the relative binding constants for the various cations with SDS. The order thus obtained for $1/K$ is $Mg^{2+} > TEA^+ > Na^+ > Li^+ > NH_4^+$. This order seems reasonable and appears to follow a decreasing charge/size ratio except for the organic cation, TEA^+. It is probable that the latter ion has additional bonding capabilities for the micelle and it would not be unreasonable to propose that much of the binding of TEA^+ to the micelle occurs as the result of both electrostatic attraction to the head groups and hydrophobic interactions with the micelle interior. In the series studied it seems clear that, due to its relative hydrophobicity, this ion is the only one which would be effective in reducing the high surface potentials associated with these interfaces. Looking at the overall series from a slightly different perspective the order obtained correlates well, except for NH_4^+, with the lyotropic series developed for SDS by Larsen and Magid[20] for quite different phenomena. Thus the effect of electrolytes on the binding equilibria appears to be relatively well-defined.

The source of the variation of the intramicellar quenching constants (Table III) with change in electrolyte appears to be less clear. Certainly the deviations observed are well outside of experimental error, but the overall differences are much smaller than those observed for the binding constants. It is reasonable that the term γ from eq 15 is unlikely to be affected by changes in the electrolyte, thus it appears that the variations in k_q must be due to changes in the rate of diffusion in the micellar pseudophase. In attempting to evaluate these values a difficulty is that it is impossible to measure k_{diff} in the micelles in the absence of added electrolyte.

Generally, adding electrolyte increases the diffusional collision rate between two ions of like charge. Making this assumption, the predicted rate of diffusion in the absence of electrolyte should be lower than the slowest rate observed, 4.8×10^7 M^{-1} s^{-1}. Thus, the greatest effect here is produced by TEA^+. The results could be interpreted as indicating that this ion affects the intramicellar diffusion of DMV^{2+} the most, while all the other ions studied have much smaller effects, paralleling the differences in the relative association of the added electrolytes with the micelles. An alternative explanation would be that TEA^+ produces an effective acceleration of k_{diff} by reducing trapping sites at the hydrocarbon-water interface such that the DMV^{2+} is much more mobile in the surface region. In any event, it is clear that the effect of the other cations, though clearly real, is relatively small and not easily interpretable in terms of previously observed phenomena. These results emphasize the caution that must be used in extrapolating reactions in homogeneous solutions to micelles or micelle-water interfaces for evaluation of physical properties of the micelle such as the micropolarity or microviscosity.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. GM15238) for support of this research.

Organo Halide Addition to $Pd_2(Ph_2PCH_2PPh_2)_3$. Preparation of Novel Methylene- and Phenylene-Bridged Complexes by Two-Center, Three-Fragment Oxidative Addition

Alan L. Balch,* Catherine T. Hunt, Chung-Li Lee, Marilyn M. Olmstead, and James P. Farr

Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received November 6, 1980*

Abstract: Dihalomethanes react with $Pd_2(dpm)_3$ (dpm = bis(diphenylphosphino)methane) to form $Pd_2(dpm)_2(\mu\text{-}CHR)X_2$ (X = I, Br, Cl; R = H, CH_3). $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$ undergoes substitution to form $Pd_2(dpm)_2(\mu\text{-}CH_2)L_2^{2+}$ (L = pyridine, methyl isocyanide). The Pd-C (methylene) bond resists insertion of carbon monoxide, isocyanides, or sulfur dioxide. Reaction of $Pd_2(dpm)_3$ with 1,2-diiodobenzene yields $Pd_2(dpm)_2(\mu\text{-}C_6H_4)I_2$. Addition of phenyl isocyanide dichloride to $Pd_2(dpm)_3$ yields $Pd_2(dpm)_2(\mu\text{-}CNPh)Cl_2$ while a corresponding reaction involving oxalyl chloride produces $Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$. Addition of methyl halide to $Pd_2(dpm)_3$ produces $Pd_2(dpm)_2(CH_3)_2X_2$ (X = Br, I) which exist as the molecular A-frame $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]^+X^-$ in solution. Protonation of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$ with fluoroboric acid yields brown, crystalline $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$ in which a bridging methylene has been converted into a terminal methyl group. Dynamic aspects of the structure of $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]^+$ and $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]^+$ are described.

