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ticular isotopomer is denoted y_i . The fraction $\alpha_i(t)$ is defined as $\alpha_i(t) = y_i/C_i$. If the water exchange is first-order in complex, we get eq 16, where c_j in the sum accounts for mole fractions,

$$dy_i/dt = \sum c_j y_j + \alpha_i(t) dC_i/dt \quad \alpha_i(0) = 1 \quad (16)$$

$j = 0, 1, 2$

statistical factors, and exchange constants for the isotopic equilibration process. The last term originates from the fact that isotopic effects on the irreversible side reaction are negligible. The time derivative of $\alpha_i(t)$ is given by eq 17, where the expression for dy_i/dt can be substituted into eq 16 to give eq 18. An identical

$$d\alpha_i(t)/dt = C_i^{-1} dy_i/dt - y_i C_i^{-2} dC_i/dt \quad (17)$$

$$d\alpha_i(t)/dt = C_i^{-1} \sum c_j y_j = \sum c_j \alpha_j(t) \quad (18)$$

equation can be derived when the substrate concentration is constant with time (divide eq 16 with C_0 and let $dC_i/dt = 0$). Thus, a complex undergoing side reactions can be treated as any stable MS_n complex as long as (i) water exchange is first-order with respect to complex and (ii) the relative concentrations $\alpha_i(t)$ of isotopomers can be measured.

Registry No. $\text{Pt}(\text{H}_2\text{O})_4^{2+}$, 60911-98-0; *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$, 13876-96-5; Pt, 7440-06-4.

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Di(phosphine)-Bridged Complexes of Palladium. Parahydrogen-Induced Polarization in Hydrogenation Reactions and Structure Determination of Tris(μ -bis(diphenylphosphino)methane)dipalladium, $\text{Pd}_2(\text{dppm})_3$

Rein U. Kirss and Richard Eisenberg*

Received October 7, 1988

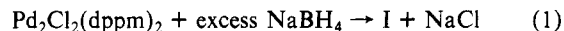
Reduction of $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$ (dppm = bis(diphenylphosphino)methane) with excess NaBH_4 produces a dark purple solid, I, which shows a reaction chemistry consistent with the stoichiometry $\text{Pd}_2\text{H}_x(\text{dppm})_2$. Reaction of I with excess dppm produces the known compound $\text{Pd}_2(\text{dppm})_3$. Crystals of $\text{Pd}_2(\text{dppm})_3$ are monoclinic in space group $P2_1/c$ with cell dimensions $a = 14.733$ (5) Å, $b = 14.760$ (5) Å, $c = 29.720$ (6) Å, and $\beta = 97.44$ (1)°. The structure of $\text{Pd}_2(\text{dppm})_3$ is similar to that of the structurally characterized $\text{Pt}_2(\text{dppm})_3$ analogue with approximate C_{3h} symmetry. A total of 1 equiv of H_2 and 1 equiv of methane is evolved per 3 $\text{Pd}(\text{dppm})$ units when I is treated with aqueous HCl and methyl iodide, respectively. The corresponding metal-containing products are $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$ and a mixture of $[\text{Pd}_2\text{I}(\text{CH}_3)(\text{dppm})_2]\text{I}$ and $\text{PdI}_2(\text{dppm})$. The latter compound is also obtained upon oxidation of I with I_2 . Reaction of I with CH_2I_2 in dichloromethane yields a mixture of $\text{Pd}_2\text{I}_2(\mu\text{-CH}_2)(\text{dppm})_2$ and $\text{Pd}_2\text{Cl}_2(\mu\text{-CH}_2)(\text{dppm})_2$, while reaction with either Me_3SiCl or Me_2SiCl_2 produces $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$. Complex I is active in the catalytic hydrogenation of alkenes and alkynes. Parahydrogen-induced polarization (PHIP) is observed in the styrene product when solutions of I and phenylacetylene in CDCl_3 are stored at -196°C under 3–4 atm of H_2 for >8 h prior to reaction at $60\text{--}70^\circ\text{C}$. Similar results are obtained when para-enriched H_2 is used without the storage time. Complex I decomposes upon heating in CDCl_3 to mixtures of $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$, $\text{PdCl}_2(\text{dppm})$, and an unidentified red palladium compound. While this mixture is also active in hydrogenation and gives rise to PHIP, $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$ by itself gives weak polarization under hydrogenation conditions and $\text{PdCl}_2(\text{dppm})$ gives no polarization.

Introduction

Binuclear di(phosphine)-bridged hydride complexes incorporate two key features for the study of metal-catalyzed reactions. First, metal hydrides play an important role in hydrogenation, hydroformylation, and CO reduction chemistry,^{1,2} and second, the proximity of two metal centers in binuclear systems can lead to unusual reactivity.^{3–5} For these reasons, the preparation and reaction chemistry of binuclear dppm -bridged (dppm = bis(diphenylphosphino)methane) hydride complexes have been a focus of our research. Recently, our interest in this class of compounds was stimulated by an unusual series of observations in the reaction chemistry of $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ with unsaturated organic substrates.^{6–9} Specifically, when hydrogenation reactions of

alkynes by $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ were monitored by ^1H NMR spectroscopy at early reaction times, extraordinary NMR absorptions and emissions were observed in the product resonances.⁷ This series of observations, which has now been shown to be due to parahydrogen-induced polarization,⁸ prompted efforts to prepare dppm -bridged complexes containing other platinum group elements that would show similar properties in hydrogenation catalysis.

In this paper, we report one such system that forms in the reaction of $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$ with excess NaBH_4 , eq 1. This system,



which we refer to as I, has not been characterized definitively, although it is an effective hydrogenation catalyst and its reaction chemistry shows it to be consistent with $\text{Pd}_2\text{H}_x(\text{dppm})_2$. In the course of characterizing I, we found that its reaction with excess dppm led to the formation of $\text{Pd}_2(\text{dppm})_3$, which we have examined by X-ray diffraction. This structure determination is fully described in this paper.

The complex $\text{Pd}_2(\text{dppm})_3$ was reported in 1972 by Stern and Maples,¹⁰ who examined its catalytic activity with regard to ho-

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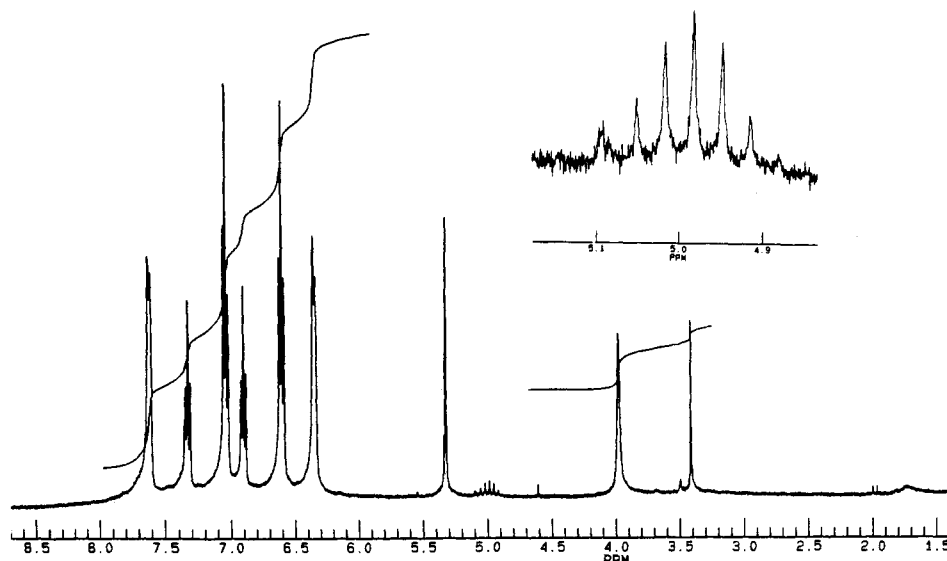


