus nuclei is shifted far downfield from the standard (85% H_3PO_4), as opposed to an upfield shift generally observed for bimetallic Pd(II) and Pt(II) phosphido-bridged complexes.^{1,10,11} This large downfield shift is characteristic of the three-membered ring created by a phosphido group that bridges a strong metal-metal bond.²⁰ Also, the chemical shift of the phosphino nuclei, 86 ppm, is farther downfield than expected; this may be due to an inductive effect of the strong $Ir=Ir$ bond and/or the M_2P_2 moiety.

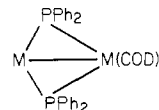
The previously unknown compound $[Ir(\mu-PPh_2)(COD)]_2$ was obtained from the reaction of $[IrCl(COD)]_2$ with lithium diphenylphosphide in THF (eq 2). The cyclooctadiene com-



plex was chosen since the COD ligand is usually displaced readily by other ligands such as CO and PR_3 to give several types of derivatives. The product is a red, air-sensitive solid that is moderately soluble in tetrahydrofuran and shows only a single $^{31}P\{^1H\}$ resonance at $\delta = 166$. The strongly deshielded,

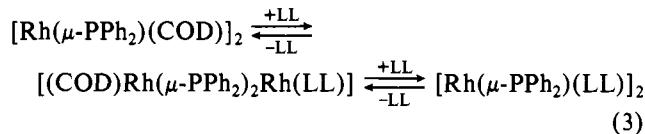
low-field position of the phosphido nuclei indicates that the complex contains an Ir-Ir bond and that it probably has a structure similar to that of $[Ir(\mu-PPh_2)(CO)(PPh_3)]_2$, with a pseudotetrahedral coordination geometry around each metal.

Since the cyclooctadiene ligand usually can be easily displaced from COD-Ir(I) complexes, several attempts were made to prepare other $Ir_2(PPh_2)_2$ complexes from $[Ir(\mu-PPh_2)(COD)]_2$. However, reactions with ligands such as carbon monoxide or 1,3-bis(diphenylphosphino)propane did not produce ligand-substituted derivatives, even at elevated temperatures. Usually, only the starting materials, contaminated with small amounts of impurities, could be isolated from the reactions. This lack of reactivity may be due to the presence of the metal-metal double bond. A decreased reactivity of a COD complex was also observed for rhodium complexes that contain the linkage (vide infra)



For synthesis of the analogous dirhodium-diphenylphosphido complex $[Rh(\mu-PPh_2)(COD)]_2$, a THF solution of $[RhCl(COD)]_2$ was treated with a THF solution of $LiPPh_2$. The resulting dark green compound gives only one resonance (a 1:2:1 triplet) in the $^{31}P\{^1H\}$ NMR spectrum at -71.7 ppm, indicating that the two phosphorus nuclei are magnetically equivalent and coupled equally to both rhodium atoms. The $^1J_{RHP}$ value of 100 Hz is considerably smaller than normal $R_3P-Rh(I)$ coupling constants,^{21,22} and the low value may indicate that the Rh_2P_2 unit is not planar but is folded along the P_2 axis to give a V-shaped molecular structure, i.e., like a partially folded book. The upfield (shielded) position of the ^{31}P signal indicates that no appreciable M-M bonding occurs; thus, each rhodium(I) retains its normal four-coordinate, planar coordination geometry. In contrast to the case for $[Ir(\mu-PPh_2)(COD)]_2$, the analogous rhodium complex reacts with a variety of phosphine ligands to give substituted dirhodium derivatives whose structures fall into three categories, each of which will be discussed below.

1. **Reactions of $[Rh(\mu-PPh_2)(COD)]_2$ with Bidentate Group 5 Donors.** The compound $[Rh(\mu-PPh_2)(COD)]_2$ reacts rapidly with a number of bidentate tertiary phosphine ligands to give stepwise replacement of the COD ligands by chelating diphenylphosphines; the equilibria can be represented by eq 3. The



resulting compounds have similar stoichiometries and $^{31}P\{^1H\}$ NMR spectra, which indicate that they are diphenylphosphido-bridged dirhodium complexes containing planar Rh(I) atoms with no metal-metal bonding.

For purposes of discussion, the reaction of $[Rh(\mu-PPh_2)(COD)]_2$ with 1,2-bis(diphenylphosphino)ethane, DPPE, is described in detail. When $[Rh(\mu-PPh_2)(COD)]_2$ is treated with 1.0 equiv of DPPE in THF, the solution changes color from green to brown, and the ^{31}P NMR spectrum of the solution shows a new doublet of triplets at $\delta = -76$ and complicated patterns at $\delta = 57.9$ and -104 as well as resonances at $\delta = -71.7$ due to the starting material $[Rh(\mu-PPh_2)(COD)]_2$. The triplet coupling (at $\delta = -76$) indicates phos-

(18) Piranino, P.; Faraone, F.; Sergi, S. *J. Organomet. Chem.* **1977**, *133*, 107.

(19) Haines, R. J.; Mason, R.; Zubieta, J. A.; Nolte, C. R. *J. Chem. Soc., Chem. Commun.* **1972**, 990.