The oxidative addition reaction represents a fundamental transformation of organometallic chemistry.[1] While oxidative addition reactions of mononuclear complexes have received considerable study, comparable studies on binuclear transition-metal complexes have only recently begun to appear. From this limited number of studies, the transannular oxidative addition summarized by eq 1 has emerged as a common type of reaction for ligand-

$$X{-}Y + M^nM^n \rightarrow X{-}M^{n+1}{-}M^{n+1}{-}Y \qquad (1)$$

bridged, binuclear complexes. This reaction results in a formal, one-electron oxidation of each metal and in the creation of a metal-metal single bond. Examples of this type of reaction include the addition of halogens to $Rh_2(dpm)_2(CO)_2Cl_2$ (dpm = bis(diphenylphosphino)methane),[2] $Rh_2(dpm)_2(CNR)_4^{2+}$,[2,3] $Rh_2[CN(CH_2)_3NC]_4^{2+}$,[4] $Pd_2(dpm)_3$,[5] and $Au_2[(CH_2)_2P(CH_3)_2]_2$,[6] the addition of methyl halides to $Rh_2[CN(CH_2)_3NC]_4^+$,[4] and $Au_2[(CH_2)_2P(CH_3)_2]_2$,[6] and the addition of dihydrogen to $Ir_2(t\text{-}BuS)_2(CO)_4$.[7]

The study reported here involves the addition of organic halides to the binuclear palladium(0) complex $Pd_2(dpm)_3$.[8] Transannular oxidative additions to give palladium(I) dimers do not occur. Rather, oxidative addition results in the formation of palladium(II) complexes. With organic dihalides this reaction results in the

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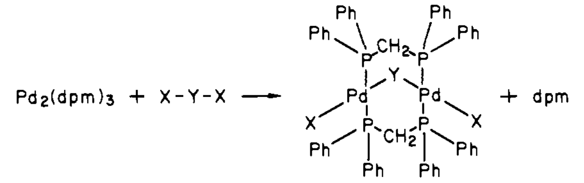
formation of a molecular A-frame[9,10] via the two-center, three-fragment addition shown in eq 2. In this fashion, novel methylene-



(2)

and phenylene-bridged molecules can be formed. Previous routes to other related A-frame complexes have involved either the insertion of small molecules into metal–metal bonds[10] or the nucleophilic attack on preformed binuclear complexes.[9,13]

Experimental Section

Preparation of Compounds. $Pd_2(dpm)_3$[8] and 1,1-diiodoethane[14] were prepared by known routes. All reactions involving $Pd_2(dpm)_3$ were performed in oxygen-free solutions under an atmosphere of purified nitrogen. All of the products, however, are air stable and can be conveniently handled without protection from the atmosphere.

$Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$. Diiodomethane (0.5 mL) was added to a solution of 0.225 g (0.164 mmol) of $Pd_2(dpm)_3$ in 15 mL of dichloromethane. After being left standing for 45 min, the red solution was filtered. Dropwise addition of ethyl ether caused the product to precipitate as bright yellow crystals. These were collected by filtration and recrystallized from dichloromethane/ether. The yield of the yellow crystalline solid was 0.14 g (68%). Anal. Calcd for $C_{51}H_{46}I_2P_4Pd_2$: C, 49.03; H, 3.71; P, 9.92; I, 20.031. Found: C, 48.70; H, 3.78; P, 9.73; I, 19.88.

$Pd_2(dpm)_2(\mu\text{-}CHCH_3)I_2\cdot CH_2Cl_2$. This complex was prepared from 1,1-diiodoethane and $Pd_2(dpm)_3$ by the method used for the preparation of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$. The orange-brown product was recrystallized from dichloromethane/ethanol. ^1H NMR spectroscopy confirmed the presence of dichloromethane in the crystalline product. Anal. Calcd for $C_{53}H_{50}Cl_2I_2P_4Pd_2$: C, 47.55; H, 3.99. Found: C, 47.72; H, 3.91.

