Synthesis and Characterization of Dinuclear Palladium(I) and Mononuclear Palladium(II) Complexes Containing 1,1-Bis(diphenylphosphino)ethane (dpmMe) and Related Mixed-Ligand Complexes Containing dpmMe with Either Bis(diphenylphosphino)methane (dpm) or 2-(Diphenylphosphino)pyridine (Ph_2Ppy). X-ray Crystal Structures of $PdCl_2$(dpmMe) and $Pd_2Cl_2(\mu\text{-dpmMe})_2$

Chung-Li Lee,[1a] Ye-Ping Yang,[1a,b] Steven J. Rettig,[1c] Brian R. James,*[1a] David A. Nelson,*[1d] and Michael A. Lilga[1d]

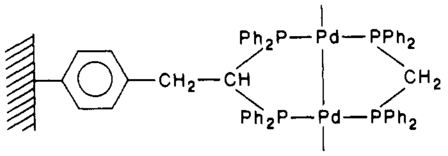
Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6, and Pacific Northwest Laboratory, Richland, Washington 99352

Received February 10, 1986

1,1-Bis(diphenylphosphino)ethane (dpmMe) has been synthesized by treating 1,1-dichloroethane with 2 equiv of $LiPPh_2$. Alkylation of bis(diphenylphosphino)methane (dpm) using *n*-BuLi and MeI occurs at the methylene carbon and one phosphorus atom to give the phosphonium salt $[Ph_2PCH(Me)P(Me)Ph_2]I$, which can be formed also by reaction of CH_3I with dpmMe. The complex $PdCl_2$(dpmMe) was prepared from $PdCl_2(PhCN)_2$, while $Pd_2X_2(\mu\text{-dpmMe})_2$ (X = Cl, Br, I, NCO), $Pd_2Cl_2(\mu\text{-dpmMe})(\mu\text{-}Ph_2Ppy)$, and $Pd_2Cl_2(\mu\text{-dpmMe})(\mu\text{-dpm})$ were prepared via ligand substitution of $Pd_2Cl_2(\mu\text{-}Ph_2Ppy)_2$ with the appropriate bidentate ligand [Ph_2Ppy = 2-(diphenylphosphino)pyridine]. The $Pd_2Cl_2(\mu\text{-dpmMe})_2$ complex crystallized as the anti form in the orthorhombic space group *Fdd*2 with $a = 22.249$ (1) Å, $b = 65.811$ (5) Å, $c = 12.833$ (1) Å, and $Z = 16$; the data were refined to $R = 0.039$ on the basis of 4470 reflections with $I \geq 3\sigma(I)$. A crystal of $PdCl_2$(dpmMe) was triclinic of space group $P\bar{1}$ with $a = 14.547$ (3) Å, $b = 19.521$ (5) Å, $c = 9.788$ (3) Å, $\alpha = 103.60$ (1)°, $\beta = 108.34$ (1)°, $\gamma = 91.89$ (2)°, and $Z = 4$ (two independent molecules); $R = 0.026$ from 7123 observed reflections with $I \geqslant 3\sigma(I)$. Of the dinuclear Pd_2Cl_2 species, only $Pd_2Cl_2(\mu\text{-dpmMe})(\mu\text{-dpm})$ reacted with CO in solution to form reversibly the A-frame complex in which the gas has inserted into the metal–metal bond. The solid-state structure of $Pd_2Cl_2(\mu\text{-dpmMe})_2$ shows that rotation of phenyl groups is somewhat inhibited by the presence of the methyl groups, but in solution rotation occurs, as evidenced by NMR data; lack of reactivity toward CO is attributed to a steric problem that would result from the required presence of one methyl group inside a boat ring conformation within a bridged carbonyl product.

Introduction

The coordination chemistry of the bis(diphenylphosphino)methane ligand (dpm), particularly its use as a bridging ligand in the development of A-frame complexes and their catalytic properties, has been reviewed.[2] We have reported recently[3] on the solution kinetics and thermodynamics of CO binding to the dinuclear palladium(I) species $Pd_2X_2(\mu\text{-dpm})_2$[4,5] and noted their potential for selective binding of CO in the presence of other gases.[3,6] The possibility of immobilizing the Pd_2 moiety on polystyrene (e.g., as shown below) led us to an interest in dpm alkylated at the methylene carbon and thus in Pd_2 mixed-ligand complexes containing both dpm and an alkylated dpm, e.g., 1,1-bis(diphenylphosphino)ethane (dpmMe).



Syntheses of the dpmMe ligand and its use in coordination chemistry within mono-, di-, and trinuclear species have been reported,[7-10] while Shaw and co-workers[11-15] have studied direct alkyl- and arylation at the methylene carbon atom of metal-coordinated dpm. Methylation (and sometimes dimethylation), for example, was carried out by deprotonation using a base such as $LiN(SiMe_3)_2$, followed by treatment with MeI; the procedure was successful synthetically with mononuclear complexes such as $M(CO)_4$(dpm) (M = Cr, Mo, W)[11,12] and PtX_2(dpm) (X = halide)[12,13] while PdI_2(dpm) showed only partial conversion

---

[1] (a) University of British Columbia. (b) On leave from Anhui University, The People's Republic of China. (c) Experimental Officer, University of British Columbia, Crystal Structure Service. (d) Pacific Northwest Laboratory.

[2] Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

[3] Lee, C. L.; James, B. R.; Nelson, D. A.; Hallen, R. T. *Organometallics* **1984**, *3*, 1360.

[4] Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.

[5] All the bidentate ligands within the dimeric species are present in the bridging mode; for convenience, the μ symbol will be subsequently omitted.

[6] Nelson, D. A.; Hallen, R. T.; Lee, C. L.; James, B. R. *Recent Developments in Separation Science*; Li, N., Calo, J. M., Eds.; CRC Press: Cleveland, 1986; Vol. IX, p 1.

[7] Kraihanzel, C. S.; Maples, P. K. *J. Organomet. Chem.* **1976**, *117*, 159.

[8] van der Ploeg, A. F. M. J.; van Koten, G. *Inorg. Chim. Acta* **1981**, *51*, 225.

[9] Sommer, K. *Z. Anorg. Chem.* **1970**, *376*, 37.

[10] Dean, P. A. W.; Srivastava, R. S. *Can. J. Chem.* **1985**, *63*, 2829.

[11] Al-Jibori, S.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 286.

[12] Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *74*, 235.

[13] Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1982**, *65*, L123.

[14] Pringle, P.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 81.

[15] Pringle, P.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 581.

into a mixture of mono- and dimethylated dpm species.[13] The possibility of similar alkylation within dinuclear species containing bridged dpm, e.g., $PdPtCl_2(dpm)_2$[14] and $Pt_2(acetylide)_4(dpm)_2$,[15] has been mentioned[13] but, to our knowledge, not reported. With a complex such as $Pd_2X_2(dpm)_2$, we would expect such a reaction to give a complex mixture because of the presence of the relatively weak Pd–Pd and Pd–X bonds.[2-4]

We report here an improved procedure for synthesis of $Ph_2PCH(Me)PPh_2$(dpmMe), and the synthesis and characterization of (a) $PdCl_2$(dpmMe), including an X-ray crystallographic analysis, (b) $Pd_2X_2(dpmMe)_2$, where X = halide or NCO, again with structural data for the chloride, and (c) Pd_2Cl_2(dpmMe)(dpm) and Pd_2Cl_2(dpmMe)(Ph_2Ppy), where Ph_2Ppy = 2-(diphenylphosphino)pyridine. Reactivity of the complexes toward CO in solution is also discussed.

Experimental Section

General Data. The sources of some of the materials used, the synthetic methods for $PdCl_2(PhCN)_2$ and $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone), and methods of measuring electronic spectra can be traced through our earlier paper.[3] Diphenylphosphine,[16] Ph_2Ppy,[17] $Pd_2Cl_2(Ph_2Ppy)_2$,[17] and $PdCl_2$(dpm)[18] were prepared by the reported procedures. *n*-BuLi (1.6 M in hexanes) and MeLi (1.56 M in ether) were used as supplied by Aldrich; *N,N,N′,N′*-tetramethylethylenediamine, tmed (Aldrich), and solvents were distilled and dried prior to use, unless noted otherwise. Syntheses of phosphines and the complexes were carried out under N_2. ^1H (5-mm tubes, 400 MHz) and ^{31}P (10-mm tubes, 32.44 MHz) NMR spectra were recorded at room temperature on Brüker WH-400 and Bruker WP-80 FT instruments, respectively; ^{31}P NMR shifts are given relative to external 85% H_3PO_4, downfield being positive, while simulation of the ^1H and ^{31}P spectra were performed by using the iterative routine of a Bruker ASPECT 200 NMR PANIC program. IR spectra were recorded as Nujol mulls on a Nicolet 5DX FT spectrometer.