(20) (a) Carty, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 5612. (b) Carty, A. J. *Adv. Chem. Ser.* **1981**, No. 196, 163. (c) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349.

(21) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266-274 and references therein.

(22) Pregosin, P. A.; Kunz, R. W. "Phosphorus-31 and Carbon-13 Nuclear Magnetic Resonance Studies of Transition Metal Complexes Containing Phosphorus Ligands"; Springer-Verlag: New York, 1979.

Table II. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectral Parameters for the Dirhodium-Diphenylphosphido Complexes^a

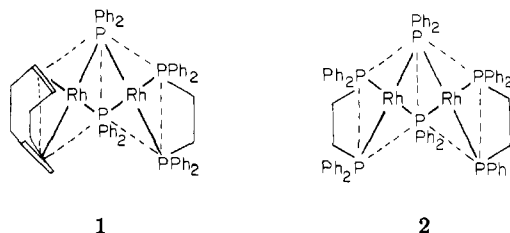
compd	phosphino		phosphido			
	δ	$^1J_{\text{RhP}}$, Hz	δ	Δ , ^b ppm	$^1J_{\text{RhP}}$, Hz	$^2J_{\text{PP}}$, Hz
$[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$			-71.7	-59.3	100	
$\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{DPPM})(\text{COD})$	-24	121	-48.0	-35.6	92	248
$[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPM})]_2$	-23.5 to -29.2 ^b		-23.5 to -29.2 ^c			
$\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{DPPE})(\text{COD})$	57.9	142	-76.0	-63.6	94	219
$[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$	57.3	141	-104.0	-91.6	90	227
$\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{DPPP})(\text{COD})$	16.3	140	-79.0	-66.6		218
$[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPP})]_2$	16.4	142	-77.7	-65.3		220
$\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{Ph}_2\text{PCH=CHPPh}_2)(\text{COD})$	66.6	141	-66.1	-53.7	94	229
$[\text{Rh}(\mu\text{-PPh}_2)(\text{Ph}_2\text{PCH=CHPPh}_2)]_2$	66.5	144	-64.5	-52.1		225
$[\text{Rh}(\mu\text{-PPh}_2)(\text{Arphos})]_2$	60.0	141	-69.4	-57.0	99	228
$\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PEtPh})(\text{COD})$	57.2	146	-60.0	-47.6	95	220
$[\text{Rh}(\mu\text{-PPh}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PEtPh})]_2$	57.8	143	-96.0	-83.6		216
$\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PPh})(\text{COD})$	10.4	129	-78.0	-65.6		222

^a Solvent THF. ^b The phosphorus coordination chemical shifts, $\Delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$, are calculated from $\delta = -12.4$ for KPPPh_2 (Quin, L. D.; Orton, W. L. *J. Chem. Soc., Chem. Commun.* 1979, 401). Thus, Δ will be negative for upfield (shielded) chemical shifts. ^c The phosphino and phosphido resonances overlap and give a complicated pattern that spans this range.

phido phosphorus coupling to two equivalent rhodium-103 nuclei. Such coupling results from either a coincidental equivalence of the rhodium atoms or from a fast exchange equilibrium (e.g., eq 3). The latter is likely, as the ^{31}P NMR spectrum becomes more complicated at low temperatures. When an additional 1.0 equiv of DPPE is added to the above solution, the color becomes bright red and red crystals precipitate. The ^{31}P NMR spectrum of this red compound consists of a doublet of doublets at $\delta = 57.3$ and a complicated resonance at $\delta = -104$. The infrared spectrum of the isolated red complex showed no absorptions due to cyclooctadiene; however, it did show peaks due to aliphatic C-H vibrations of the DPPE ligand. The ^1H NMR spectrum shows resonances at $\delta = 7.5$ – 6.5 (aromatic) and at $\delta = 1.8$ – 1.4 (aliphatic, DPPE). All attempts to isolate the intermediate brown complex failed, producing only $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ and the red compound just described. On the basis of the spectral data and the elemental analysis, the red complex is $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$ and the intermediate brown compound is $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{DPPE})]$. A solution that contains 1 equiv of DPPE per $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ actually contains all three of the bis(diphenylphosphido)-dirhodium complexes in equilibrium (eq 3). This equilibrium is observed for all of the diphosphine ligands examined; the rapid interconversions preclude isolation of the intermediates, $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{LL})]$, since the bis(diphosphine) complexes $[\text{Rh}(\mu\text{-PPh}_2)_2(\text{LL})]_2$ are less soluble in all the organic solvents tried. The ^{31}P NMR data of the monosubstituted complexes $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{LL})]$ were recorded in situ on the reaction mixtures that resulted from addition of 1.0 equiv of the appropriate chelating ligand.