$Pd_2(dpm)_2(\mu\text{-}CH_2)Br_2$. This complex was prepared from dibromomethane and $Pd_2(dpm)_3$ by using the route described for the preparation of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$. Anal. Calcd for $C_{51}H_{46}Br_2P_4Pd_2$: C, 53.02; H, 4.01. Found: C, 53.48; H, 4.19.

$[Pd_2(dpm)_2(\mu\text{-}CH_2)(CNCH_3)_2][PF_6]_2$. Methyl isocyanide was added dropwise to a stirred suspension of 100 mg (0.080 mmol) of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$ in 5 mL of methanol until all of the solid had dissolved. The very pale yellow solution was filtered. A saturated methanolic solution of ammonium hexafluorophosphate was added dropwise to the filtrate to precipitate the product. The white crystalline product was collected and washed with methanol and ether. Purification was accomplished by dissolving the product in 5 mL of acetone, filtering the solution, and precipitating the product by adding ethyl ether; yield 96 mg (88%). Anal. Calcd for $C_{55}H_{52}F_{12}N_2P_6Pd_2$: C, 48.30; H, 3.83. Found: C, 48.46; H, 3.96.

$[Pd_2(dpm)_2(\mu\text{-}CH_2)(C_5H_5N)_2][PF_6]_2$. A 100-mg sample was dissolved in 3 mL of warm pyridine. A saturated methanolic solution containing 0.4 g of ammonium hexafluorophosphate was added to the pyridine solution. Water was added dropwise to this light yellow solution to precipitate the white crystalline product. This was collected by filtration and washed with water and ethyl ether. The product may be recrystallized from acetone/ether or dichloromethane/ether. Anal. Calcd for $C_{61}H_{56}F_{12}N_2P_6Pd_2$: C, 50.75; H, 3.91; N, 1.94. Found: C, 50.88; H, 4.02; N, 2.03.

$Pd_2(dpm)_2(\mu\text{-}o\text{-}C_6H_4)I_2$. *o*-Diiodobenzene (724 mg, 2.220 mmol) in 5 mL of oxygen-free benzene was added dropwise over a period of 30 min to a refluxing solution of 300 mg (0.220 mmol) of $Pd_2(dpm)_3$ in 15 mL of benzene. The resulting mixture was heated under reflux for an additional 90 min during which the color changed from red to orange. After the solution was cooled ethyl ether was added dropwise to precipitate the product. After the yellow-orange crystalline product was collected by filtration, it was purified by recrystallization from dichloromethane/ether; yield 227 mg (79%). Anal. Calcd for $C_{56}H_{48}I_2P_4Pd_2$: C, 51.36; H, 3.54; I, 19.38. Found: C, 51.39; H, 3.95; I, 18.82.

$[Pd_2(dpm)_2(\mu\text{-}o\text{-}C_6H_4)(CH_3NC)_2][PF_6]_2$. Methyl isocyanide was added dropwise to a suspension of 200 mg (0.152 mmol) of $Pd_2(dpm)_2(\mu\text{-}C_6H_4)I_2$ in 10 mL of methyl alcohol until dissolution was complete. The color of the solution turned from yellow to colorless when the reaction was completed. Addition of 52.2 mg (0.320 mmol) of NH_4PF_6 in 3 mL of methyl alcohol to the solution caused the product to precipitate as white crystals. These were collected by filtration and vacuum dried. The product was purified by recrystallization from dichloromethane/diethyl ether; yield 207 mg (95%). Anal. Calcd for $C_{60}H_{54}F_{12}N_2P_6Pd_2$: C, 50.41; H, 3.81; N, 1.96. Found: C, 50.36; H, 3.96; N, 1.95.