Syntheses. $Ph_2PCH(Me)PPh_2$ (dmpMe). A solution of MeLi (18.4 mL, 28.8 mmol), added dropwise to Ph_2PH (5.35 g, 28.7 mmol) dissolved in benzene (50 mL), generated a yellow solution with concomitant evolution of CH_4. The solution was stirred for 3 h, and 1,1-dichloroethane (1.41 g, 14.3 mmol) was then added; a white precipitate (LiCl) formed immediately, but the mixture was stirred for 3 h prior to filtration through Celite. The benzene filtrate was concentrated under vacuum to give a yellow oil; addition of EtOH (95%, 300 mL) yielded white crystals that were purified by dissolution in 30 mL of CH_2Cl_2 followed by reprecipitation via addition of 100 mL of EtOH: yield 4.6 g, 80%; mp 113 °C (lit.[7] 111–113 °C). Anal. Calcd for $C_{26}H_{24}P_2$: C, 78.38; H, 6.07. Found: C, 78.38; H, 6.23.

[$Ph_2PCH(Me)P(Me)Ph_2$]I. (a) A solution of *n*-BuLi (9.5 mL, 15.2 mmol) was added slowly to dpm (3.85 g, 10 mmol) and tmed (1.82 mL, 12 mmol) dissolved in benzene (50 mL). The resulting yellow solution was stirred for 3 h prior to addition of excess MeI (2.5 mL). A white precipitate formed immediately, but the mixture was stirred overnight, before the white solid was collected by filtration. Separation from LiI was effected by dissolution in 30 mL of CH_2Cl_2, filtration, and reprecipitation by addition of 100 mL of ether, this procedure being repeated three times: yield 4.3 g, 79%. Anal. Calcd for $C_{27}H_{27}P_2I$: C, 60.01; H, 5.04. Found: C, 60.07; H, 5.12.

(b) Addition of MeI (2.28 g, 16 mmol) to $Ph_2PCH(Me)PPh_2$ (0.5 g, 1.25 mmol) dissolved in benzene (5 mL) yielded a white preciptate within 10 min. The mixture was stirred overnight, before the white solid was collected, vacuum dried, and purified by reprecipitation from 15 mL of CH_2Cl_2 via addition of 50 mL of benzene: yield 0.68 g, 99%.

$PdCl_2$(dpmMe) (1). The dpmMe ligand (312 mg, 0.79 mmol) in 10 mL of CH_2Cl_2 was added with stirring to $PdCl_2(PhCN)_2$ (300 mg, 0.78 mmol) dissolved in 10 mL of CH_2Cl_2, and stirring then continued for 2 h. Addition of diethyl ether (50 mL) to the final yellow solution yielded yellow crystals that were purified by reprecipitation (twice) from 30 mL of CH_2Cl_2 via addition of ~100 mL of ether: yield 400 mg, 89%. Anal. Calcd for $C_{26}H_{24}P_2Cl_2Pd$: C, 54.24; H, 4.20. Found: C, 54.08; H, 4.21.

$Pd_2Cl_2(dpmMe)_2$ (2). (a) The dpmMe ligand (295 mg, 0.74 mmol) in 20 mL of CH_2Cl_2 was added slowly to $Pd_2Cl_2(Ph_2Ppy)_2$ (300 mg, 0.43 mmol) dissolved in 20 mL of CH_2Cl_2. The resulting solution was stirred for 3 h and the volume reduced to 15 mL. Addition of diethyl ether (65 mL) yielded yellow-orange crystals that were reprecipitated from 15 mL of $CHCl_3$ via addition of 60 mL of methanol: yield 403 mg, 87%. Anal. Calcd for $C_{52}H_{48}Pd_2P_2Cl_2$: C, 57.80; H, 4.48. Found: C, 57.39; H, 4.48.

(b) $Pd_2(dba)_3{\cdot}CHCl_3$ (405 mg, 0.39 mmol), $PdCl_2(PhCN)_2$ (300 mg, 0.78 mmol), and dpmMe (635 mg, 1.59 mmol) were dissolved in 40 mL of CH_2Cl_2, and the solution was refluxed for 1 h. After being cooled to room temperature and filtered, the solution was reduced by evacuation to a volume of 15 mL; slow addition of diethyl ether (50 mL) gave orange crystals (600 mg), but even after two reprecipitations from CH_2Cl_2 using ether, the high-yield product was a mixture of the desired compound $Pd_2Cl_2(dpmMe)_2$ and $PdCl_2$(dpmMe) in about a 2:1 ratio as judged by ^1H and ^{31}P NMR. An attempted corresponding synthesis using $Pd_2(bda)_3{\cdot}CHCl_3$, $PdCl_2$(dpmMe), and dpmMe in a 1:2:2 mole ratio again gave a similar product mixture of the dinuclear and precursor mononuclear species.

$Pd_2Cl_2(dpm)_2$. $PdCl_2$(dpm) (300 mg, 0.53 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (276 mg, 0.27 mmol), and dpm (205 mg, 0.53 mmol) were dissolved in 40 mL of CH_2Cl_2, and the solution was refluxed for 30 min. The final red solution was filtered and reduced to 15 mL by evacuation; slow addition of 50 mL of MeOH gave orange-red crystals that were reprecipitated twice from CH_2Cl_2 (15 mL) by using MeOH (50 mL): yield 430 mg, 77%. The pure compound was identified by comparison with an authentic sample.[3,4]

$Pd_2X_2(dpmMe)_2$ (X = Br, I, and NCO). To $Pd_2Cl_2(dpmMe)_2$ (200 mg, 0.19 mmol) dissolved in 15 mL of CH_2Cl_2 was added with stirring ~1.0 g of NaX dissolved in 15 mL of MeOH and 30 mL of H_2O. The solution turned orange-red immediately; N_2 was bubbled through the solution to effect concentration, and fine crystals of product precipitated within 1 h. The bromide was purified by reprecipitation twice from 10 mL of $CHCl_3$ by using 50 mL of MeOH: yield 180 mg, 85%. Anal. Calcd for $C_{52}H_{48}P_4Br_2Pd_2$: C, 53.41; H, 4.14. Found: C, 52.71; H, 4.11. The iodide and isocyanate were purified by reprecipitation from 20 mL of CH_2Cl_2 by using 50 mL of aqueous methanol ($MeOH:H_2O$ = 4, v/v): yields 190 and 200 mg, respectively, >95%. Anal. Calcd for $C_{52}H_{48}P_4I_2Pd_2{\cdot}{}^1/_2CH_2Cl_2$: C, 48.30; H, 3.78. Found: C, 48.43; H, 3.51. Calcd for $C_{53}H_{48}ONP_4Pd_2{\cdot}{}^1/_2CH_2Cl_2$: C, 57.56; H, 4.34. Found: C, 57.55; H, 3.95.

$Pd_2Cl_2(dpmMe)(Ph_2Ppy){\cdot}{}^1/_2CH_2Cl_2$ (3). To $Pd_2Cl_2(Ph_2Ppy)_2$ (400 mg, 0.49 mmol) dissolved in 60 mL of CH_2Cl_2 was added dropwise over 40 min, with vigorous stirring, dpmMe (190 mg, 0.48 mmol) dissolved in 60 mL of CH_2Cl_2. The final solution was concentrated to 15-mL volume by rotovap; addition of 50 mL of ethyl ether precipitated an orange product that was purified by reprecipitation twice from 15 mL of CH_2Cl_2 using 50 mL of ether: yield 400 mg, 86%. Anal. Calcd for $C_{43}H_{38}NP_3Cl_2Pd_2{\cdot}{}^1/_2CH_2Cl_2$: C, 52.88; H, 3.98; N, 1.42. Found: C, 52.64; H, 4.09; N, 1.50.

Pd_2Cl_2(dpmMe)(dpm) (4). A CH_2Cl_2 solution of dpm (160 mg, 0.42 mmol in 60 mL) was added dropwise over 1 h, with vigorous stirring, to $Pd_2Cl_2(dpmMe)(Ph_2Ppy)$ (400 mg, 0.42 mmol) dissolved in 60 mL of CH_2Cl_2. The workup procedure was as described above for $Pd_2Cl_2(dpmMe)(Ph_2Ppy)$: yield 405 mg, 90%. Anal. Calcd for $C_{51}H_{46}P_4Cl_2Pd_2$: C, 57.43; H, 4.35; Cl, 6.65. Found: C, 57.31; H, 4.37; Cl, 6.80.

Reactions with CO. Of the three "Pd_2Cl_2" complexes containing dpmMe, only Pd_2Cl_2(dpmMe)(dpm) showed reactivity toward CO. The complex (220 mg, 0.21 mmol) was dissolved in 20 mL of CH_2Cl_2 and CO bubbled through the solution at ambient temperatures; the color rapidly turned from yellow-orange to red (and this could be reversed rapidly by switching to an N_2 supply). Addition to the carbonylated solution of 40 mL of ethyl ether saturated with CO yielded red crystals that were filtered off and vacuum dried. ^1H NMR showed a mixture of the insertion product

---

(16) Bianco, V. D.; Doronzo, S. *Inorg. Synth.* **1976**, *16*, 161.

(17) Maisonnet, A.; Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 3961.

(18) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.