Some general observations about the ^{31}P NMR spectra of these diphosphine derivatives of $[\text{Rh}(\mu\text{-PPh}_2)_2(\text{COD})]$ will be useful before considering the specific ligands. The ^{31}P NMR data are summarized in Table II; the ^{31}P δ values for the phosphino phosphorus atoms are all within normal ranges for chelating phosphine ligands.^{21–23} The phosphido ligands display resonances that are significantly upfield (shielded) from the standard; thus the compounds in Table II do not contain M–M bonds in solution. Due to the complexity of the phosphido ^{31}P NMR resonances in the $[\text{Rh}(\mu\text{-PPh}_2)_2(\text{LL})]_2$ complexes, the rhodium–phosphido coupling constants, $^1J_{\text{RhP}}$, could not be accurately determined in these cases. The phosphido–rhodium coupling constants are generally lower in the

$(\text{LL})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$ complexes than previously observed for Rh(I) complexes; we believe that the compounds retain a folded M_2P_2 unit, as in $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$.^{23c} We expect the rhodium(I) atoms to maintain their usual four-coordinate, planar geometry in these compounds. The trans phosphino–phosphido coupling constants (see **1** and **2**) are of



comparable magnitude to those couplings in previously described Rh(I)–phosphine complexes.^{21–23} However, the cis phosphino–phosphido coupling constants are not observable, even though the ^{31}P NMR spectra are “first order”. Thus, these cis $^2J_{\text{PP}}$ couplings must be less than 2 Hz. This coupling is lower than expected; however, precedent for zero cis P–P coupling has been reported for other planar, heavy-metal complexes, e.g., *cis*-PtCl₂(PR₃)₂.^{20a} In the case of our $(\text{LL})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$ complexes, the low cis $^2J_{\text{PP}}$ values may result from nonoptimal rhodium–phosphorus orbital overlap in the Rh_2P_2 ring. It is worth noting that the rhodium–phosphorus coupling constants for the phosphido groups are significantly lower than those for the phosphino groups. We are in the process of determining the crystal structures of some of these dirhodium diphenylphosphido complexes to ascertain whether there is a correlation of the Rh–P bond distances with the Rh–P coupling constants in mixed phosphino–phosphido complexes. Distinguishing specific details of the ^{31}P NMR spectra are given below for each chelating diphosphine ligand.

(a) **DPPM.** The ligand bis(diphenylphosphino)methane bridges two metal atoms more often than it chelates to one metal atom.²⁴ This tendency for bridging probably results from the strain in a four-membered chelate ring. In the present study, however, the only products that were obtained with DPPM give ^{31}P NMR spectra that are consistent only with a chelating DPPM ligand. Note from Table II that the δ values for the phosphino (–24 ppm) and the phosphido nuclei

(23) (a) Garrou, P. E. *Inorg. Chem.* 1975, 14, 1435. (b) Garrou, P. E. *Chem. Rev.* 1981, 81, 229–266. (c) Such a structure has been found for the $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$ complex: Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem.*, in press.

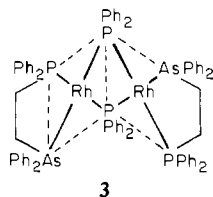
(24) (a) Brown, M. P.; Fisher, J. R.; Hill, R. H.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* 1981, 20, 3516. (b) Cowie, M.; Dwight, S. K. *Ibid.* 1980, 19, 209. (c) Lee, C.-L.; Hunt, C. T.; Balch, A. L. *Ibid.* 1981, 20, 2498.

(-48 ppm) for $(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2(\text{DPPM})$ occur closer together than in the other diphosphino complexes. This similarity of the chemical shifts for both types of phosphorus nuclei in separate four-membered rings lends credence to the "ring contribution" to the coordination chemical shift.²³ This point is demonstrated even more dramatically in $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPM})]_2$, where the ^{31}P NMR resonances for the phosphino and phosphido nuclei are so similar that the resonances overlap and cannot be clearly distinguished from each other (Table II).

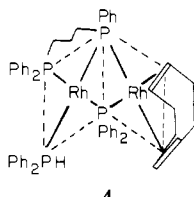
(b) **DPPE and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$.** The bimetallic phosphido-bridged complexes of DPPE and $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ were prepared to study the effect of the conformational flexibility of the chelate ring on the complex as a whole. The introduction of the carbon-carbon double bond in $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ changes the C-C-P bond angles from the values found in chelated 1,2-bis(diphenylphosphino)ethane. The ^{31}P NMR patterns are almost identical for the DPPE and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ complexes; however, the chemical shift values are different (Table II). The δ values of both the phosphino and phosphido nuclei are affected; it is somewhat surprising that the chemical shift of the phosphido nuclei should be affected, unless an inductive effect is operative. Also, when the DPPE data are compared with those of *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$, it is again surprising that the metal-phosphorus coupling constants are so similar, since the coupling constants are expected to be very sensitive to any changes in the chelate ring orientation.²⁰ However, the similar $^2J_{\text{PP}}$ values for these DPPE and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ rhodium complexes are consistent with Carty's results on planar $\text{MX}_2(\text{P}^-\text{P}^+)$ complexes (M = Ni, Pd, Pt), where the presence of a saturated $-\text{CH}_2\text{CH}_2-$ or an unsaturated $>\text{C}=\text{C}<$ linkage between two phosphorus atoms had little effect on the $^2J_{\text{PMP}}$ coupling constants.^{20a}

(c) **DPPP.** The phosphido resonance in $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{DPPP})]$ is very complicated, whereas the phosphido resonances in the $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{LL})]$ compounds (where LL = DPPE and DPPM) are relatively simple patterns; apparently the *cis* phosphino-phosphido coupling constants are significant in the DPPP compound and cause the observed complicated pattern. Owing to the complexity of this phosphido resonance, it was not possible to extract the rhodium-phosphido coupling from the spectrum.