$Pd(PPh_3)_2(o\text{-}C_6H_4I)I$. Under an atmosphere of purified nitrogen 856 mg (2.59 mmol) of *o*-diiodobenzene in 5 mL of benzene was added dropwise over a period of 30 min to a refluxing solution of 300 mg (0.259 mmol) of $Pd(Ph_3P)_4$ in 10 mL of benzene. After the solution was further heated under reflux for an additional 90 min, the volume of the solution was reduced to 5 mL by the use of a rotary evaporator. Addition of ethyl ether to the solution caused the product to separate as pale yellow crystals. After the product was isolated by filtration, it was recrystallized two times from dichloromethane/ethyl ether; yield 235 mg (94%). Anal. Calcd for $C_{42}H_{34}I_2P_2Pd$: C, 52.50; H, 3.57; I, 26.41. Found: C, 52.62; H, 3.58; I, 26.44.

$Pd_2(dpm)_2(CH_3)_2I_2$. Methyl iodide (0.5 mL) was added to a solution of 209 mg (0.153 mmol) of $Pd_2(dpm)_3$ in 15 mL of dichloromethane. After being left standing for 1 h, the pale orange solution was filtered and ether was added to the filtrate to precipitate the product. After the product was collected by filtration, it was washed with ether and dissolved in dichloromethane. Reprecipitation by the slow addition of ether gave the product as fine dull yellow crystals; yield 0.180 g (93%). Anal. Calcd for $C_{52}H_{50}I_2P_4Pd_2$: C, 49.36; H, 3.98; I, 20.05. Found: C, 48.78; H, 4.02; I, 20.58.

$Pd_2(dpm)_2(CH_3)_2Br_2$. This compound was prepared from methyl bromide and $Pd_2(dpm)_3$ by the route used to prepare $Pd_2(dpm)_2(CH_3)_2I_2$. Anal. Calcd for $C_{52}H_{50}Br_2P_4Pd_2$: C, 53.31; H, 4.30; Br, 13.64. Found: C, 53.17; H, 4.48; Br, 14.29.

$[Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)_2][PF_6]\cdot{}^1/_2CH_2Cl_2$. A solution of 0.15 g (0.92 mmol) of ammonium hexafluorophosphate was added to a solution of 0.15 g (0.13 mmol) of $Pd_2(dpm)_2(CH_3)_2Br_2$ in 20 mL of methanol. The white, crystalline product which precipitated was collected by filtration and washed with methanol. It was purified by dissolving the solid in dichloromethane, filtering the solution, and reprecipitating the product by the gradual addition of ether; yield 0.138 g (87%). The presence of dichloromethane in the crystalline solid was verified by ^1H NMR spectroscopy. Anal. Calcd for $C_{52}H_{50}BrF_6P_5Pd_2\cdot{}^1/_2CH_2Cl_2$: C, 49.30; H, 4.02; P, 12.11. Found: C, 49.14; H, 4.13; P, 11.70.

$[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2][PF_6]\cdot{}^1/_2CH_2Cl_2$. This salt was prepared from $Pd_2(dpm)_2(CH_3)_2I_2$ by the route used to make $[Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)_2][PF_6]$. The presence of dichloromethane in the white crystalline product was verified by ^1H NMR spectroscopy. Anal. Calcd for $C_{52}H_{50}F_6IP_5Pd_2\cdot{}^1/_2CH_2Cl_2$: C, 47.54; H, 3.72. Found: C, 47.20; H, 3.96.

$[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$. A 1-mL sample of aqueous 40% fluoroboric acid was added to a solution of 100 mg (0.080 mmol) of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$ in 7 mL of dichloromethane. Sufficient methanol was added to the mixture to give a homogeneous solution. After filtration the yellow solution was allowed to stand in an open Erlenmeyer flask for 18 h. During this period, the solution turned brown, evaporated to about half its volume, and produced a brown crystalline solid. The solid was collected by filtration and washed with methanol. The brown product was purified by recrystallization from dichloromethane/ethyl ether; yield 76 mg (71%). Anal. Calcd for $C_{51}H_{47}BF_4I_2P_4Pd_2$: C, 45.81; H, 3.54; P, 9.27. Found: C, 45.25; H, 3.49; P, 8.99.