Figure 1. ^1H NMR spectrum of compound I in CD_2Cl_2 . The septet that integrates to 1:3 dppm ligands is expanded in the inset.

mogeneous hydrogenation. More recently, Balch and co-workers have studied the oxidative addition chemistry of $\text{Pd}_2(\text{dppm})_3$ with halogens and organic halides.⁴ While the chemistry and catalytic properties of $\text{Pd}_2(\text{dppm})_3$ have thus been reported previously, the structure of this Pd(0) system was known only from spectroscopic data and by analogy to the related Pt system.

The chemistry of Pt dppm complexes has been studied extensively by Puddephatt and co-workers. In a reaction analogous to the preparation of I, they found that $\text{Pt}_2\text{Cl}_2(\text{dppm})_2$ reacts with NaBH_4 to yield a binuclear cationic species, $[\text{Pt}_2\text{H}_3(\text{dppm})_2]\text{Cl}$, which has been extensively studied.¹¹ The chemistry of this species has some similarities to that of I, but, in terms of hydrogenation catalysis, some differences. Specifically, $[\text{Pt}_2\text{H}_3(\text{dppm})_2]\text{Cl}$ does not catalyze hydrogenation with the occurrence of PHIP under conditions similar to those seen for I.

Results and Discussion

Synthesis and Characterization of I. Sodium borohydride reduction of a slurry of $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$ in methanol precipitates the dark purple solid I, which is thermally stable up to 180 °C and air stable for months as a solid. Compound I is insoluble in both aliphatic and aromatic hydrocarbons and diethyl ether, sparingly soluble in acetone, acetonitrile, and tetrahydrofuran, and most soluble in dimethylformamide, dichloromethane, and chloroform. However, the dark blue solutions of I in the latter solvents slowly turn red over a period of hours (CHCl_3) to days (CH_2Cl_2 or DMF) with decomposition accelerated by air. In this decomposition, $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$, $\text{PdCl}_2(\text{dppm})$, and an unidentified red compound (see Experimental Section) form initially with the red compound, eventually decomposing to the former two products.

The ^1H NMR spectrum of I in CD_2Cl_2 (Figure 1) shows six aryl proton resonances in the region δ 6.3–7.7 ppm (four doublets and two pseudotriplets in a 2:2:1:1:2:2 ratio) and a broad singlet at δ 3.98 ppm for the dppm methylene protons in the expected 10:1 ratio. The methylene resonance remains unchanged down to -80 °C, suggesting a rapid fluxional process to equilibrate the CH_2 protons. One additional resonance is observed at 5.01 ppm as a septet with 14-Hz coupling, integrating in a ratio of 3 dppm to 1 proton for this multiplet. Irradiation of this resonance has no effect on the rest of the ^1H NMR spectrum. When NaBD_4 is used in the reaction with $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$, the 5.01-ppm resonance is absent, while the remainder of the spectrum is unchanged. Treatment of a slurry of I in CD_3OD with CD_3ONa leads to the disappearance of the multiplet at 5.01 ppm in CD_2Cl_2 . These results suggest the presence of either a metal hydride or a metal

borohydride that is coupled to the dppm phosphorus nuclei. The unusual chemical shift of the proposed hydride is not unprecedented in that Puddephatt and co-workers have reported the hydride resonance in the related species $[\text{Pt}_3(\mu_3\text{-H})(\text{dppm})_3]^+$ at δ 4.16 ppm.^{12a} A single resonance is observed at δ -5.82 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum obtained in CD_2Cl_2 for compound I. Recently, a compound of formula $\text{Pd}_2(\text{dppm})_2$ has been identified spectroscopically by Stille and co-workers,^{12b} but this complex shows a ^{31}P NMR resonance (δ 22 ppm in CD_2Cl_2) significantly different from that of compound I.

While compound I can be obtained spectroscopically pure as a purple powder from rapid recrystallization in CH_2Cl_2 /hexane mixtures, analytically pure samples have not been obtained, possibly because of the solid to solid nature of the synthetic reaction. The growth of X-ray-quality crystals has also been unsuccessful. Elemental analysis for palladium and phosphorus on independently prepared samples of I reveal that the stoichiometry of Pd to dppm is 1:1. The samples also contain C and H in ratios consistent with this stoichiometry.

To test the presence of a hydride or hydride-like species chemically, the identities and quantities of gases produced in reactions of I with excess HCl and CH_3I were determined by gas chromatography. When I is treated with aqueous HCl, H_2 is produced in the amount of 1 equiv of hydrogen/3 $\text{Pd}(\text{dppm})$ units along with $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$. Similarly, treatment of I with methyl iodide produces methane in the amount of 1 equiv of methane/3 $\text{Pd}(\text{dppm})$ units along with a mixture of $[\text{Pd}_2\text{I}(\text{CH}_3)(\text{dppm})_2]\text{I}$ and $\text{PdI}_2(\text{dppm})$.

Other reactions also provide insight into the nature if not the identity of I. Treatment of I with CO in a variety of solvents gives rapid reaction but does not lead to the formation of a readily identifiable species. Surprisingly, the cation $\text{Pd}_3(\mu_3\text{-CO})(\text{dppm})_3^{2+}$ ¹³ is formed upon treatment of a sample of I with 4 equiv of $\text{Ag}(\text{CF}_3\text{CO}_2)$ in acetone under CO. This product was identified by comparison of its NMR spectral data with published data for $[\text{Pd}_3(\mu_3\text{-CO})(\text{dppm})_3](\text{CF}_3\text{CO}_2)_2$. In addition, oxidation of I with excess I_2 yields $\text{PdI}_2(\text{dppm})$ as the only metal-containing product; however, no H_2 was observed in a sealed reaction tube by ^1H NMR spectroscopy.

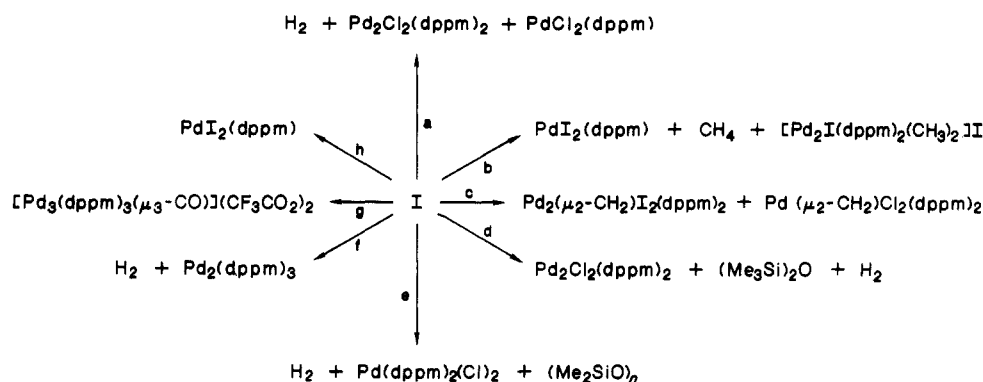
Scheme I summarizes the reactions of I with aqueous HCl, alkyl halides, and halogens to produce mono- and dinuclear products.