(d) **$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$.** The reaction of $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ with 1-(diphenylphosphino)-2-(diphenylarsino)ethane was studied in an attempt to simplify the ^{31}P NMR phosphido resonances of the complexes $[\text{Rh}(\mu\text{-PPh}_2)(\text{LL})]_2$ and to determine accurately the magnitude of the phosphido-rhodium coupling constant in the complex. Addition of 1.0 equiv of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ to $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ gives a solution that shows a doublet of doublets for the phosphino nuclei and a doublet of triplets for the phosphido nuclei. Addition of 2.0 equiv of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ to $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ produces red crystals that exhibit the same ^{31}P NMR spectrum as above, minus the triplet due to the starting material $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$. Thus, the equilibrium in eq 3 is shifted far to the right and the only product observed is $[\text{Rh}(\mu\text{-PPh}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2)]_2$, even in the presence of 1.0 equiv of $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$. Also, the phosphorus-31 NMR pattern indicates that the two arsine-phosphine ligands coordinate in a *trans* manner, as shown in 3. The rhodium-



3



4

phosphido coupling, 99.7 Hz, is very similar to the rhodium-phosphorus coupling in $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$. The phosphorus-phosphorus coupling constants are similar to those observed for the DPPE complexes.

2. **Reaction of $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ with the Tertiary-Secondary Phosphine 1-(Diphenylphosphino)-3-(phenylphosphino)propane.** When $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ is treated with 1.0 equiv of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (PPH) in THF, the ^{31}P NMR spectrum of the resulting solution exhibits a number of features that are different from the spectra of the complexes that result from the symmetrical $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ligands. First, the phosphido resonance at -77.8 ppm is very complicated compared to that of $(\text{DPPE})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$. Second, the phosphino resonances of $\delta \approx 15$ appear to result from overlapping signals. Third, a resonance at -41 ppm is due to free diphenylphosphine, Ph_2PH . Confirmation that this resonance is due to free Ph_2PH was obtained by recording a proton-coupled ^{31}P NMR spectrum; in that case, the resonance at $\delta = -41$ was a doublet with $^1J_{\text{PH}} = 214$ Hz, which is identical with the P-H coupling from an authentic sample of Ph_2PH . The only source of diphenylphosphine in this solution is the diphenylphosphido bridge in $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$. The presence of the free diphenylphosphine implies that the μ -diphenylphosphido group was displaced, presumably by the secondary phosphine end of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$. Replacement of the Ph_2P^- ligand by the phosphido group of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2^-$ presumably reflects the increased basicity of the alkylphenylphosphido ligand vs. that of the diphenylphosphido ligand and the advantages of the chelating ligand. The structural representation of the proposed product is shown in 4. The resulting diphenylphosphine bonds at the second coordination position that was vacated by the 1,5-cyclooctadiene ligand, and the ^{31}P NMR multiplet of Ph_2PH ($\delta = 15$) appears to overlap the multiplet of the tertiary phosphino portion of PPH. Addition of more than 1.0 equiv of PPH to $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ did not produce any significant changes in the ^{31}P NMR spectrum; thus, further substitution of the cyclooctadiene ligand did not occur at room temperature. Displacement of the diphenylphosphido ligand by PPH provides an unusual example of reactivity of a bridging organophosphido ligand. Thus, the diphenylphosphido bridge is not as chemically inert as has been assumed.^{5a} In fact, after this paper was submitted, Carty reported that bridging diphenylphosphido groups undergo hydrogenation reactions to break the $\mu\text{-PPh}_2$ bridge, particularly under mild catalytic hydrogenation conditions.²⁵

3. **Reaction of $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ with Monodentate Phosphines.** In contrast to the stepwise replacement of 1,5-cyclooctadiene (COD) from $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ by chelating diphosphine ligands, reactions with monodentate phosphines (e.g., PPh_3 , PMePh_2 , PCy_3 , and PET_3) give products of a very different nature, as evidenced by their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The three monodentate phosphines PPh_3 , PMePh_2 , and PET_3 function similarly, and the details of the triphenylphosphine case are presented below for illustration.

(a) **PPh_3 .** Addition of 2.0 equiv of PPh_3 to a THF solution of $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ at room temperature caused the color to change from green to brown; in addition, the ^{31}P NMR peaks of $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ completely disappear. If more PPh_3 is added to the solution, the ^{31}P spectrum shows resonances due to $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{PPh}_3)_2]$ and free PPh_3 ; surprisingly, the second COD molecule is not displaced by monodentate phosphines, even if the solutions are heated. In solutions containing 2.0 equiv of PPh_3 and $[\text{Rh}(\mu\text{-PPh}_2)-$

(25) We thank a reviewer for pointing out the similarity and relevance of Carty's results, which were published after we submitted this paper (McLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* 1982, 60, 87. Carty, A. J. *Pure Appl. Chem.* 1982, 54, 113).