Table I. NMR Spectral Data[a]

compd	methine proton[b]			methyl protons[b]			$^{31}P\{H\}$, δ_P
	δ_H	J_{HH}	J_{HP}	δ_H	J_{HH}	J_{HP}	
dpmMe	3.20 (q)	7.08	<1	0.99			
$[Ph_2PCH(Me)P(Me)Ph_2]I$	5.30 (dq)	7.22	14.47[c]	1.29 (ddd)	7.22	9.70 19.50[c]	29.54, −9.66[g]
				2.53[d] (d)		13.01[c]	
$PdCl_2(dpmMe)$ (**1**)	4.75 (tq)	7.64	12.03	1.12 (ddt)	7.64	17.53	−36.77 (s)
$Pd_2Cl_2(dpmMe)_2$ (**2**)	4.94 (qqn)	6.80	6.17	1.02 (dqn)	6.80	6.14	17.16 (b s)
$Pd_2Br_2(dpmMe)_2$ (**2a**)	4.95 (qqn)	6.90	6.55	0.97 (dqn)	6.90	6.12	16.12 (b s)
$Pd_2I_2(dpmMe)_2$ (**2b**)	5.04 (qqn)	6.59	6.60	0.88 (dqn)	6.59	6.22	12.34 (b s)
$Pd_2(NCO)_2(dpmMe)_2$ (**2c**)	4.88 (qqn)	6.47	6.10	1.05 (dqn)	6.47	6.47	17.46 (b s)
$Pd_2Cl_2(dpmMe)(Ph_2Ppy)$ (**3**)	4.86 (tq)	7.07	13.64	1.00 (dt)	7.07	12.26	18.11 (dd), 8.35 (d), 4.48 (d)[h]
$Pd_2Cl_2(dpmMe)(dpm)$ (**4**)	4.96 (tq)	7.11	12.84	1.03 (dt)	7.11	11.32	*i*
	4.56 (dt)	13.52	9.81 [e]				
	3.69 (dt)	13.52	9.40				
$Pd_2Cl_2(dpmMe)(dpm)(\mu\text{-}CO)$ (**5**)[f]	2.88 (tq)	7.10	11.40	1.24 (dt)	7.10	8.80	*i*
	2.77 (dtt)	13.48	10.80 [e]				
			5.60				
	2.18 (dt)	13.48	9.20				

[a] Measured at ambient temperatures in CD_2Cl_2 (for the Pd complexes) or $CDCl_3$ (for the free phosphines): b = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet. [b] *J* in Hz; the integrations were correct in every system. [c] Coupling to quaternary P. [d] Me at quaternary P. [e] CH_2 protons of dpm. [f] Prepared in situ by using **4** and 1 atm of CO. [g] AB quartet, J_{AB} = 64 Hz. [h] P_a, δ 18.11 (*J* = 17.58, 24.41 Hz); P_c, δ 8.35 (*J* = 24.41 Hz); P_b, δ 4.48 (*J* = 17.58 Hz). [i] See Figure 6; AA′BB′ system.

Table II. Electronic Absorption Spectral Data[a]

complex	λ_{max}, nm (log ϵ, M^{-1} cm^{-1})
1	256 sh (4.36), 345 (3.87)
anti-**2**	250 sh (4.59), 292 (4.48), 342 (4.32), 402 (3.97)
2a	255 sh (4.53), 280 sh (4.39), 300 (4.38), 360 (4.30), 415 (4.08)
2b	262 sh (4.52), 280 sh (4.45), 313 (4.36), 395 (4.18), 432 (4.17), 482 (4.13), 565 (3.61)
2c	250 sh (4.56), 285 (4.56), 323 (4.17), 375 (3.94)
3	255 sh (4.46), 277 sh (4.37), 344 (4.08), 430 (3.80)
4	252 sh (4.53), 291 (4.44), 342 (4.25), 410 (3.91)
5[b]	250 sh (3.90), 300 (1.99), 340 (0.96), 437 (1.00)

[a] In CH_2Cl_2 at ambient temperatures; sh = shoulder. [b] Prepared in situ by using **4** and 1 atm of CO; solution contains **5** and **4** in an approximate ratio of 2:1; values in parentheses are relative intensities on a nonlogarithmic scale.

$Pd_2Cl_2(dpmMe)(dpm)(\mu\text{-}CO)$ (**5**) and unreacted starting material.

Spectroscopic data for the ligands and complexes are summarized in Tables I and II. The presence of CH_2Cl_2 in the crystalline samples of $Pd_2X_2(dpmMe)_2$ (X = I and NCO) and **3** was verified by ^1H NMR.

Crystal Preparation and X-ray Crystallographic Analysis of $PdCl_2(dpmMe)$ (1) and $Pd_2Cl_2(dpmMe)_2$ (2). Single crystals were prepared by placing test tubes containing saturated CH_2Cl_2 solutions of the complex in a closed vessel (400 mL) containing 100 mL of anhydrous ethyl ether. Overnight equilibration of the solvent vapors yielded pale yellow crystals of **1** and orange crystals of **2**.

Crystallographic data for both compounds appear in Table III. Final unit-cell parameters were obtained by least-squares on (2 sin θ)/λ values for 25 reflections (with 2θ = 40–47° for **1** and 35–42° for **2**). The intensities of three check reflections, measured each hour of X-ray exposure time throughout both data collections, showed only small random fluctuations. Absorption corrections[19] were applied by using the Gaussian integration method,[20,21] transmission factor ranges being given in Table III.

Both structures were solved by conventional heavy-atom methods, the coordinates of the Pd, Cl, and P atoms being determined from the Patterson functions. For **1**, which contained two crystallographically independent molecules, the centrosymmetric space group $P\bar{1}$ was suggested by the Patterson function and confirmed by subsequent analysis. The remaining non-hydrogen atoms were positioned from subsequent difference maps. In the final stages of full-matrix least-squares refinement, the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included as fixed contributors in idealized positions (methyl groups staggered; $C(sp^3)$–H = 0.98 Å; $C(sp^2)$–H = 0.97 Å), recalculated after each cycle of refinement. Neutral atom scattering factors and anomalous scattering corrections for Pd, P, and Cl were taken from ref 22. The polarity of the structure of **2** (for the particular crystal used) was determined by parallel refinement; the *R* and R_w ratios of 1.0075 and 1.0088, respectively, suggest that the correct polarity has been chosen at a confidence level exceeding 99.5%.

Final positional and equivalent isotropic thermal parameters are given in Table IV. Bond lengths, bond angles, and intraannular torsion angles for **1** and **2** appear in Tables V, VI, and VII, respectively; Tables V and VI are included as supplementary material. Calculated hydrogen atom parameters, anisotropic thermal parameters, torsion angles, and measured and calculated structure factor amplitudes (Tables VII–XII), as well as a listing (Table XIII) of weak C–H···Cl interactions in **1**, are also included as supplementary material.

Results and Discussion

Ligand Synthesis. The reports from Shaw's group[11-15] (see Introduction) suggested that alkylation of dpm bridging two metals could give difficulties, and thus we investigated routes to the free ligand $Ph_2PCH(Me)PPh_2$.

Deprotonation at the methylene C atom of dpm yields the intermediate methanide $PPh_2C^-HPPh_2$, which is an ambident nucleophile,[23,24] as evidenced further by our isolation of $[Ph_2PCH(Me)P(Me)Ph_2]I$, where methylation has occurred at the carbon and one phosphorus; the same phosphonium salt was prepared also in quantitative yield by treatment of dpmMe (see below) with MeI. Similar direct methylation of dpm using MeI has been shown to give $[Ph_2PCH_2P(Me)Ph_2]I$,[25] although $PPh_2(CH_2)_2PPh_2$ (dpe) undergoes direct methylation at both phosphorus atoms.[26] The NMR data for $[Ph_2PCH(Me)P(Me)Ph_2]I$

---

(19) The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson.

(20) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(21) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1967**, *22*, 457.

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

(23) Appel, R.; Wander, M.; Knoll, F. *Chem. Ber.* **1979**, *112*, 1093.

(24) Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456.

(25) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.