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Scheme 1^a

^a Conditions: (a) Aqueous HCl/acetone; (b) CH₃I/CH₂Cl₂; (c) CH₂I₂/CH₂Cl₂; (d) Me₃SiCl/CH₂Cl₂; (e) Me₂SiCl₂/CH₂Cl₂; (f) dppm/C₆H₆; (g) Ag(CF₃CO₂)/CO/acetone; (h) I₂/CH₂Cl₂.

In each case, the products were identified by ¹H and ³¹P NMR spectroscopy and their spectra were compared with spectra of known samples prepared by independent routes.^{4,14}

When an excess of CH₂I₂ is used in reaction with I, a mixture of Pd₂I₂(μ-CH₂)(dppm)₂ and Pd₂Cl₂(μ-CH₂)(dppm)₂ is observed. The latter product may arise from the oxidative addition of dichloromethane solvent to a dppm-bridged Pd(0) intermediate or by metathesis. A small amount of CH₃I is also detected by ¹H NMR spectroscopy, while low concentrations of H₂ and methane may be produced as well by analogy to other reactions.

Reactions of I with alkylchlorosilanes were observed to be much faster than with alkyl halides, leading to complete consumption of I within minutes, compared to hours or days for the corresponding alkyl halides. When I is reacted with 6 equiv of Me₃SiCl in CD₂Cl₂, a rapid color change from blue to red is observed immediately upon thawing, with gas evolution being noticed as well. By ¹H NMR spectroscopy, the only metal species observed is Pd₂Cl₂(dppm)₂. After 1 h, no Me₃SiCl remains nor is Me₃SiH observed in the reaction; however, the resonance for H₂ is seen in the ¹H NMR spectrum. The fate of the trimethylsilyl group is the formation of Me₃SiOSiMe₃ by comparison with spectra of pure samples. The formation of siloxane is facilitated by the presence of trace oxygen or water in the reaction system. While NMR solvents were rigorously dried and degassed, the other reagents were vacuum-transferred without exhaustive degassing. Reaction with dimethyldichlorosilane proceeds equally rapidly, yielding PdCl₂(dppm) as the major Pd-containing product, a small amount of Pd₂Cl₂(dppm)₂, and H₂; the Me₂Si residues are presumed to form oligomeric or cyclic (Me₂SiO)_n siloxanes.

In a sealed reaction carried out in C₆D₆, heating a mixture of I with dppm produces Pd₂(dppm)₃ quantitatively by ¹H NMR spectroscopy. The choice of benzene as solvent for this reaction, despite the insolubility of I, was prompted by a desire to exclude any sources of halide, such as halogenated solvents, in ruling out chloride as a constituent of I. Again, H₂ was observed as a reaction product by ¹H NMR spectroscopy. The identity of Pd₂(dppm)₃ obtained in this reaction has been unambiguously established by a single-crystal X-ray structure determination of this complex obtained in an analogous reaction done in acetonitrile.

In summary, compound I is composed of Pd, dppm, and hydride or hydride-like ligands with a Pd:dppm ratio of 1:1. The hydride or hydride-like ligands have been verified both spectroscopically and chemically. Despite the lack of an unambiguous formula, compound I is interesting because of its ability to catalyze hydrogenation reactions with the occurrence of parahydrogen-induced polarization. This aspect is discussed further below.

Crystal Structure of Pd₂(dppm)₃. Orange crystals of Pd₂(dppm)₃ suitable for X-ray study were grown from acetonitrile solution of I and dppm. The details of the structure analysis are presented in Table I, and final refined positional parameters and equivalent isotropic temperature factors are given in Table II. The

Table I. Crystallographic Data for Pd₂(dppm)₃

formula	Pd ₂ P ₆ C ₇₅ H ₆₆	V, Å ³	6410
fw	1438.56	Z	4
cryst syst	monoclinic	d _{calcd} , g/cm ³	1.49
space group	P2 ₁ /c (No. 14)	T, °C	23
a, Å	14.733 (5)	μ(Mo Kα), cm ⁻¹	7.47
b, Å	14.760 (5)	transm coeff	0.854–1.125
c, Å	29.720 (6)	R	0.033
β, deg	97.44 (1)	R _w	0.039
λ(Mo Kα), Å	0.71069		

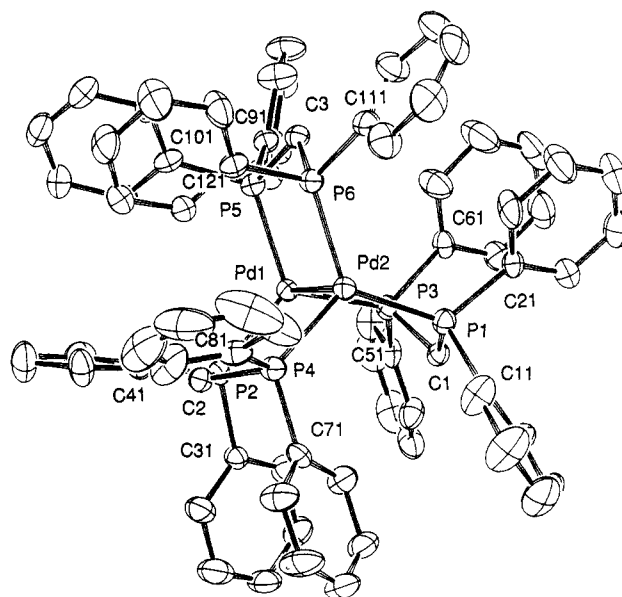


Figure 2. Molecular structure of Pd₂(dppm)₃, showing its approximate C₃ symmetry and atom-labeling scheme. Only the ipso carbon atoms Cx1 of the phenyl rings are numbered; the other phenyl carbons are numbered sequentially (e.g., C11 is bonded to C12 and C16).

molecular structure of Pd₂(dppm)₃ is shown in Figures 2 and 3 and consists of two trigonally coordinated Pd(0) atoms bridged by three dppm ligands. The structure is thus similar to that previously reported for Pt₂(dppm)₃, which has been described as a manxane-like structure, manxane being bicyclo[3.3.3]undecane.¹⁵ Selected bond distances and angles for the structure are presented in Tables III and IV, with complete tabulations being given in the supplementary material.