$Pd_2(dpm)_2(\mu\text{-}CNC_6H_5)Cl_2$. Phenyl isocyanide dichloride (1 mL) was added to a solution of 0.20 g (0.15 mmol) of $Pd_2(dpm)_3$ in 10 mL of dichloromethane. After filtration in a nitrogen atmosphere, the solution was allowed to stand for 1 h. During that period the solution first darkened and then lightened to orange. The yellow-orange crystalline solid which precipitated was collected by filtration and washed with dichloromethane, yield 0.085 g (49%). The product was identified by comparison with an authentic sample.[10]

$Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$. Oxalyl chloride (0.15 mL) was added to a solution of 0.23 g (0.17 mmol) of $Pd_2(dpm)_3$ in 10 mL of dichloromethane. Copious gas evolution ensued and an orange-red crystalline solid formed. This was collected by filtration and washed with dichloromethane and ether. The solid was identified as $Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$ by comparison of infrared and electronic spectra with those of authentic samples.[10]

Physical Measurements. ^1H (5-mm tubes, 200 MHz) and $^{31}P\{^1H\}$ (12-mm tubes, 81 MHz) NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer. An external 85% phosphoric

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Table I. Characteristic ^{1}H and ^{31}P{^{1}H} NMR Spectral Features of Palladium Complexes

	^{1}H^a (25 °C)					
	P-CH$_2$-P			methyl		
compd	δ	J(P-H), Hz	J(H-H), Hz	δ	J(P-H), Hz	^{31}P^b (25 °C) δ
$Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$	3.70 2.93	4.8 3.5	14.4			18.45
$Pd_2(dpm)_2(\mu\text{-}CH_2)Br_2$	3.60 2.85	4.6 3.6	14.4			16.60
$Pd_2(dpm)_2(\mu\text{-}CH_2)Cl_2$	3.52 2.84	4.7 3.4	14.4			
$Pd_2(dpm)_2(\mu\text{-}CHCH_3)I_2{}^c$	3.56, 3.47 3.13, 2.79	*c* *c*	*c* *c*			21.37, 25.64^d
$[Pd_2(dpm)_2(\mu\text{-}CH_2)(CNCH_3)_2][PF_6]_2{}^e$	4.53 4.04	5.2 4.1	14.8	2.92		26.4
$[Pd_2(dpm)_2(\mu\text{-}CH_2)(NC_5H_5)_2][PF_6]_2{}^e$	4.49 4.18	4.6 4.4	14.0			24.8
$Pd_2(dpm)_2(\mu\text{-}C_6H_4)I_2$	2.63 1.70	3.65 5.56	12.4			11.3^f
$[Pd_2(dpm)_2(\mu\text{-}C_6H_4)(CNCH_3)_2][PF_6]_2$	2.73 1.59	3.95 6.06	12.4	3.39		21.2^f
$Pd_2(dpm)_2(CH_3)_2I_2$	4.49	4.0		0.83 (q)	2.8	17.04
$Pd_2(dpm)_2(CH_3)_2Br_2$	4.11	4.11		0.71 (q)	2.7	17.66
$[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2][PF_6]$	4.68 4.43	5.5 3.45	13.8	0.92 (q)	2.7	
$[Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)_2][PF_6]$	4.39 3.95	5.5 3.6	13.8	0.81 (q)	2.7	17.41
$[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$	4.64	4.3		0.97 (t)	5.7	13.1, 3.1^g
$[Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)Br][BF_4]$	4.11	4.4		0.89 (t)	5.8	14.0, 9.5^h
$[Pd_2(dpm)_2(\mu\text{-}I)(C_2H_5)I][CF_3CO_2]$	4.61	4.24		−0.08^i (q) (2.13)^{i,j}	6.7 7.5	