Table III. Crystallographic Data[a]

	$PdCl_2[CH_3CH(PPh_2)_2]$ ($PdCl_2$(dpmMe))	$Pd_2Cl_2[CH_3CH(PPh_2)_2]_2$ ($Pd_2Cl_2(dpmMe)_2$)
formula	$C_{26}H_{24}Cl_2P_2Pd$	$C_{52}H_{48}Cl_2P_4Pd_2$
fw	575.7	1080.6
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$[b]	*Fdd*2
a, Å	14.547 (3)	22.2490 (7)
b, Å	19.521 (5)	65.811 (5)
c, Å	9.788 (3)	12.8328 (6)
α, deg	103.60 (1)	90
β, deg	108.34 (1)	90
γ, deg	91.89 (2)	90
V, Å^3	2547 (1)	18 790 (2)
Z	4 (2 independent molecules)	16
D_{calcd}, g/cm^3	1.501	1.528
F(000)	1160	8736
μ(Mo Kα), cm^{-1}	10.66	10.39
cryst dimens, mm	0.46 × 0.50 × 0.58	0.33 × 0.46 × 0.54
transmissn factors	0.496–0.556	0.572–0.738
scan type	$\omega-2\theta$	$\omega-2\theta$
scan range, deg in ω	0.85 + 0.35 tan θ	0.60 + 0.35 tan θ
scan speed, deg/min	1.34–10.06	0.91–10.06
data collected	$\pm h,\pm k,-l$	$+h,+k,+l$
$2\theta_{max}$, deg	50	55
unique reflctns	8967	5786
reflctns with $I \geq 3\sigma(I)$	7123	4470
no. of variables	559	540
R	0.026	0.039
R_w	0.036	0.048
S	1.453	2.024
mean Δ/σ (final cycle)	0.10	0.07
max Δ/σ (final cycle)	0.92	0.62
residual density, e/Å^3	−0.75 to +0.61	−2.37 to +3.96

[a] Temperature 22 °C; Enraf-Nonius CAD4-F diffractometer; Mo Kα radiation ($\lambda_{K\alpha_1}$ = 0.709 30; $\lambda_{K\alpha_2}$ = 0.713 59 Å); graphite monochromator; takeoff angle 2.7°; aperture (2.00 + tan θ) × 4.0 mm at a distance of 173 mm from the crystal; scan range extended by 25% on both sides for background measurement; $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (*S* = scan count; *B* = normalized background count); function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$. Values given for *R*, R_w, and *S* are based on those reflections with $I \geq 3\sigma(I)$. [b] Reduced cell; conventional orientation.

(Table I) are in line with those discussed for other phosphonium–phosphine systems.[25]

Despite its ambident character, the methanide $PPh_2C^-HPPh_2$ has been used successfully to synthesize other neutral bidentate ligands such as $Ph_2PCH(R)PPh_2$ (R = $SiMe_3$,[27] Ph_2P[23]) and *cis*- and *trans*-$PPh_2CH{=}CHPPh_2$.[28] The best route we found to $Ph_2PCH(Me)PPh_2$ is outlined in eq 1, with an overall yield of 80%; the ^{1}H

$$2Ph_2PH \xrightarrow[-2CH_4]{2MeLi} 2Li^+PPh_2^- \xrightarrow{Cl_2CHCH_3} \underset{\text{dpmMe}}{Ph_2PCH(Me)PPh_2} \quad (1)$$

and $^{31}P\{H\}$ NMR spectra (Table I) agree with those reported.[7,8] A method[9] utilizing Cl_2CHCH_3 with $Li^+PPh_2^-$ formed from PPh_3 and Li has been noted recently[10] to furnish a 10% yield; a modification using Br_2CHCH_3 with $Na^+PPh_2^-$ formed from PPh_3 and Na/liq. NH_3 gave a yield of 44%.[7] Another method, based on a procedure used for synthesis of $Ph_2PCH(SiMe_3)PPh_2$,[27] stated no yield.[8]

The $PdCl_2$(dpmMe) Complex. Reaction of dpmMe with $PdCl_2(PhCN)_2$ yielded $PdCl_2$(dpmMe) (1). The ^{1}H NMR (Figure 1; Table I) (Figures 1, 3, and 7 are available as supplementary material) shows the methine proton as a triplet of quartets (J_{HP} = 12.03, J_{HH} = 7.64 Hz), while there is no measurable P–H coupling in the free ligand, as noted by others.[7] The ^{1}H NMR data, and the large upfield shift in the ^{31}P spectrum, are comparable to those given for PtI_2(dpmMe).[12,13] The downfield shifts of the methine proton, and increased P–H coupling on coordination, are analogous to the data found within the $PdCl_2$(dpm) system (δ 4.28 (J_{HP} = 10.8 Hz) vs. δ 2.86 (J_{HP} = 1.3 Hz) for free dpm).[29] In the reported partial conversion of PdI_2(dpm) to PdI_2(dpmMe) via methylation, no NMR data were given for the product.[11]

A stereoview of 1 is shown in Figure 2. The crystal structure consists of discrete molecules, associated by weak C–H···Cl interactions (see Table XIII). All other intermolecular distances represent normal van der Waals contacts.

The two crystallographically independent molecules of $PdCl_2$(dpmMe) differ significantly with respect to the planarity of both the chelate ring and the metal coordination groups. In each case the Pd atoms are displaced from their respective P_2Cl_2 mean planes by amounts greater than for any of the substituent atoms, the overall deviation from planarity being considerably greater for the unprimed molecule [deviations of Pd, Cl(1), Cl(2), P(1), and P(2) from the mean P_2Cl_2 plane are 0.0675 (2), 0.0397 (8), −0.0440 (8), 0.0440 (7), and −0.0441 (7) Å, respectively; for the primed molecule, the deviations are 0.0257 (2), −0.0040 (10), 0.0034 (9), −0.0035 (8), and 0.0035 (7) Å, respectively]. The data in Table V show that the bond lengths involving Pd are generally shorter for the primed molecule, which has the more nearly ideal square-planar coordination geometry (e.g., Pd–Cl(1) = 2.3673 Å, Pd′–Cl(1′) = 2.3489 Å, Pd–P(2) = 2.2340 Å, Pd′–P(2′) = 2.2234 Å; Cl(1)–Pd–P(2) = 98.13°, Cl(1′)–Pd′–P(2′) = 95.69, Cl(1)–Pd–Cl(2) = 94.78°, Cl(1′)–Pd′–Cl(2′) = 93.84°).

An earlier structural investigation[18] of the complexes $PdCl_2[Ph_2P(CH_2)_nPPh_2]$, where *n* = 1 (dpm), 2 (dpe), and 3 (dpp), rationalized significant variations in Pd–P bond lengths in terms of steric constraints associated with cis bidentate chelating ligands: the length of the Pd–P bonds increased with increasing distance of the P atom from the $PdCl_2$ plane and, in general, the Pd–Cl bonds showed a trans effect. In complex 1, which would be expected to be even more sterically strained than $PdCl_2$(dpm), the mean Pd–P bond length of 2.227 Å is shorter than in any of the above complexes (mean Pd–P = 2.242, 2.230, and 2.246 Å for the dpm, dpe, and dpp complexes, respectively). This is consistent with the relatively small displacements of the P atoms from the respective $PdCl_2$ planes in 1 (P(1), −0.067, P(2), −0.222, P(1′), −0.061, and P(2′), −0.048 Å) compared to those in $PdCl_2$(dpm) (−0.136, +0.242 Å), $PdCl_2$(dpe) (−0.070, +0.087 Å), and $PdCl_2$(dpp) (−0.053, +0.312 Å). It is noteworthy that in both molecules of 1, the two P atoms lie on the same side of the $PdCl_2$ plane, in contrast with data for the dpm, dpe, and dpp complexes.[18] The Pd–Cl distances for each molecule of 1 are significantly different, but the mean value of 2.358 Å

---

(26) (a) Brophy, J. J.; Gallagher, M. J. *Aust. J. Chem.* **1967**, *20*, 503. (b) Carty, A. J.; Harris, R. K. *J. Chem. Soc., Chem. Commun.* **1967**, 234.

(27) Appel, R.; Geisler, K.; Schöler, H.-F. *Chem. Ber.* **1979**, *112*, 648.

(28) Hietkamp, S.; Stelzer, O. *Inorg. Chem.* **1984**, *23*, 258.

(29) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267.

Table IV. Final Positional (Fractional, ×10^4; Pd, Cl, and P, ×10^5) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses

$PdCl_2(dpmMe)$

atom	x	y	z	U_{eq}[a]	atom	x	y	z	U_{eq}[a]
Pd	80651 (1)	22294 (1)	30932 (2)	37	C(22)	6486 (2)	459 (2)	1784 (4)	55
Pd	36985 (1)	26922 (1)	55857 (2)	39	C(23)	5990 (2)	−220 (2)	1126 (4)	64
Cl(1)	89716 (6)	12942 (4)	24538 (9)	55	C(24)	5596 (2)	−558 (2)	1906 (5)	68
Cl(2)	89089 (6)	30669 (4)	23985 (9)	56	C(25)	5664 (3)	−231 (2)	3344 (5)	72
Cl(1′)	47588 (6)	37028 (4)	59531 (11)	62	C(26)	6163 (3)	444 (2)	4029 (4)	68
Cl(2′)	49702 (5)	20452 (4)	65803 (10)	58	C(1′)	1470 (2)	2406 (1)	4552 (3)	39
P(1)	71166 (5)	29909 (4)	38689 (8)	40	C(2′)	860 (2)	2578 (2)	5574 (4)	49
P(2)	71904 (5)	16747 (4)	41084 (8)	41	C(3′)	2328 (2)	1091 (1)	3597 (3)	46
P(1′)	24771 (5)	18638 (4)	51294 (8)	40	C(4′)	3156 (2)	831 (2)	3366 (4)	53
P(2′)	23345 (5)	31507 (4)	46418 (8)	38	C(5′)	3060 (3)	216 (2)	2243 (4)	66
C(1)	6289 (2)	2326 (2)	4113 (3)	46	C(6′)	2167 (3)	−119 (2)	1366 (4)	72
C(2)	5342 (2)	2082 (2)	2801 (4)	58	C(7′)	1341 (3)	147 (2)	1577 (5)	79
C(3)	7742 (2)	3583 (2)	5683 (3)	50	C(8′)	1423 (2)	752 (2)	2690 (4)	67
C(4)	8708 (2)	3823 (2)	6064 (4)	63	C(9′)	2386 (2)	1574 (2)	6715 (4)	50
C(5)	9204 (3)	4262 (3)	7477 (5)	91	C(10′)	2814 (3)	2018 (2)	8123 (4)	72
C(6)	8736 (3)	4455 (3)	8473 (5)	110	C(11′)	2678 (4)	1842 (3)	9354 (5)	92
C(7)	7784 (4)	4208 (3)	8105 (5)	136	C(12′)	2150 (4)	1219 (3)	9148 (6)	101
C(8)	7281 (3)	3763 (3)	6734 (4)	95	C(13′)	1742 (3)	756 (3)	7766 (7)	92
C(9)	6410 (2)	3473 (2)	2619 (3)	46	C(14′)	1853 (3)	934 (2)	6524 (5)	68
C(10)	6240 (3)	3216 (2)	1105 (4)	59	C(15′)	2084 (2)	3288 (1)	2802 (3)	43
C(11)	5631 (3)	3546 (2)	108 (4)	73	C(16′)	2818 (2)	3597 (2)	2455 (4)	66
C(12)	5207 (3)	4115 (2)	625 (5)	78	C(17′)	2626 (3)	3749 (3)	1092 (5)	84
C(13)	5370 (3)	4373 (2)	2129 (5)	75	C(18′)	1702 (3)	3596 (2)	65 (4)	72
C(14)	5968 (2)	4054 (2)	3135 (4)	60	C(19′)	979 (3)	3285 (2)	394 (4)	69
C(15)	7893 (2)	1707 (2)	6010 (3)	47	C(20′)	1161 (2)	3125 (2)	1755 (4)	59
C(16)	8805 (2)	1489 (2)	6284 (4)	65	C(21′)	2151 (2)	3959 (1)	5831 (3)	41
C(17)	9380 (3)	1527 (3)	7737 (5)	85	C(22′)	2735 (2)	4171 (2)	7310 (3)	50
C(18)	9042 (3)	1774 (2)	8897 (4)	77	C(23′)	2594 (3)	4776 (2)	8242 (4)	58
C(19)	8148 (3)	1977 (2)	8620 (4)	84	C(24′)	1892 (3)	5181 (2)	7709 (4)	59
C(20)	7568 (3)	1951 (2)	7189 (4)	74	C(25′)	1310 (3)	4972 (2)	6238 (5)	78
C(21)	6572 (2)	789 (2)	3228 (3)	46	C(26′)	1435 (3)	4367 (2)	5293 (4)	70

$Pd_2Cl_2(dpmMe)_2$

atom	x	y	z	U_{eq}[a]	atom	x	y	z	U_{eq}[a]
Pd(1)	−4915 (2)	19643 (1)	0	30	C(23)	−1361 (4)	1250 (1)	789 (8)	49
Pd(2)	−2229 (2)	15717 (1)	−1219 (6)	35	C(24)	−1610 (5)	1153 (1)	−80 (9)	65
Cl(1)	−7304 (8)	23210 (3)	1937 (17)	44	C(25)	−1784 (5)	953 (2)	−27 (11)	79
Cl(2)	328 (11)	12173 (3)	−1382 (30)	71	C(26)	−1701 (6)	846 (2)	853 (13)	95
P(1)	−14903 (8)	18984 (3)	−3028 (16)	37	C(27)	−1416 (5)	936 (2)	1735 (11)	75
P(2)	−11208 (9)	15148 (3)	7073 (17)	38	C(28)	−1254 (4)	1132 (1)	1657 (8)	58
P(3)	5126 (8)	20383 (3)	1698 (14)	30	C(29)	764 (3)	2100 (1)	1488 (6)	35
P(4)	6181 (8)	16574 (3)	−10581 (17)	36	C(30)	385 (4)	2201 (2)	2125 (7)	61
C(1)	−1723 (3)	1634 (1)	−75 (7)	45	C(31)	579 (5)	2276 (2)	3095 (8)	73
C(2)	−2378 (4)	1597 (1)	213 (9)	61	C(32)	1133 (5)	2242 (2)	3425 (8)	74
C(3)	1061 (3)	1844 (1)	−284 (6)	37	C(33)	1526 (5)	2141 (3)	2799 (10)	112
C(4)	1644 (4)	1920 (1)	−746 (8)	51	C(34)	1344 (5)	2076 (2)	1812 (9)	86
C(5)	−1701 (3)	1954 (1)	−1634 (6)	43	C(35)	710 (3)	2264 (1)	−591 (6)	36
C(6)	−1984 (4)	1816 (1)	−2296 (7)	52	C(36)	513 (4)	2275 (1)	−1605 (7)	47
C(7)	−2128 (4)	1874 (2)	−3314 (8)	64	C(37)	696 (4)	2440 (1)	−2230 (8)	59
C(8)	−2010 (5)	2070 (2)	−3671 (8)	68	C(38)	1022 (5)	2590 (2)	−1846 (12)	86
C(9)	−1740 (5)	2203 (2)	−3042 (9)	74	C(39)	1179 (7)	2586 (2)	−844 (14)	123
C(10)	−1580 (5)	2149 (2)	−2021 (9)	68	C(40)	1049 (6)	2419 (2)	−219 (11)	97
C(11)	−2010 (3)	2047 (1)	513 (7)	45	C(41)	464 (4)	1774 (1)	−2308 (7)	43
C(12)	−2488 (5)	2162 (2)	122 (10)	91	C(42)	−133 (4)	1809 (1)	−2581 (8)	58
C(13)	−2863 (5)	2262 (3)	777 (13)	111	C(43)	−290 (6)	1917 (2)	−3479 (9)	81
C(14)	−2797 (5)	2257 (2)	1823 (13)	91	C(44)	175 (7)	1989 (2)	−4138 (10)	87
C(15)	−2344 (5)	2148 (2)	2228 (9)	71	C(45)	748 (6)	1953 (2)	−3892 (8)	75
C(16)	−1936 (5)	2049 (2)	1553 (8)	61	C(46)	913 (4)	1845 (1)	−2986 (7)	51
C(17)	−1211 (4)	1609 (1)	2046 (7)	46	C(47)	1186 (3)	1463 (1)	−1320 (7)	43
C(18)	−1706 (4)	1558 (1)	2648 (8)	57	C(48)	1527 (5)	1387 (1)	−485 (9)	63
C(19)	−1761 (5)	1634 (2)	3669 (9)	74	C(49)	1967 (5)	1241 (2)	−664 (11)	82
C(20)	−1304 (6)	1761 (2)	4035 (8)	78	C(50)	2047 (5)	1162 (1)	−1631 (12)	77
C(21)	−826 (5)	1805 (2)	3490 (9)	69	C(51)	1717 (5)	1232 (1)	−2465 (12)	80
C(22)	−772 (4)	1733 (1)	2463 (8)	57	C(52)	1277 (4)	1378 (1)	−2316 (8)	56

[a] $U_{eq} = {}^1/_3$trace(diagonalized U).

compares well with the corresponding means of 2.357, 2.359, and 2.354 Å observed for the dpm, dpe, and dpp complexes.

The results of the present structure analysis show that the magnitude of steric strain is less important than the extent to which this strain causes out-of-plane deformation of the four coordinating atoms. The primed $PdCl_2$(dpmMe) molecule has a relatively planar, four-membered chelate ring (fold angle 5.6°), which results in near eclipsing of phenyl and methyl substituents (mean stagger angle 7.5°). The unprimed molecule is less strained in this respect (fold and stagger angles of 16.3 and 27.6°, respectively) as is the unsubstituted $PdCl_2$(dpm) molecule. The primed $PdCl_2$(dpmMe), however, has the most nearly