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Table II. Refined Positional and Isotropic Thermal Parameters for Pd₂(dppm)₃^a

atom	x	y	z	B(eq), Å ²	atom	x	y	z	B(eq), Å ²
Pd1	0.31579 (3)	0.22314 (3)	0.16048 (2)	2.53 (2)	C62	0.3345 (6)	0.4412 (6)	0.2372 (3)	5.5 (5)
Pd2	0.18301 (3)	0.33739 (3)	0.10262 (2)	2.72 (2)	C63	0.3532 (8)	0.5239 (6)	0.2583 (4)	7.8 (6)
P1	0.1016 (1)	0.3721 (1)	0.16137 (7)	3.04 (9)	C64	0.3218 (7)	0.5419 (6)	0.2981 (4)	6.7 (6)
P2	0.2661 (1)	0.0956 (1)	0.11938 (6)	2.95 (9)	C65	0.2746 (6)	0.4778 (7)	0.3184 (3)	6.5 (6)
P3	0.2521 (1)	0.2722 (1)	0.22336 (6)	2.91 (8)	C66	0.2567 (5)	0.3946 (6)	0.2971 (3)	5.2 (4)
P4	0.1338 (1)	0.2166 (1)	0.05641 (6)	3.10 (8)	C71	0.0249 (4)	0.1583 (4)	0.0613 (2)	3.2 (3)
P5	0.4399 (1)	0.3036 (1)	0.14099 (6)	2.91 (8)	C72	-0.0015 (5)	0.1480 (5)	0.1037 (2)	4.2 (4)
P6	0.3012 (1)	0.4220 (1)	0.08052 (7)	3.00 (9)	C73	-0.0815 (6)	0.1035 (6)	0.1103 (3)	4.9 (4)
C1	0.1291 (4)	0.2956 (4)	0.2099 (2)	2.8 (3)	C74	-0.1381 (5)	0.0721 (6)	0.0736 (3)	5.2 (5)
C2	0.2122 (4)	0.1185 (4)	0.0604 (2)	3.3 (3)	C75	-0.1152 (6)	0.0846 (7)	0.0316 (3)	7.0 (6)
C3	0.4091 (4)	0.4185 (4)	0.1202 (2)	2.9 (3)	C76	-0.0343 (6)	0.1277 (6)	0.0250 (3)	5.3 (5)
C11	-0.0233 (4)	0.3594 (4)	0.1511 (3)	3.5 (4)	C81	0.1217 (5)	0.2401 (6)	-0.0048 (3)	4.1 (4)
C12	-0.0671 (6)	0.3796 (6)	0.1087 (3)	5.5 (5)	C82	0.0841 (8)	0.3223 (7)	-0.0180 (4)	8.1 (6)
C13	-0.1624 (6)	0.3685 (8)	0.0986 (3)	7.6 (6)	C83	0.073 (1)	0.3453 (8)	-0.0656 (5)	11.3 (9)
C14	-0.2113 (6)	0.3351 (7)	0.1306 (4)	6.8 (6)	C84	0.099 (1)	0.288 (1)	-0.0961 (5)	10 (1)
C15	-0.1702 (5)	0.3160 (6)	0.1725 (3)	5.8 (5)	C85	0.1377 (8)	0.209 (1)	-0.0823 (4)	9.5 (8)
C16	-0.0766 (5)	0.3280 (5)	0.1830 (3)	4.4 (4)	C86	0.1485 (6)	0.1823 (8)	-0.0368 (3)	6.9 (5)
C21	0.1063 (4)	0.4869 (5)	0.1861 (2)	3.1 (3)	C91	0.5277 (4)	0.3242 (5)	0.1900 (2)	3.2 (3)
C22	0.0803 (5)	0.5079 (5)	0.2275 (3)	4.6 (4)	C92	0.5852 (5)	0.3977 (6)	0.1950 (3)	5.3 (4)
C23	0.0842 (6)	0.5966 (7)	0.2432 (3)	5.5 (5)	C93	0.6492 (6)	0.4076 (6)	0.2325 (3)	5.9 (5)
C24	0.1149 (6)	0.6643 (6)	0.2178 (3)	5.8 (5)	C94	0.6588 (5)	0.3450 (6)	0.2653 (3)	4.9 (4)
C25	0.1408 (8)	0.6435 (6)	0.1772 (4)	7.5 (6)	C95	0.6016 (6)	0.2710 (6)	0.2620 (3)	5.9 (5)
C26	0.1371 (6)	0.5551 (6)	0.1618 (3)	5.6 (5)	C96	0.5370 (5)	0.2614 (5)	0.2244 (3)	5.1 (4)
C31	0.1850 (4)	0.0144 (4)	0.1401 (2)	3.1 (3)	C101	0.5168 (4)	0.2624 (5)	0.1006 (2)	3.2 (3)
C32	0.1664 (5)	0.0223 (5)	0.1830 (3)	3.6 (4)	C102	0.5567 (5)	0.3154 (5)	0.0707 (3)	4.1 (4)
C33	0.1060 (6)	-0.0380 (6)	0.2006 (3)	4.9 (4)	C103	0.6134 (5)	0.2793 (6)	0.0416 (3)	4.7 (4)
C34	0.0638 (5)	-0.1032 (6)	0.1728 (4)	5.5 (5)	C104	0.6342 (5)	0.1897 (7)	0.0445 (3)	5.1 (5)
C35	0.0825 (6)	-0.1126 (6)	0.1290 (3)	6.3 (5)	C105	0.5972 (6)	0.1354 (5)	0.0748 (3)	5.7 (5)
C36	0.1434 (6)	-0.0549 (5)	0.1124 (3)	5.1 (4)	C106	0.5373 (5)	0.1715 (5)	0.1028 (3)	4.5 (4)
C41	0.3558 (4)	0.0140 (5)	0.1101 (3)	3.3 (4)	C111	0.2833 (5)	0.5447 (5)	0.0720 (3)	3.8 (4)
C42	0.4098 (5)	-0.0184 (5)	0.1477 (3)	4.1 (4)	C112	0.3352 (6)	0.6106 (6)	0.0957 (3)	5.4 (5)
C43	0.4821 (5)	-0.0778 (6)	0.1463 (3)	5.4 (5)	C113	0.3133 (8)	0.7018 (6)	0.0888 (4)	7.4 (6)
C44	0.4999 (6)	-0.1050 (6)	0.1046 (4)	6.2 (5)	C114	0.2402 (8)	0.7257 (6)	0.0582 (4)	7.3 (6)
C45	0.4483 (6)	-0.0774 (7)	0.0664 (3)	6.6 (5)	C115	0.1894 (7)	0.6614 (7)	0.0350 (4)	7.1 (6)
C46	0.3764 (5)	-0.0170 (6)	0.0692 (3)	5.2 (5)	C116	0.2098 (6)	0.5703 (6)	0.0423 (3)	5.5 (5)
C51	0.2555 (5)	0.1936 (5)	0.2714 (2)	3.5 (4)	C121	0.3447 (4)	0.3913 (5)	0.0282 (2)	3.3 (3)
C52	0.1816 (5)	0.1467 (5)	0.2831 (3)	4.4 (4)	C122	0.3490 (5)	0.3007 (5)	0.0173 (3)	4.4 (4)
C53	0.1917 (7)	0.0869 (5)	0.3192 (3)	5.2 (5)	C123	0.3866 (5)	0.2695 (6)	-0.0195 (3)	5.2 (4)
C54	0.274 (1)	0.0754 (7)	0.3454 (3)	7.2 (6)	C124	0.4214 (6)	0.3289 (7)	-0.0476 (3)	5.7 (5)
C55	0.3490 (7)	0.1232 (7)	0.3338 (3)	6.5 (5)	C125	0.4166 (7)	0.4194 (6)	-0.0391 (3)	7.4 (6)
C56	0.3407 (5)	0.1801 (6)	0.2970 (3)	4.9 (4)	C126	0.3801 (6)	0.4503 (5)	-0.0013 (3)	5.7 (5)
C61	0.2850 (5)	0.3764 (5)	0.2557 (2)	3.2 (3)					