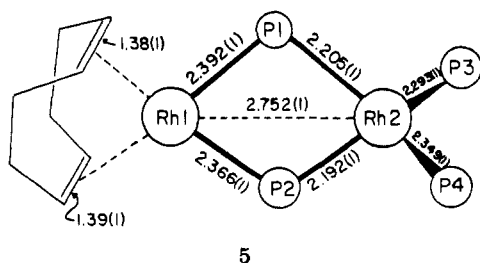
Table III. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectral Parameters for the $(\text{R}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$ Complexes

compd	phosphino		phosphido			$^2J_{\text{PP}}$, Hz
	δ	$^1J_{\text{RhP}}$, Hz	δ	Δ , ppm ^a	$^1J_{\text{RhP}}$, Hz	
$(\text{Ph}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$	51.0	190	216	228	94, 166	0
$(\text{MePh}_2\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$	24.1	190	219	231	95, 168	0
$(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$	25.0	182	217	229	97, 169	0
$(\text{Cy}_3\text{P})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$	71.5	231	207	219	87, 202	38

^a The coordination chemical shift, Δ , is defined in footnote *b* of Table II.

(COD)]₂, the ^{31}P spectra show a doublet of doublets at 216 ppm and a doublet at 51 ppm. The magnitudes of the spin-spin splitting are unique to each resonance multiplet, and no phosphorus-phosphorus coupling is observed. The large downfield chemical shift of the organophosphido resonance is evidence that these phosphorus atoms are bridging across a metal-metal (i.e., Rh-Rh) bond. The lack of trans phosphino-phosphido coupling precludes a planar geometry about rhodium, since a trans P-P coupling is expected to be 250–400 Hz.^{21,24} Also, one of the Rh-P coupling constants is significantly larger than usually observed in planar Rh(I) complexes, which implies a greater amount of “s” orbital character in the Rh-P bond of the PPh_3 complex. The infrared and proton NMR spectra show that one COD molecule remains bonded to rhodium.

Thus, we postulated¹ on the basis of the total spectroscopic evidence in solution that the monodentate PR_3 ligands form bis(diphenylphosphido)-bridged dirhodium complexes that contain a Rh-Rh bond and a pseudotetrahedral rhodium atom bonded to two PR_3 phosphines. The lack of observable P-P coupling provided the basis for a tetrahedral structure around one of the rhodium atoms. In an earlier study, Mazanec and Meek^{26a} had noted the absence of P-P coupling in several tetrahedral rhodium (d^{10} , 1-) complexes of the type $\text{Rh}(\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2)(\text{PR}_3)(\text{NO})$. An X-ray structure determination of the triethylphosphine complex (i.e., $(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$) has confirmed that these “mixed” 1,5-cyclooctadiene-bis(tertiary phosphine)-dirhodium complexes possess a number of remarkable structural features that account for their unusual ^{31}P NMR spectra.^{1,26b} For example, the $(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$ complex contains a rhodium-rhodium bond, two dissymmetrically bridging diphenylphosphido groups that are reminiscent of nonsymmetrical bridging CO ligands, and two distinctly different stereochemistries around the rhodium atoms. One rhodium is tetrahedral and surrounded by four phosphorus atoms, and the other rhodium (bonded to COD) is nearly planar. The important structural features are given in the schematic drawing 5; a preliminary structural report has been published.^{26b}



5

(b) PMePh_2 and PEt_3 . Both methylphenylphosphine and triethylphosphine react with $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ to give products that have a stoichiometry and ^{31}P NMR pattern similar to those of the product obtained from the reaction of PPh_3 . The ^{31}P NMR spectral parameters are summarized in

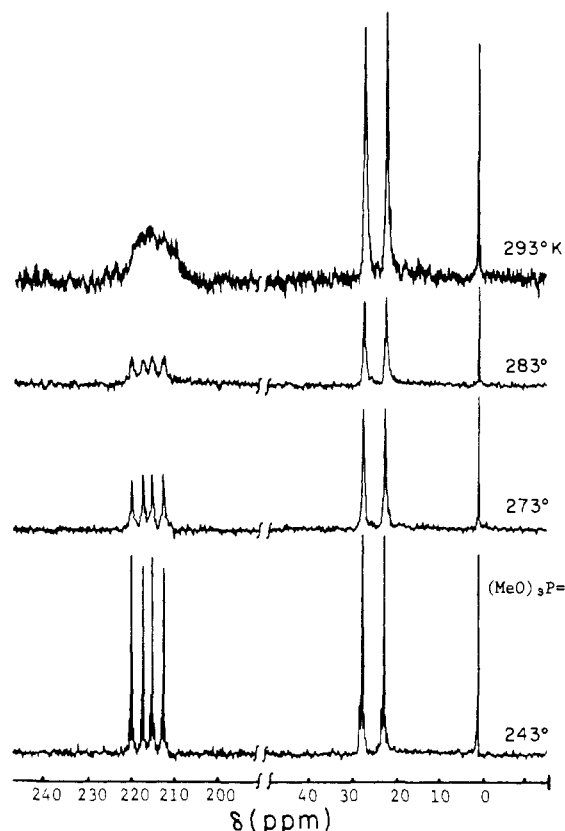
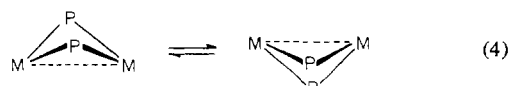


Figure 1. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ from 243 to 293 K. $(\text{MeO})_3\text{P}=\text{O}$ is contained in a separate coaxial tube as a secondary standard; the reported chemical shifts are relative to 85% H_3PO_4 .