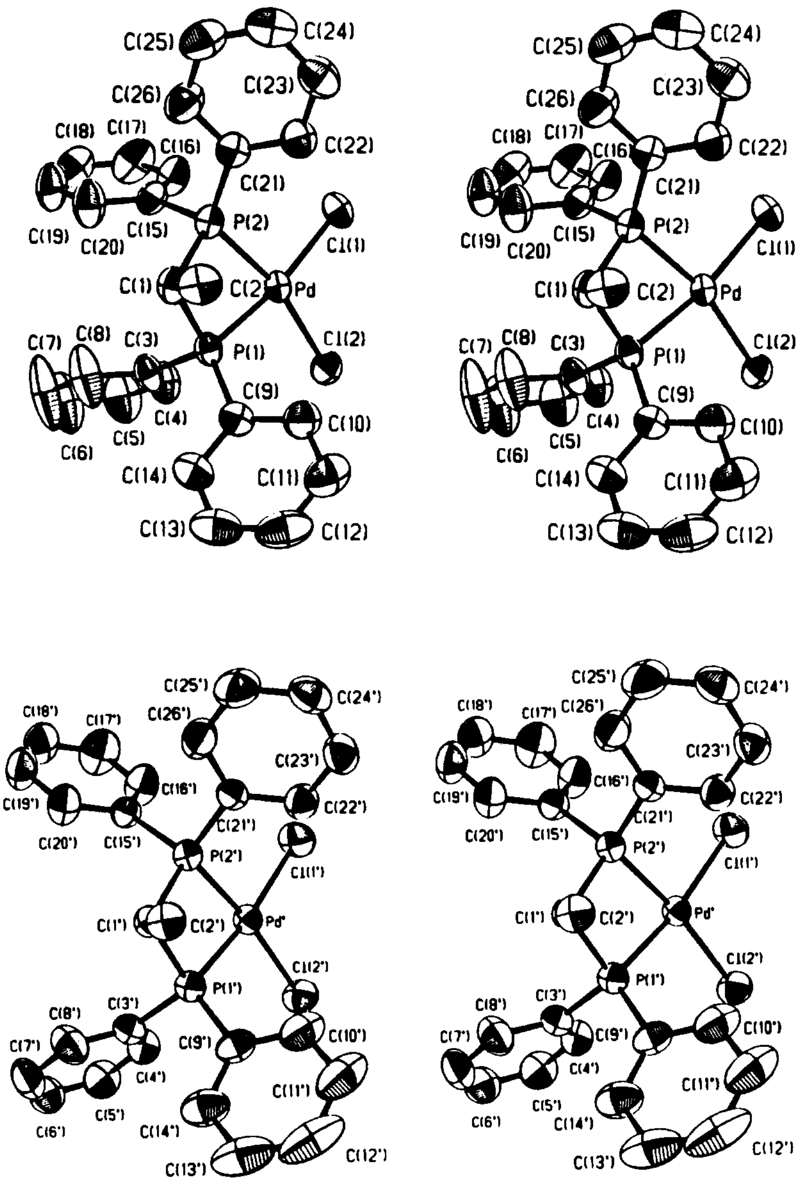
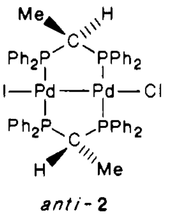


Figure 2. A stereoview of the two crystallographically independent molecules of $PdCl_2(dpmMe)$ (1) with 50% thermal ellipsoids (H atoms omitted).

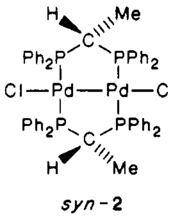
planar coordination about the metal and hence the shortest Pd–P bonds.

Another striking difference between the structures of $PdCl_2(dpm)$ and $PdCl_2(dpmMe)$ is the orientation of the phenyl rings. In the former molecule, the phenyl rings are asymmetrically disposed, but in the latter the phenyl rings are symmetrically oriented so as to impart overall C_s symmetry, this being a direct result of steric interaction between the C(2) methyl group and the C(9) and C(21) phenyl rings; this effectively locks these two phenyl rings in the observed orientation.[30] Of note, of the four structures being discussed, those which possess some degree of higher overall symmetry, namely, $PdCl_2(dpmMe)$ ($\sim C_s$) and $PdCl_2(dpe)$ ($\sim C_2$), show the smallest out-of-plane distortion of the coordinating atoms and have the shortest Pd–P bonds.

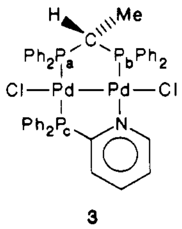
The Dinuclear Pd_2X_2 Complexes. Attempts to prepare $Pd_2Cl_2(dpmMe)_2$ (2) from the correct stoichiometric mixture of $PdCl_2(PhCN)_2$ and $Pd_2(dba)_3$ precursors in the presence of dpmMe, as used for the dpm analogue,[4] gave only a product mixture of 2 and 1. The same product mixture resulted on using 1 itself as the Pd(II) precursor instead of $PdCl_2(PhCN)_2$, although such a method again worked well for the dpm system with 77% yield of $Pd_2Cl_2(dpm)_2$, as described in the Experimental Section. An effective, high-yield synthesis of 2 resulted, however, by simple substitution of the pyridylphosphine ligands of $Pd_2Cl_2(Ph_2Ppy)_2$[17] with dpmMe. Complex 2 can exist as two possible isomers with the methyl groups on the opposite (*anti*-2) or same (*syn*-2) sides of the Pd–C–Pd plane.



anti-2



syn-2



3

The $^{31}P\{H\}$ NMR shows a broad singlet at δ 17.16, indicating equivalent P atoms, while the ^1H NMR (Figure 3; Table I) reveals virtual coupling[31] of the Me and CH

---

[30] Steric barriers to rotation were assessed using a locally written computer program, MOVE, by S. V. Evans.

[31] Becker, E. D. *High Resolution NMR*; Academic Press: New York, 1980; p 163.

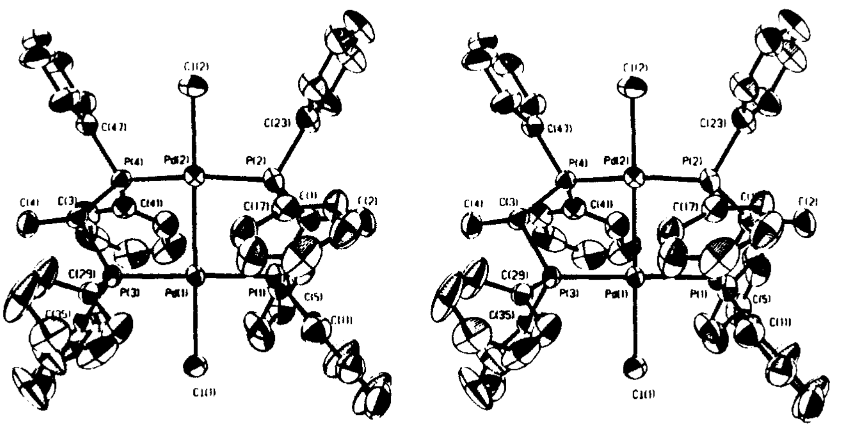


Figure 4. A stereoview of $Pd_2Cl_2(dpmMe)_2$ (2) with 50% thermal ellipsoids (H atoms omitted).

Table VII. Intraannular Torsion Angles (deg)[a]

$PdCl_2(dpmMe)$	
P(2)-Pd-P(1)-C(1)	-15.15 (9)
Pd-P(1)-C(1)-P(2)	17.45 (10)
Pd-P(2)-C(1)-P(1)	-17.37 (10)
P(1)-Pd-P(2)-C(1)	15.07 (9)
P(2′)-Pd′-P(1′)-C(1′)	-5.18 (9)
Pd′-P(1′)-C(1′)-P(2′)	5.95 (10)
Pd′-P(2′)-C(1′)-P(1′)	-5.95 (10)
P(1′)-Pd′-P(2′)-C(1′)	5.17 (9)
$Pd_2Cl_2(dpmMe)_2$	
P(1)-Pd(1)-Pd(2)-P(2)	-37.34 (8)
Pd(1)-Pd(2)-P(2)-C(1)	56.3 (3)
Pd(2)-P(2)-C(1)-P(1)	-52.0 (5)
Pd(1)-P(1)-C(1)-P(2)	16.4 (5)
Pd(2)-Pd(1)-P(1)-C(1)	18.5 (3)
P(3)-Pd(1)-Pd(2)-P(4)	-37.22 (7)
Pd(1)-Pd(2)-P(4)-C(3)	54.8 (2)
Pd(2)-P(4)-C(3)-P(3)	-47.8 (4)
Pd(1)-P(3)-C(3)-P(4)	12.9 (5)
Pd(2)-Pd(1)-P(3)-C(3)	20.3 (3)

[a] Standard deviations in parentheses.

protons to the remote P atoms, as seen by the partially overlapping doublet of quintets (δ 1.02) and quartet of quintets (δ 4.94). The observed single resonance pattern for the methyl, and for the methine, protons shows the presence of a single isomer, which is shown by the X-ray study to be the anti form (Figure 4). The corresponding syn and anti arrangements of the methyl groups within $Ag_2(dpmMe)_2^{2+}$[8] and $Hg_2(dpmMe)_2^{4+}$[10] have been detected by ^1H and ^{31}P NMR studies, but assignments to the respective isomers could not be made.