^aB values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

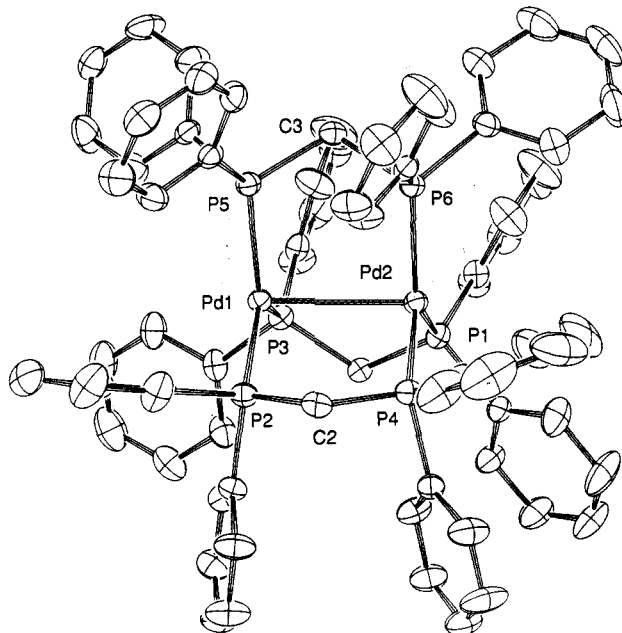
Table III. Selected Intramolecular Distances for Pd₂(dppm)₃^a

Pd1-P2	2.311 (2)	P1-C1	1.837 (7)
Pd1-P3	2.314 (2)	P2-C2	1.861 (7)
Pd1-P5	2.316 (2)	P3-C1	1.837 (7)
Pd1-Pd2	2.959 (2)	P4-C2	1.846 (7)
Pd2-P1	2.300 (2)	P5-C3	1.842 (7)
Pd2-P6	2.307 (2)	P6-C3	1.853 (7)
Pd2-P4	2.310 (2)		

^aDistances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Each Pd atom possesses approximate trigonal-planar coordination with Pd-P distances in the range 2.300–2.316 Å and P-Pd-P angles of 116.1–125.6°. The Pd-P distances are similar to those in other dppm-bridged palladium dimers, and the P-Pd-P angles are similar to those in Pt₂dppm₃.¹⁵ The conformation of the PdP₃ fragments is practically eclipsed, leading to a structure of nearly C_{3h} symmetry with the mirror plane passing through the dppm CH₂ groups, as seen in Figure 3. The two PdP₃ planes are approximately parallel with a Pd-Pd distance of 2.959 (2) Å, a distance marginally too long for a single bond between metal centers.

The Pd-Pd distance is longer than those found in Pd₂Br₂(dppm)₂ (2.699 Å)^{15c} and Pd₂Cl(SnCl₃)(dppm)₂ (2.644 Å),² where metal-metal bonds are required to maintain a 16e configuration for each Pd center. The 2.959-Å distance is, however, shorter than the nonbonding Pd...Pd distances found for Pd₂(μ-S)Cl₂(dppm)₂ (3.258 Å), Pd₂(μ-SO₂)Cl₂(dppm)₂ (3.221 and 3.383 Å),

**Figure 3.** Molecular structure of Pd₂(dppm)₃ perpendicular to the Pd-Pd vector.

and Pd₂(μ-NCMe)(MeCN)₂(dppm)₂²⁺ (3.215 Å).⁴ The Pd...Pd separation in the present structure is similar to the value of 3.023

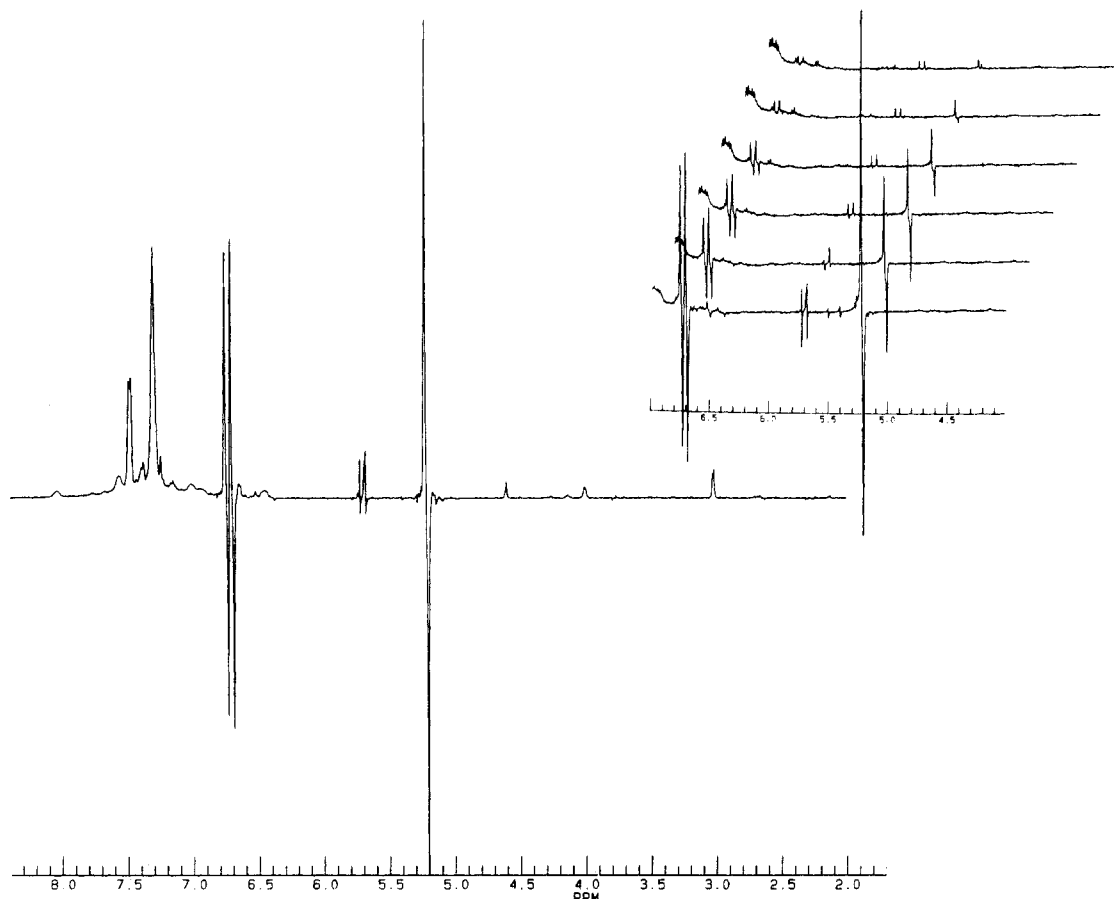


Figure 4. Hydrogenation of $\text{PhC}\equiv\text{CH}$ with **I** in CDCl_3 at 60°C under 3–4 atm of H_2 . The inset shows the decay of the polarization over 6 min; the initial spectrum is obtained ~ 40 s after thawing with subsequent spectra at 1-min intervals.