Table III. However, the ^{31}P NMR spectra of the “mixed” COD-bis(phosphine) complexes of PEt_3 and PMePh_2 , i.e., $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{PR}_3)_2]$, differ in one very important aspect from that of the PPh_3 case, i.e., the signal for the far-downfield multiplet is temperature dependent. Figure 1 shows that the resonance due to the bridging diphenylphosphido group ($\delta = 217$) begins to coalesce above 243 K. The Rh-P coupling in this resonance appears to be maintained through the temperature range, which indicates that the coalescence process does not involve Rh-P bond breaking. Also, since the phosphino resonance ($\delta = 26$) does not change throughout the temperature range, the monodentate phosphine ligands apparently do not dissociate and become involved in the dynamic process. Thus, it is concluded that all three monodentate ligands (PPh_3 , PMePh_2 , and PEt_3) form complexes similar to 5 with a Rh-Rh bond and that the coalescence behavior of the organophosphido resonance in the PMePh_2 and PEt_3 cases can be ascribed to a “flapping” of the organophosphido ligands, as shown in eq 4. This motion causes an



averaging of the positions of the phosphido nuclei with respect

(26) (a) Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 85. (b) Meek, D. W.; Kreter, P. E., Jr.; Christoph, G. G. *J. Organomet. Chem.* **1982**, *231*, C53–58.

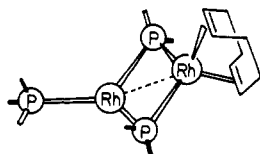
Table IV. Hydrogenation Data for the Diphenylphosphido-Bridged Rhodium Complexes^a

catalyst	substrate ^b	solvent			
		tetrahydrofuran		benzene	
		rel rate	turnover, ^c min ⁻¹	rel rate	turnover, min ⁻¹
[RhCl(PPh ₃) ₃]	1-octene	1.0	8.5	1.0	5.9
[Rh(μ-PPh ₂)(COD)] ₂	1-octene	1.8	15.6	1.6	9.5
[Rh(μ-PPh ₂)(COD)] ₂	cyclohexene	0.76	6.5		
[Rh(μ-PPh ₂)(COD)] ₂	2,3-dimethylbut-2-ene	0.04	0.36		
[(DPPE)Rh(μ-PPh ₂) ₂ Rh(COD)]	1-octene	2.7	23.1	1.9	11.0
[(DPPE)Rh(μ-PPh ₂) ₂ Rh(COD)]	cyclohexene	0.52	4.4		
[(PPh ₃) ₂ Rh(μ-PPh ₂) ₂ Rh(COD)]	1-octene	1.3	11.0	1.2	6.9
[Rh(μ-PPh ₂)(DPPE)] ₂ ^d	1-octene			1.3	7.8

^a At 25 °C and 750 torr H₂ pressure. ^b [substrate]/[Rh] = 500. ^c Turnover = (moles of substrate converted per minute)/(moles of Rh).
^d Three-hour induction period before significant catalysis.

to the rest of the molecule and causes a decrease in the intensity of the resonances of these phosphorus atoms.²⁷ Since the chemical shift does not change, this flapping motion does not average nuclei that are in different chemical environments; it only causes a perturbation of the nuclear magnetic resonance conditions. A similar behavior has been reported for [Fe(μ-PMe₂)(CO)₃]₂.²⁸ This dynamic behavior is not observed in the analogous PPh₃ complex; perhaps the steric requirements of the triphenylphosphine ligand constrain the Rh₂P₂ core to a static structure.

(c) PCy₃. Treatment of [Rh(μ-PPh₂)(COD)]₂ with tricyclohexylphosphine in THF produces in situ a complex that is formulated as (Cy₃P)Rh(μ-PPh₂)₂Rh(COD) on the basis of its ³¹P NMR spectrum. This complex, containing both three- and four-coordinate Rh(I), could not be isolated as a pure solid owing to its high sensitivity to oxygen. The ³¹P NMR spectrum of the PCy₃ complex (Table III) consists of a doublet of triplets at 71.5 ppm (due to PCy₃) and a doublet of doublets of doublets at 207 ppm (due to μ-PPh₂). The additional coupling (as compared to the case for the (R₃P)₂Rh(μ-PPh₂)₂Rh(COD) complexes) of 38 Hz is also observed in the phosphino resonance at 71.5 ppm and is due to P-P coupling, which is not observed in the three [(R₃P)₂Rh(μ-PPh₂)₂Rh(COD)] complexes. The Cy₃P-Rh coupling constant, 231 Hz, is larger than normally observed for four-coordinate Rh(I)-PR₃ complexes. The phosphido-rhodium coupling constants are both larger, 202 Hz, and smaller, 87 Hz, than those in the [(R₃P)₂Rh(μ-PPh₂)₂Rh(COD)] complexes. These observations, when combined with the observed P-P coupling, suggest that one rhodium is three-coordinate and that it may approximate a trigonal-planar coordination geometry. Thus, the structure of the PCy₃ complex is proposed to be like 6. The bulky PCy₃ ligand has



6

produced other coordinatively unsaturated and reactive transition-metal complexes,^{29,30} which can serve as precedents for the three-coordinate Rh(I) structure proposed here.