The $Pd_2X_2(dpmMe)_2$ complexes (X = Br (**2a**), I (**2b**), NCO (**2c**), made from the chloro complex **2** by metathesis, have NMR data that closely resemble those of **2** (Tables I and II). Differences exist in the electronic spectra of the $Pd_2X_2(dpmMe)_2$ complexes, X = halide and NCO (Table II), but in each case the spectrum is similar to that of the dpm analogue, where trends have been discussed.[3,4]

An attempt to synthesize the dinuclear, mixed-ligand complex $Pd_2Cl_2(dpmMe)(dpm)$ (4) from a $PdCl_2(dpmMe)/Pd_2(dba)_3$/dpm mixture was unsuccessful, giving only a mixture of products (not described in the Experimental Section). A high-yield synthesis, however, was accomplished by successive displacement of Ph_2Ppy, first from $Pd_2Cl_2(Ph_2Ppy)_2$ by dpmMe to give $Pd_2Cl_2(dpmMe)(Ph_2Ppy)$ (3) and then from 3 by dpm to give 4. The $^{31}P\{H\}$ NMR of 3 shows three discrete resonances of inequivalent P atoms, and the assignments given in Table I are based on the larger coupling constant being associated with trans P atoms. The ^1H NMR reveals the expected triplet of quartets for the single CH proton and the doublet of triplets for the single Me group. The J_{HP} coupling constants are roughly twice the magnitude of those noted for the $Pd_2(dpmMe)_2X_2$ complexes (Table I); this is because with virtual coupling the observed coupling constant is the average of the couplings to the adjacent and remote phosphorus atoms, and the latter is zero.[32]

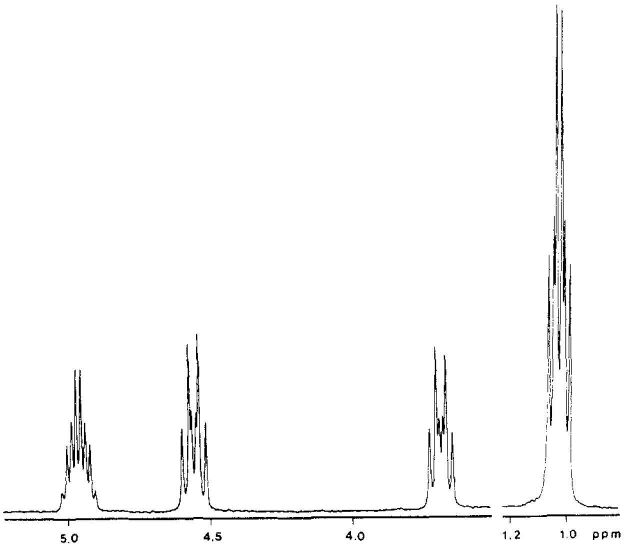


Figure 5. The ^1H NMR spectrum of the methine, methylene, and methyl regions of $Pd_2Cl_2(dpmMe)(dpm)$ (4) in CD_2Cl_2 at ~20 °C. The simulated spectra (data in Table I) are identical.

Very similar ^1H NMR findings are noted for complex 4 (Figure 5) which also shows each of the two inequivalent CH_2 protons as a doublet of triplets; as for 3, the inequivalence of the trans P atoms again rules out any virtual coupling. The $^{31}P\{H\}$ NMR of complex 4 (Figure 6) is in accord with an AA′BB′ system with large trans coupling ($J_{AB} = J_{A'B'} \approx 440$ Hz). Related systems have been analyzed similarly,[33] but we have not been able to analyze for the smaller couplings for complete simulation of the spectrum.

As noted in the Introduction, our interest in the Pd–dpmMe chemistry developed from the potential of such complexes to bind CO reversibly and selectively; however, as noted in the Experimental Section, of the three complexes *anti*-**2**, **3**, and **4** tested for solution reactivity toward 1 atm CO, only **4**, $Pd_2Cl_2(dpmMe)(dpm)$, gave evidence for partial and reversible formation of a bridged carbonyl

---

[32] Lee, C. L. Ph.D. Dissertation, University of California, Davis, 1981.

[33] Balch, A. L.; Hunt, C. T.; Lee, C. L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

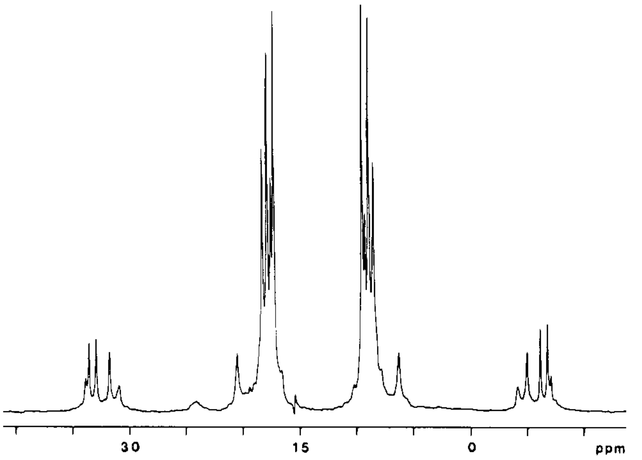


Figure 6. The ^{31}P{H} NMR spectrum of $\mathrm{Pd_2Cl_2}$(dpmMe)(dpm) (4) in $\mathrm{CD_2Cl_2}$ at ~20 °C.

adduct, $\mathrm{Pd_2Cl_2}$(dpmMe)(dpm)(μ-CO) (**5**). This A-frame complex is formed by insertion of CO into the Pd–Pd bond, chemistry that is well-known for the $\mathrm{Pd_2Cl_2(dpm)_2}$ system.[2-4] The ^{1}H NMR data, measured under CO, show that about 65% of **4** is converted to the bridged carbonyl, which is detected also in the IR at 1704 cm^{-1} (Nujol). The ^{1}H NMR (Figure 7; Table I) of **5** is complicated by long-range coupling of one of the $\mathrm{CH_2}$ protons to the two remote P atoms ($^4J_{HP}$ = 5.60 Hz). The carbonylation results in an upfield shift of the $\mathrm{CH_2}$ protons, as noted with $\mathrm{Pd_2Cl_2(dpm)_2}$,[34] and the CH proton, while the Me proton experiences a small downfield shift. The ^{31}P{H} spectrum reveals an AA′BB′ pattern similar to that of complex **4** (Figure 6). The $\mathbf{4} \rightleftharpoons \mathbf{5}$ equilibrium can be monitored also by changes in the electronic absorption spectra.[3] The ^{1}H NMR or visible spectral data yield an equilibrium constant of ~500 M^{-1} for the carbonylation reaction at ~20 °C in $\mathrm{CH_2Cl_2}$ (assuming a CO solubility of 8 × 10^{-3} M atm^{-1}).[3,35] This equilibrium value is some 500 times less than that for carbonylation of $\mathrm{Pd_2Cl_2(dpm)_2}$ under corresponding conditions,[3,36] and the observed nonreactivity (K < 5 M^{-1}) of *anti*-**2**, $\mathrm{Pd_2Cl_2(dpmMe)_2}$, fits into a pattern revealing decreasing reactivity with incorporation of a methyl substituent at the methylene group(s) of bridging dpm.

The crystal structure of **2** consists of discrete molecules, linked by weak C–H···Cl interactions [C(37)–H(37)···Cl(1) ($-x$, $^1/_2 - y$, $z - {}^1/_2$) and C(6)–H(6)···Cl(2) ($x - {}^1/_4$, $^1/_4 - y$, $z - {}^1/_4$); H···Cl = 2.85 and 2.87 Å; C···Cl = 3.658 (10) and 3.706 (9) Å; C–H···Cl = 141 and 146°]. There is also a close intermolecular contact involving a pair of phenyl rings that results in the H···H contacts H(12)···H(33) ($x - {}^1/_2$, y, $z - {}^1/_2$) = 2.09 Å and H(13)···H(32) ($x - {}^1/_2$, y, $z - {}^1/_2$) = 2.16 Å. All other intermolecular distances correspond to normal van der Waals interactions.

The overall molecular structure is remarkably similar to that of $\mathrm{Pd_2Br_2(dpm)_2}$,[37] the most important difference being the shorter Pd–Pd distance in the chloride (2.6639 (7) vs. 2.699 (5) Å), which is rationalized in terms of a structural trans effect. The Pd–P distances in **2** are equal within experimental error, the mean value of 2.291 (2) Å being in good agreement with the corresponding value of 2.29 (3) Å observed for $\mathrm{Pd_2Br_2(dpm)_2}$. The two Pd–Cl distances (Pd(1)–Cl(1) = 2.427 Å; Pd(2)–Cl(2) = 2.408 Å) differ by 6.7σ, possibly as a result of the involvement of Cl(1) in a pair of weak intramolecular C–H···Cl interactions [C(10)–H(10)···Cl(1) and C(30)–H(30)···Cl(1); H···Cl = 2.73 and 2.78 Å; C···Cl = 3.590 (11) and 3.589 (9) Å; C–H···Cl = 148 and 142°, respectively].