Table IV. Selected Bond Angles for $\text{Pd}_2(\text{dppm})_3^a$

P2–Pd1–P3	123.23 (7)	C51–P3–Pd1	117.2 (2)
P2–Pd1–P5	119.48 (7)	C51–P3–C1	102.4 (3)
P2–Pd1–Pd2	90.97 (7)	C1–P3–Pd1	112.0 (2)
P3–Pd1–P5	117.22 (7)	C61–P3–Pd1	125.1 (2)
P3–Pd1–Pd2	89.10 (7)	C2–P4–Pd2	114.9 (2)
P5–Pd1–Pd2	92.66 (7)	C81–P4–C2	101.0 (4)
P1–Pd2–P6	125.64 (7)	C81–P4–Pd2	115.2 (3)
P1–Pd2–P4	117.95 (7)	C71–P4–C2	100.0 (3)
P1–Pd2–Pd1	93.23 (7)	C71–P4–Pd2	121.6 (2)
P6–Pd2–P4	116.06 (8)	C101–P5–Pd1	124.1 (2)
P6–Pd2–Pd1	90.41 (7)	C3–P5–C91	103.4 (3)
P4–Pd2–Pd1	92.21 (7)	C3–P5–C101	103.3 (3)
C11–P1–C1	100.5 (3)	C3–P5–Pd1	112.8 (2)
C11–P1–Pd2	117.5 (3)	C91–P5–Pd1	112.5 (2)
C1–P1–C21	105.0 (3)	C3–P6–Pd2	114.9 (2)
C1–P1–Pd2	112.1 (2)	C121–P6–Pd2	118.2 (2)
C21–P1–Pd2	120.7 (2)	C121–P6–C3	99.8 (3)
C41–P2–C2	101.9 (3)	C111–P6–C3	102.1 (3)
C41–P2–Pd1	115.4 (2)	C111–P6–Pd2	118.1 (2)
C31–P2–C2	102.5 (3)	P5–C3–P6	113.1 (3)
C31–P2–Pd1	121.7 (2)	P1–C1–P3	113.4 (3)
C2–P2–Pd1	114.7 (2)	P4–C2–P2	113.0 (3)

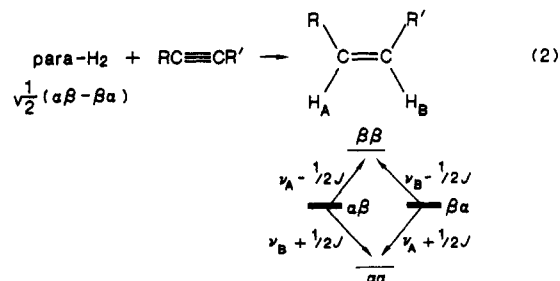
^a Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Å found for the Pt...Pt separation in $\text{Pt}_2(\text{dppm})_3$, which was taken to indicate some metal–metal interaction although less than that of a single bond.^{15c} All other distances and angles for the $\text{Pd}_2(\text{dppm})_3$ structure appear normal. The $\text{Pd}_2\text{P}_4\text{C}_2$ rings adopt boat–chair conformations similar to those observed in Pt_2dppm_3 .

Hydrogenation and Parahydrogen-Induced Polarization Using I. In the absence of added hydrogen, compound **I** appears to hydrogenate alkynes or alkenes stoichiometrically, while under H_2 , catalytic hydrogenation is observed. The reaction using $\text{PhC}\equiv\text{CH}$ as substrate is slow at room temperature and H_2 pressures of less than 1 atm but becomes significantly faster at

$60\text{--}70^\circ\text{C}$ and H_2 pressures of 3–4 atm.

The original stimulus for the present study was the observation of parahydrogen-induced polarization in the hydrogenation of alkynes and simple alkenes using the binuclear complex $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$. Compound **I** is also effective in generating PHIP. The basis of PHIP has been put forth by Weitekamp¹⁶ and involves the pairwise transfer of para-enriched H_2 to the substrate. If this occurs rapidly relative to proton relaxation, then the transferred protons will initially reflect the nuclear spin populations of the starting dihydrogen. This is shown schematically in eq 2 for hydrogenation of an internal alkyne with para- H_2 .



Since only the $\alpha\beta$ and $\beta\alpha$ states of the product olefin correlate with the para- H_2 nuclear spin function, these states will be overpopulated relative to a normal Boltzmann distribution (as shown in the diagram of eq 2), giving rise to polarized A/E or E/A resonances similar to those seen in a CIDNP multiplet effect.

When solutions of **I** and $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ in CDCl_3 are stored at -196°C under 3–4 atm of H_2 for >8 h before thawing, shaking, and immediate insertion into the probe of a 400-MHz NMR instrument, large multiplet type polarizations are observed in the

(16) (a) Bowers, C. R.; Weitekamp, D. P. *Phys. Rev. Lett.* **1986**, *57*, 2645.
(b) Bowers, C. R.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541.

H_{trans} and H_{gem} protons of the product styrene, as shown in Figure 4. The polarization decays exponentially with a first-order rate constant of 0.012 s^{-1} (see Figure 4, inset). After the polarization has disappeared (usually $<10\text{ min}$), storage of the tube at -196°C for $>8\text{ h}$ regenerates the polarization when the tube is thawed, shaken, and inserted into the NMR probe a second time. This can be repeated through several cycles. Storage at -78°C for 24 h gives the same effect, but the magnitude of the polarization is qualitatively weaker. Failure to store the samples under these conditions leads to the observation of hydrogenation, but without polarization.

Addition of para-enriched H_2 (prepared by storage of H_2 over a Fe_2O_3/C /silica catalyst at -196°C for $2\text{--}24\text{ h}$) to a solution of I and $PhC\equiv CH$ in $CDCl_3$ followed by immediate insertion into the NMR magnet leads to the observation of the same polarization as seen when the reaction tubes were stored under H_2 at -196°C . These results confirm that during the storage period ortho- H_2 /para- H_2 conversion is occurring leading to a para-enriched H_2 atmosphere above the reaction solution when thawed. The observed polarization in the hydrogenated products thus results from the transfer of H_2 to substrate in a pairwise fashion from a nonequilibrium mixture of ortho- and parahydrogen.

Polarization has been observed in a variety of solvents (C_6D_6 , $CDCl_3$, CD_3COCD_3 , and CD_3CN) for both alkynes (phenylacetylene, *tert*-butylacetylene, and 1-phenyl-1-propyne) and alkenes (styrene- d_8 and ethylene- d_4), although the hydrogenation of alkenes requires higher temperatures. From the hydrogenation of $C_6H_5C\equiv CD$, H_2 addition to substrate appears to be *cis*. At elevated temperatures in $CDCl_3$, I is observed to decompose to a mixture of $Pd_2Cl_2(dppm)_2$, $PdCl_2(dppm)$, and the unidentified red Pd compound (*vide supra*).¹⁷ These species form in the presence of either substrate or H_2 alone and are equally active as hydrogenation catalysts upon addition of the other component to the solution, as judged by the generation of PHIP. The mononuclear $PdCl_2(dppm)$ complex, however, is inactive as a hydrogenation catalyst under these conditions, and while $Pd_2Cl_2(dppm)_2$ has been shown to be an active hydrogenation catalyst, much higher temperatures are required to observe the polarization. In general, PHIP observed with $Pd_2Cl_2(dppm)_2$ is much less intense than in reactions involving compound I.