4. Catalytic Hydrogenation of Olefins. The catalytic activities of a tremendously large number of phosphine-rhodium complexes have been studied, particularly for hydrogenation catalysis.³¹ Schrock and Osborn found that [Rh(diene)-(PR₃)₂]⁺ complexes are active hydrogenation catalysts;³² more recently, Crabtree has shown that [Ir(COD)(PR₃)₂]⁺ complexes are even more active under certain conditions.³³ Thus, we routinely screened our phosphido-bridged dirhodium complexes for hydrogenation catalysis under mild conditions, i.e., at 25 °C and ~750 torr H₂ pressure. Most of these complexes are quite active hydrogenation catalysts; the data are summarized in Table IV, and the rates are compared to that of the Wilkinson catalyst, RhCl(PPh₃)₃, under comparable conditions.

The mechanism of hydrogenation with [Rh(μ-PPh₂)(COD)]₂ has not been elucidated, but it probably involves initial hydrogenation of 1,5-cyclooctadiene to cyclooctane, followed by coordination of the added olefin. Cyclooctane was found in the product mixture, along with octane, which results from the 1-octene substrate. When hydrogenation was carried out in benzene as a solvent, a small amount (<1%) of the hydrogenation products was cyclohexane. The cyclohexane apparently results from hydrogenation of the benzene solvent, which is likely to occur via a rhodium complex that contains coordinated benzene as a ligand.

The rate of reaction for each of the complexes in Table IV is dependent on the solvent used. The polar solvent THF causes a higher rate of reaction, as well as longer catalyst life, than does the weakly coordinating solvent benzene. The better coordinating properties of THF apparently leads to longer catalyst life by binding to vacant coordination sites on the metal, thus preventing side reactions that may lead to catalyst deactivation.^{33c} Hydrogenation reactions with [Rh(μ-PPh₂)(COD)]₂ in CH₂Cl₂ were attempted, but this system lost all activity after less than 10% olefin conversion.

Since [Rh(μ-PPh₂)(COD)]₂ has two coordinated cyclooctadiene ligands, it is possible that both are removed during hydrogenation to produce active sites on both rhodium atoms. To determine the effect of blocking one rhodium atom, we investigated the catalytic activity of (DPPE)Rh(μ-PPh₂)₂Rh(COD). It was expected that the chelating ligand DPPE would not dissociate readily during hydrogenation; thus, the number of active sites available in (DPPE)Rh(μ-

- (27) Jackman, L. M.; Cotton, F. A., Eds. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Academic Press: London, 1975.
(28) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 746.
(29) Moers, F. G.; deJong, J. A. M.; Beaumont, P. M. H. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1915.
(30) James, B. R.; Preece, N.; Robinson, S. D. *Inorg. Chim. Acta* **1979**, *34*, L219.

- (31) (a) Marko, L. *Pure Appl. Chem.* **1979**, *51*, 2211. (b) Harmon, R. E.; Gupta, S. K.; Brown, D. J. *Chem. Rev.* **1973**, *73*, 21. (c) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. (d) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.
(32) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816.
(33) (a) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205. (b) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331. (c) Crabtree, R. H. *Platinum Met. Rev.*, in press.

$\text{PPh}_2)_2\text{Rh}(\text{COD})$ should be half the number in $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$, if both COD ligands are lost from the latter. The rate of hydrogenation of 1-octene with $[(\text{DPPE})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ is actually greater than the rate for $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$ (Table IV), and the effective catalyst life is much longer for $[(\text{DPPE})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$. The increased rate is apparently due to the increased basicity of the complex on coordination of the diphosphine ligand,^{31d} and the longer catalyst life is due probably to a greater stability of the DPPE portion of the complex, which diminishes side reactions that deactivate the catalyst.

With bimetallic complexes or clusters, the possibility always exists for cleavage to a monometallic species that becomes the actual catalyst. Thus, to test our assumption that DPPE did not dissociate readily from the "mixed" COD-DPPE complex $[(\text{DPPE})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$, we examined the H_2 catalyst activity of $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$. Unfortunately, the results obtained with the latter complex are somewhat ambiguous; clearly, the complex is not active at ambient conditions for approximately 3 h, in contrast to immediate catalysis by $[(\text{DPPE})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$; however, after 3 h under H_2 , solutions containing $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$ begin to hydrogenate 1-octene at a rate comparable to that of $\text{RhCl}(\text{PPh}_3)_3$. The nonactivity for the first 3 h suggests that the dimer is not cleaved rapidly to a monomer and that DPPE dissociation is slow. The activity observed for $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$ after 3 h may result from a slow dissociation of DPPE to produce an intermediate that can coordinate and then hydrogenate the olefin substrate. Even after the 3-h induction period, the rate of hydrogenation by $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$ is slower than the rate for $[(\text{DPPE})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$; the slower rate may be due to competition between the olefin and the dissociated DPPE ligand for coordination sites on rhodium. These data suggest that the bimetallic nature of the complexes in Table IV is retained

during hydrogenation and that cleavage of the phosphido bridges does not occur to produce the active catalyst in solution.³⁴

Acknowledgment. We are grateful to the OSU Small Grants Program and Johnson Matthey Co. for partial financial support of this research and to the National Science Foundation (Grant No. CHE-7910019) and the National Institutes of Health (Grant No. GM-27431) for recent instrumentation grants that aided the purchase of the 300- and 200-MHz NMR instruments, respectively. We also thank Professor G. G. Christoph for help with the X-ray structure determination and the John Simon Guggenheim Foundation for a fellowship to D.W.M. for 1981-1982.