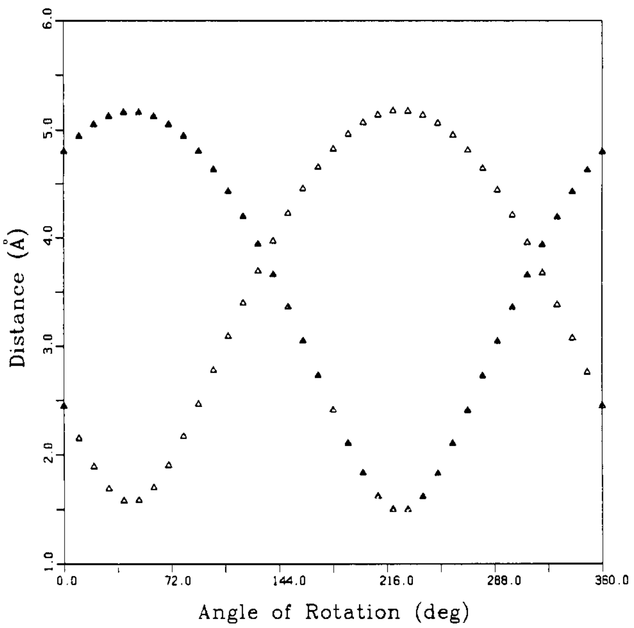


Figure 8. The ortho-hydrogen contacts as a function of rotation of the phenyl rings for the $\mathrm{Pd_2Cl_2(dpmMe)_2}$ (*anti*-**2**) complex: △, H(18)–H(2a); ▲, H(22)–H(2a).

The coordination geometries around each metal atom in **2** are significantly nonplanar, showing tetrahedral distortions in which the P atoms are displaced to the opposite side of the mean, as are the Pd and Cl ligands (mean displacement = 0.07 Å). The dihedral angle between the two coordination planes is 37°, similar to the value of 39° found for $\mathrm{Pd_2Br_2(dpm)_2}$. The orientation of the phenyl rings in **2**, despite the presence of the methyl groups, is very similar to that in $\mathrm{Pd_2Br_2(dpm)_2}$. The nonplanar five-membered chelate rings allow for staggering of the methyl and phenyl groups with respect to the intraannular P–C bonds. In addition, this anti isomer has both methyl groups in the less sterically crowded pseudoequatorial positions. The presence of the C(2) and C(4) methyl groups does inhibit rotation of C(17) and C(41) phenyl groups about the respective P–C bonds, at least in the solid state. Calculations[30] show that simple rotations of these phenyl rings, which would certainly assist an axial approach of CO to either metal atom, are prevented by steric interactions between the ortho-hydrogen atoms of the phenyl rings and methyl group (Figure 8). The solution NMR data, however, reveal that both dpmMe ligands and all four phosphorus atoms are equivalent, which means that rotation of the phenyl groups is no longer inhibited. The lack of reactivity toward CO may result from a steric problem in a bridged carbonyl product. The A-frame species generally, and certainly for example $\mathrm{Pd_2Cl_2(dpm)_2}$(μ-CO), adopt boat conformations for both of the two fused rings,[2,17] and for the anti isomer of **2** this would necessitate the location of one methyl group in the inside of the boat with considerable steric consequences. Alternatively, the fused rings could adopt chair/boat or chair/chair conformations, and such changes could well alter the stability of the product. The intermediate re-

---

[34] For $\mathrm{Pd_2Cl_2(dpm)_2}$, $\delta_{\mathrm{CH_2}}$ 4.28; for $\mathrm{Pd_2Cl_2(dpm)_2}$(μ-CO), the $\mathrm{CH_2}$ protons occur at δ 2.78 and 2.33 (Lee, C. L.; James, B. R., unpublished data).

[35] Chang, C. K.; Traylor, T. G. *J. Am. Chem. Soc.* **1973**, *95*, 8475, 8477.

[36] The carbonylation of $\mathrm{Pd_2Cl_2(dpm)_2}$ was studied in dimethylacetamide solution,[3] but equilibrium data are similar in $\mathrm{CH_2Cl_2}$ (Lee, C. L.; James, B. R., unpublished data).

[37] Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. J. *J. Chem. Soc., Chem. Commun.* **1976**, 485.

activity of $Pd_2Cl_2(dpmMe)(dpm)$ (4), containing a single methyl group, toward CO can be rationalized similarly.

We note also that $Pd_2Cl_2(dpmMe)(dpm)$ reacts with H_2S to form the bridged sulfide complex and molecular H_2,[38] exactly analogous to the $Pd_2Cl_2(dpm)_2$ system;[39] however, as with CO, the $Pd_2Cl_2(dpmMe)_2$ complex is unreactive toward H_2S.

Conclusions

An improved synthetic procedure for 1,1-bis(diphenylphosphino)ethane (dpmMe) has been found, and some mono- and dinuclear palladium complexes of this ligand have been synthesized and characterized, as well as dinuclear species with mixed-ligand systems (dpm or Ph_2Ppy). Structures of $PdCl_2(dpmMe)$ (two independent molecules within the crystal lattice) are compared to those reported previously for the dpm, dpe, and dpp analogues; variations in Pd–P bond lengths correlate with displacement of the P atoms from the $PdCl_2$ plane and not, as suggested earlier, with steric constraints associated with the cis-bidentate ligands. The anti form of $Pd_2Cl_2(dpmMe)_2$ shows no reactivity in solution toward CO probably because an A-frame, bridged-carbonyl product would experience a steric problem associated with the presence of one of the methyl groups. The $Pd_2Cl_2(dpmMe)(dpm)$ complex does bind CO reversibly, but with lower overall affinity than $Pd_2Cl_2(dpm)_2$; the data suggest that the mixed-ligand species, modified by attachment to a support through the methyl substituent, should bind CO reversibly.

Acknowledgment. We thank the U.S. Department of Energy, Morgantown Energy Technology Center, and the Natural Sciences and Engineering Research Council of Canada for financial support and Johnson Matthey Ltd. for loan of the palladium. We are grateful also to one reviewer who provided helpful comments regarding the CO reactivity pattern.

Supplementary Material Available: Figures 1, 3, and 7 (^1H NMR spectra of 1, 2, and 5) and tables of bond lengths, bond angles, torsion angles, hydrogen coordinates, and anisotropic thermal parameters for 1 and 2 and C–H···Cl interactions for 1 (21 pages); listings of structure factors for 1 and 2 (64 pages). Ordering information is given on any current masthead page.

---

(38) Besenyei, G.; Lee, C. L.; James, B. R.; Nelson, D. A.; Lilga, M. A., to be submitted for publication.

(39) Lee, C. L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175.

Addition of the Os–CH_2 Bond in $Os_3(CO)_{11}(\mu\text{-}CH_2)$ to $Pt(PPh_3)_2$ To Give the Spiked Triangular Cluster $Os_3Pt(\mu\text{-}CH_2)(CO)_{11}(PPh_3)_2$. An NMR Investigation of the Fluxional Properties of $Os_3(CO)_{11}(\mu\text{-}CH_2)$

Gregory D. Williams, Marie-Chantal Lieszkovszky, Chad A. Mirkin, and Gregory L. Geoffroy*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received February 19, 1986

$Os_3(CO)_{11}(\mu\text{-}CH_2)$ (1) reacts with $(Ph_3P)_2Pt(C_2H_2)$ to give the new tetranuclear cluster $Os_3Pt(\mu\text{-}CH_2)(CO)_{11}(PPh_3)_2$ (2) in which the methylene ligand bridges an Os–Pt bond. Compound 2 has been characterized spectroscopically and by an X-ray diffraction study. It crystallizes in the space group $C2/c$ with $a = 39.18$ (2) Å, $b = 15.200$ (6) Å, $c = 18.532$ (7) Å, $\beta = 91.17$ (3)°, $V = 11034$ (8) Å^3, and $Z = 8$. The structure has been refined for the 3258 reflections with $F_o > 5\sigma(F_o)$ to R and R_{wF} values of 0.0557 and 0.0624. The cluster has a "spiked triangular" geometry with the Pt atom bonded to only one Os of the Os_3 triangle. The methylene ligand bridges the Os–Pt bond, and the Pt is further coordinated by two PPh_3 ligands. Compound 2 readily and reversibly exchanges CO for PPh_3 at the Pt center. Magnetization-transfer experiments (^1H, ^{13}C) have shown that the inequivalent methylene hydrogens in the parent cluster 1 undergo slow exchange, but the spectral evidence does not imply the intermediacy of a terminal Os=CH_2, in contrast to the recently reported fluxional properties of $Ru_3(CO)_{11}(\mu\text{-}CH_2)$.

The methylene-bridged cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (1)[1] has proven to be unusually reactive. Even though it is coordinatively saturated, it readily reacts with CO,[2a] SO_2,[2b] $SnCl_2$,[2c] N_3^-, NO_2^-, Cl^-, Br^-, and I^-[2d] under mild conditions to give a variety of new products. We have been interested

---

(1) (a) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559–2564. (b) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975–6977. (c) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* **1982**, *231*, C65–C67. (d) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 364–365.

(2) (a) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783–4789. (b) Morrison, E. D. Ph.D. Thesis, The Pennsylvania State University, 1985. (c) Viswanathan, N.; Morrison, E. D.; Geoffroy, G. L.; Gieb, S. J.; Rheingold, A. L., *Inorg. Chem.*, submitted for publication. (d) Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1985**, *4*, 1413–1418.

0276-7333/86/2305-2228$01.50/0