Conclusions. The reaction of $Pd_2Cl_2(dppm)_2$ with $NaBH_4$ leads to the formation of a purple species I that is an active catalyst for the homogeneous hydrogenation of simple substrates including $PhC\equiv CH$, styrene, and C_2D_4 . In these hydrogenations using para-enriched H_2 , the observation of parahydrogen-induced polarization shows that the transfer of hydrogen to substrate occurs pairwise and fast relative to proton relaxation. The stereochemistry of the addition appears to be *cis*. Studies directed at quantifying the magnitude of polarization in these and related hydrogenations and at using PHIP to obtain kinetic data regarding the relative rate of hydrogen transfer are continuing. The characterization of compound I includes its reaction with dppm to form $Pd_2(dppm)_3$, which has been shown crystallographically to have a C_{3h} structure like its Pt analogue.

Experimental Section

Reagents. Palladium dichloride (Johnson-Matthey), sodium borohydride (J. T. Baker), bis(diphenylphosphino)methane, methyl iodide, diiodomethane, chlorotrimethylsilane, dichlorodimethylsilane, sodium borodeuteride, styrene- d_8 , alkynes (Aldrich), and ethylene- d_4 (MSD) were used as purchased. Reagent grade solvents were degassed prior to use but were not exhaustively dried or purified. Benzene- d_6 (MSD), chloroform- d_3 , acetonitrile- d_3 , acetone- d_6 , and dichloromethane- d_2 (Aldrich) were dried over calcium hydride and distilled prior to use. H_2 , D_2 , and CO (Matheson) were used as received.

Physical Measurements. Infrared spectra were recorded on a Mattson Sirius 100 FT IR spectrometer in KBr pellets. 1H and ^{31}P NMR spectra were recorded on a Bruker WH400 spectrometer at 400 and 162 MHz, respectively. Gases were analyzed on a Hewlett-Packard 5700A gas

chromatograph with a thermal conductivity detector and a helium carrier gas (40 mL/min). Gas samples (0.5 mL) were withdrawn from the reaction flask through septa by using a gastight Pressure-Lok syringe. A $12\text{ ft} \times 1/4\text{ in.}$ Porapak Q column was used for both H_2 and CH_4 measurements. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and Desert Analytics, Tucson, AZ.

Preparation of Complexes. All syntheses were routinely performed under an atmosphere of dry nitrogen with modified Schlenk techniques. $Pd_2Cl_2(dppm)_2$, $Pd_2(dppm)_3$, $PdCl_2(dppm)Cl$, $Pd_2I_2(\mu-CH_2)(dppm)_2$, and $[Pd_2I_2(CH_3)(dppm)_2]I$ were prepared by published procedures.^{4,10,14,18}

Compound I. A 1.14-g (1.1-mmol) quantity of $Pd_2Cl_2(dppm)_2$ and 0.33 g (8.7 mmol) of $NaBH_4$ were stirred together as solids under a nitrogen atmosphere. Addition of 35 mL of methanol at 0°C led to the rapid evolution of gas and a darkening of the reaction mixture from a yellow slurry to green and finally to a dark purple color. After 30 min of reaction, the purple product was collected by filtration and washed with water and diethyl ether. The product was dried under vacuum overnight to yield 0.51 g of dark purple I. Mp: decomposes above 180°C . 1H NMR, ppm: (CD_2Cl_2) 3.98 br s (6), 5.01 septet (1, $J = 13.6\text{ Hz}$), 6.36 d (12), 6.61 t (6), 7.02 t (12), 7.32 t (6), 7.61 d (12); ($CDCl_3$) 4.05 br s (6), 5.00 septet (1), 6.43 br s (12), 6.68 t (12), 7.00 t (6), 7.08 t (12), 7.38 t (6), 7.66 br s (12); (CD_3CN) 3.96 br s (6), 5.03 septet (1), 6.31 d (12, $J = 6.4\text{ Hz}$), 6.56 t (12, $J = 7.5$), 6.85 t (6, $J = 7.2$), 7.09 t (12, $J = 7.5$), 7.34 t (6, $J = 7.2$), 7.69 d (12, $J = 6.4$); (CD_3COCD_3) 4.10 br s (6), 6.42 d (12, $J = 7.3$), 6.62 t (12, $J = 7.8$), 6.90 t (6, $J = 7.5$), 7.39 t (6, $J = 7.3$), 7.78 d (12, $J = 7.8$); no Pd-H resonance is seen, probably due to the low solubility of I in acetone. ^{31}P NMR, ppm: (CD_2Cl_2) -5.82 s ; ($CDCl_3$) -7.50 ; (CD_3CN) -5.07 s ; (CD_3COCD_3) -2.43 s . Substitution of $NaBD_4$ in the above reaction yields a product identical with I, but the 5.01-ppm resonance is missing in CD_2Cl_2 . Anal. Found: 57.28, C; 4.68, H; 11.57, P; 19.84, Pd.

Reactions with Organic and Inorganic Halides. These reactions were performed in NMR tubes and on preparative scale. Similar procedures were used for the reactions with CH_3I , CH_3I_2 , aqueous HCl , I_2 , $(C-H_3)_3SiCl$, and $(CH_3)_2SiCl_2$ and are illustrated with a single example.

Typically, 0.20 g (0.068 mmol) of I was dissolved in 15 mL of CH_2Cl_2 under nitrogen. A large excess of the organic or inorganic halide was added (e.g., 1 mL, 16 mmol of CH_3I), and the reaction was allowed to stir at room temperature until the dark blue color of I had disappeared completely. The volume of the red solution was reduced, and hexane was added to precipitate the products.

NMR tubes were prepared by adding about 3 mg (1 μmol) of I to an NMR tube. The tube was evacuated, and a solution of the volatile substrates in CD_2Cl_2 was vacuum-transferred into the tube. The tube was flame sealed under vacuum. The reactions were monitored by 1H and ^{31}P NMR spectroscopy.

Reaction of I with dppm. A 4.6-mg (1.5- μmol) quantity of I and 1.8 mg (4.7 μmol) of dppm were placed in an NMR tube in 0.5 mL of benzene- d_6 . The solution was degassed with three freeze/pump/thaw cycles before flame-sealing the tube under vacuum. The purple slurry was heated at 80°C until the solution turned red. The products were analyzed by 1H and ^{31}P NMR spectroscopies.

Crystal Structure Determination of $Pd_2(dppm)_3$. A crystal was grown from the reaction mixture of I and dppm in CD_3CN . The crystal was found to be monoclinic, space group $P2_1/c$, with cell dimensions $a = 14.733(5)\text{ \AA}$, $b = 14.760(5)\text{ \AA}$, $c = 29.720(6)\text{ \AA}$, and $\beta = 97.44(1)^\circ$. Data were collected as summarized in Table I. Direct methods (Mulan) were employed to locate the two palladium and six phosphorus atoms. Subsequent cycles of least-squares refinements and difference Fourier maps located the remaining non-hydrogen atoms. In the final model, all non-hydrogen atoms were described with anisotropic thermal parameters. Hydrogen atoms were placed at calculated positions around the phenyl rings. Table II contains the final refined positional and isotropic thermal parameters for the structure. The supplementary material contains final anisotropic thermal parameters, calculated hydrogen positional parameters, complete tabulations of bond distances and angles, and a listing of observed and calculated structure factor amplitudes for the structure. (See paragraph regarding supplementary material at end of paper.)