Registry No. $[\text{Ir}(\mu\text{-PPh}_2)(\text{CO})(\text{PPh}_3)]_2$, 39732-63-3; Ph_2PH , 829-85-6; $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, 14871-41-1; $[\text{Ir}(\mu\text{-PPh}_2)(\text{COD})]_2$, 83681-88-3; $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$, 12112-67-3; $[\text{RhCl}(\text{COD})]_2$, 12092-47-6; $\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2$, 83681-89-4; $[\text{Rh}(\mu\text{-PPh}_2)(\text{COD})]_2$, 82829-24-1; $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPM})]_2$, 83681-90-7; $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPE})]_2$, 83681-91-8; $[\text{Rh}(\mu\text{-PPh}_2)(\text{DPPP})]_2$, 83681-92-9; $[\text{Rh}(\mu\text{-PPh}_2)(\text{Arphos})]_2$, 83681-93-0; $(\text{PEt}_3)_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$, 83681-94-1; $(\text{PMePh}_2)_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$, 82847-79-8; $[\text{Rh}(\mu\text{-PPh}_2)(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)]_2$, 83681-95-2; $[\text{Rh}(\mu\text{-PPh}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PEtPh})]_2$, 83681-96-3; $\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{DPPM})(\text{COD})$, 83681-97-4; $\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{DPPE})(\text{COD})$, 83681-98-5; $\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{DPPP})(\text{COD})$, 83681-99-6; $\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PEtPh})(\text{COD})$, 83682-00-2; $\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PPH})(\text{COD})$, 83682-01-3; $(\text{Ph}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$, 82847-80-1; $(\text{Cy}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$, 83682-02-4; $\text{RhCl}(\text{PPh}_3)_3$, 14694-95-2; 1-octene, 111-66-0; cyclohexene, 110-83-8; 2,3-dimethylbut-2-ene, 563-79-1.

(34) In view of Carty's recent results under catalytic hydrogenation conditions,²⁵ one should be cautious about extrapolating the noncleavage of the $\mu\text{-PPh}_2$ group under hydrogen at 1 atm pressure to higher temperatures and pressures of H_2 .

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

Crystal Structure and Magnetic Properties of $\text{Cu}_2\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_2(\text{OCH}_3)_2$: A Catalytic Species Related to the Copper(II)-Induced Oxidation of Phenols

R. D. WILLETT and G. L. BRENEMAN*

Received April 29, 1982

The crystal structure of a catalytic precursor in the oxidation of phenols, $\text{Cu}_2\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_2(\text{OCH}_3)_2$, has been determined. The unit cell is triclinic, space group $P\bar{1}$, with $a = 8.280(3) \text{ \AA}$, $b = 6.089(2) \text{ \AA}$, $c = 9.302(5) \text{ \AA}$, $\alpha = 62.67(2)^\circ$, $\beta = 94.67(3)^\circ$, and $\gamma = 70.81(2)^\circ$. The structure consists of methoxy-bridged dimers connected to each other through asymmetric chlorine bridges, forming a one-dimensional chain. The copper coordination sphere is distorted square pyramidal. The Cu-O distances are 1.932(4) and 1.940(6) \AA , the intradimer Cu-Cu distance is 3.037(2) \AA , and the bridging Cu-O-Cu angle is 103.2(1)°. Magnetic susceptibility studies indicate antiferromagnetic coupling within dimers in the solid state with a singlet-triplet splitting of 1030 K. The implications of this with respect to mechanisms of exchange coupling are discussed. The EPR spectrum is characteristic of an exchange-coupled system. The g values are consistent with the observed stereochemistry.

Introduction

It is known that copper(I) chloride in pyridine/methanol in the presence of oxygen catalyzes the oxidation of phenols and catechols.¹ It has been suggested that this represents a nonenzymatic model reaction for oxygenases such as pyro-

catechase.^{2,3} The four-electron oxidation of catechol to *cis,cis*-muconic acid, monomethyl ester, proceeds with equal

- (1) (a) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959); (b) A. S. Hay, *J. Polym. Sci.*, **58**, 581 (1962); (c) G. F. Endres and J. Kwiatek, *ibid.*, **58**, 593 (1962); (d) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963); (e) A. S. Hay and G. F. Endres, *J. Polym. Sci., Part B*, **3**, 887 (1965); (f) H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).

* To whom correspondence should be addressed at the Department of Chemistry, Eastern Washington University, Cheney, WA 99004.