Hydrogenation Reactions and Parahydrogen-Induced Polarization Experiments. The hydrogenation reactions were carried out in 5-mm NMR tubes equipped with a resealable Teflon valve (Wilmad). After introduction of $\sim 5\text{ mg}$ (1.6 μmol) of I and any other solid reagents, solvents and volatile substrates were vacuum-transferred. Generally about 10 μL of liquid alkynes and alkenes and about 200 Torr of C_2D_4 were used. Hydrogen, deuterium, and/or CO were added to the tubes while the maximum amount of the tube was cooled at -196°C . Introduction of 1 atm of gas at this temperature, followed by closing the valve,

(17) This compound has not been cleanly isolated but has the following spectroscopic properties in $CDCl_3$ solution. 1H NMR: 4.31 (br d, $J = 12\text{ Hz}$), 4.69 (br d, $J = 13\text{ Hz}$), 6.8–7.8 ppm (multiplets). ^{31}P NMR: -10.9 ppm .

(18) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889.

makes the effective room-temperature pressure 3–4 atm.

Para-enriched H_2 was generated either by storing the tubes for longer than 8 h at $-196^\circ C$ or by adding para-enriched H_2 immediately before carrying out the NMR experiments. Para-enriched hydrogen can be readily prepared by storage of H_2 at $-196^\circ C$ in a bulb containing Fe_2O_3/C /silica catalyst for more than 2 h.

Gas Evolution Studies. The amount of H_2 produced in the reaction of **1** with acids was measured as follows. Complex **1** was suspended in a minimum of acetone under N_2 . Aqueous HCl was quickly added through a septum. Gas chromatographic measurements were made until a constant value was obtained for the H_2 pressure. Since the volume of the gas above the reaction mixture was greater than 100 mL, the withdrawal of 0.5-mL aliquots for sampling affected the total sample pressure by only 0.5%. Methane evolution was monitored in a similar fashion for the reaction of **1** in neat methyl iodide.

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Registry No. $Pd_2Cl_2(dppm)_2$, 64345-29-5; $Pd_2(dppm)_3$, 37266-95-8; $PdI_2(dppm)$, 77462-40-9; $[Pd_2I(dppm)_2(CH_3)_2]I$, 81457-54-7; $Pd_2(\mu_2-CH_2)_2I_2(dppm)_2$, 78274-36-9; $Pd_2(\mu_2-CH_2)Cl_2(dppm)_2$, 78274-94-9; $[Pd_3(dppm)_3(\mu_3-CO)](CF_3CO_2)_2$, 89189-81-1; $PdCl_2(dppm)$, 38425-01-3; CH_3I , 74-88-4; CH_3I_2 , 75-11-6; HCl, 7647-01-0; I_2 , 7553-56-2; $(C-H_3)_3SiCl$, 75-77-4; $(CH_3)_2SiCl_2$, 75-78-5; CH_4 , 74-82-8; $(Me_3Si)_2O$, 107-46-0; H_2 , 1333-74-0; $PhC\equiv CH$, 536-74-3; *tert*-butylacetylene, 917-92-0; 1-phenyl-1-propyne, 673-32-5; styrene- d_8 , 19361-62-7; ethylene- d_4 , 683-73-8.

Supplementary Material Available: Tables of data collection and refinement parameters, anisotropic thermal parameters, calculated hydrogen positional parameters, and complete bond distances and angles for non-hydrogen atoms (12 pages); a listing of observed and calculated structure factors for $Pd_2(dppm)_3$ (31 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Magnetic Properties of μ -Oxalato- and μ -Oxamido-Bridged Copper(II) Dimers. Crystal and Molecular Structures of $[Cu_2(mepirizole)_2(C_2O_4)(H_2O)_2](PF_6)_2 \cdot mepirizole \cdot 3H_2O$ and $[Cu_2(mepirizole)_2(C_2O_4)(NO_3)_2(H_2O)_2]_2[Cu_2(mepirizole)_2(C_2O_4)(NO_3)_2]$

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Four complexes, $[Cu_2L_2(ox)(H_2O)_2](PF_6)_2 \cdot 3H_2O$ (**1**), $[Cu_2L_2(ox)(NO_3)_2(H_2O)_2]_2[Cu_2L_2(ox)(NO_3)_2]$ (**2**), $Cu_2L_2(ox)(ClO_4)_2$ (**3**), and $Cu_2L_2(oxamd)(NO_3)_2 \cdot H_2O$ (**4**), with *ox* = oxalato, *oxamd* = oxamido, and *L* = mepirizole (4-methoxy-2-(5-methoxy-3-methyl-pyrazol-1-yl)-6-methylpyrimidine), have been synthesized. The structures of **1** and **2** have been determined. **1** crystallizes in the orthorhombic system, space group *Pnma*, with *Z* = 8 and *a* = 21.864 (3) Å, *b* = 20.881 (5) Å, and *c* = 11.451 (3) Å. **2** crystallizes in the monoclinic system, space group *P2₁/n*, with *Z* = 4 and *a* = 20.073 (4) Å, *b* = 13.842 (4) Å, *c* = 20.070 (4) Å, and β = 119.09 (2)°. The structure of **1** consists of centrosymmetric binuclear cations $[L(H_2O)Cu(ox)Cu(H_2O)L]^{2+}$ separated by PF_6^- anions and molecules of free mepirizole and water of crystallization. The structure of **2** is composed of two crystallographically independent dimers $[L(NO_3)Cu(ox)Cu(NO_3)(H_2O)L]$ and $[L(NO_3)Cu(ox)Cu(NO_3)L]$. The four complexes have been studied with IR, UV-visible, and EPR spectroscopies and magnetic susceptibility measurements in the 360–5 K range. The four complexes exhibit strong antiferromagnetic exchange interactions ranging from -156 to -201 cm⁻¹. Magnetic and EPR results are discussed with respect to the crystal structures of **1** and **2**.

Introduction

It is now well-known that multiatom bridges can propagate magnetic exchange interactions between paramagnetic metal ions.² The dependence of the magnetic exchange upon the nature of the bridging species and/or stereochemical factors has been the subject of several recent studies.^{3–5}

The oxalato anion and related groups as oxamido, oxamato, etc., have been incorporated as bis-bidentate bridges into complexes containing a variety of metal ions. However the factors controlling the magnitude of superexchange interactions have been best il-

lustrated with copper(II) complexes.^{2,3} Only net antiferromagnetic interactions have been observed in these complexes, the magnitude of which basically depends upon two factors: (i) the nature and magnitude of the overlap between the metal d orbitals containing the unpaired electrons and the bridging ligand orbitals; (ii) the energy difference between the two magnetic orbitals.

In this paper, we report the synthesis, characterization, and structural and magnetic study of three copper-oxalato (*ox*) complexes and one copper-oxamido (*oxamd*) complex containing the binuclear $[LCu(ox)CuL]^{2+}$ and $[LCu(oxamd)CuL]^{2+}$ entities, respectively. Mepirizole (4-methoxy-2-(5-methoxy-3-methyl-pyrazol-1-yl)-6-methylpyrimidine, herein abbreviated *L*), a biologically active compound,⁶ has been used as terminal ligand in these new materials. This ligand, including both the pyrimidyl

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