[a] Run in CD_2Cl_2 unless otherwise noted; s = singlet, t = triplet, q = quintet. In all the A-frame complexes the P–CH$_2$–P protons are inequivalent and each appears as a doublet of quintets, unless otherwise indicated. [b] Run in 1:1 mixture of $CDCl_3/CHCl_3$ unless otherwise noted. All lines are singlets unless noted. [c] Due to complex splitting patterns, the J's cannot be determined. [d] $J(AA') = \pm 104.5$ Hz, $J(BB') = \pm 44.9$ Hz, $J(AB) = \pm 363.6$ Hz and $J(AB') = \pm 5.5$ Hz. [e] Run in acetone-d_6. [f] Run in CD_2Cl_2. [g] $J(AB) = J(AB') = 20.1$ Hz. [h] $J(AB) = J(AB') = 20.8$ Hz. [i] In the ethyl group, J(H–H) = 7.2. The -CH$_3$ appears as a quintet. [j] The -CH$_2$ in the ethyl group appears as a sextet.

Table II. ^{1}H NMR Characteristics of Bridging Ligands in A-Frame Complexes^a

compd	δ	J(PH), Hz	J(H-H), Hz
$Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$	2.45 (q)	7.0	
$Pd_2(dpm)_2(\mu\text{-}CH_2)Br_2$	1.86 (q)	7.4	
$Pd_2(dpm)_2(\mu\text{-}CH_2)Cl_2$	1.64 (q)	7.5	
$Pd_2(dpm)_2(\mu\text{-}CHCH_3)I_2$	4.29 (o) 1.20 (m)	13.0 *c*	7.0 *c*
$[Pd_2(dpm)_2(\mu\text{-}CH_2)(CNCH_3)_2][PF_6]_2{}^b$	2.43 (q)	7.8	
$[Pd_2(dpm)_2(\mu\text{-}CH_2)(NC_5H_5)_2][PF_6]_2{}^b$	2.50 (q)	8.5	
$Pd_2(dpm)_2(\mu\text{-}C_6H_4)I_2$	6.11 (qt) 5.56 (qt)		5.5, 3.5
$[Pd_2(dpm)_2(\mu\text{-}C_6H_4)(CNCH_3)_2][PF_6]_2$	6.15 (qt) 5.22 (qt)		5.4, 2.9

[a] Run in CD_2Cl_2 unless otherwise indicated; m = multiplet, o = octet, q = quintet, qt = quartet. [b] Run in acetone-d_6. [c] J cannot be determined.

acid reference was used for ^{31}P NMR spectra, and the high-frequency positive convention, recommended by IUPAC, is used in reporting chemical shifts. Simulations of the entire ^{31}P spectra were performed by using the noniterative simulation routine of the Nicolet software on a Model 1180 Nicolet data system. This simulation routine is a modified version of Laocoon III. The fit of the simulation was based on matching the individual peak positions and intensities of the observed and the calculated spectra.

Infrared spectra were recorded from Nujol mulls on a Perkin-Elmer 180 infrared spectrometer. Electrical conductivities were determined by use of an Industrial Instruments conductivity bridge with 10^{-3} M solutions. Electronic spectra were recorded on a Cary 17 spectrometer.

Results

Addition of Geminal Dihalides to $Pd_2(dpm)_3$. Addition of diiodomethane or dibromomethane to $Pd_2(dpm)_3$ in dichloromethane solution at room temperature yields yellow crystalline **1** and **2** in good yield after a reaction time of 30 min. The reaction between $Pd_2(dpm)_3$ and dichloromethane is sufficiently slow so that dichloromethane can be used as a solvent for these reactions. However, small quantities of **3** have been detected after solutions of $Pd_2(dpm)_3$ in dichloromethane were allowed to stand for 6 h. Both **1** and **2** form air-stable solids which dissolve readily in dichloromethane and chloroform but otherwise have poor solubility in common organic solvents. In solution they behave as air-stable non-electrolytes. The infrared spectra of these methylene-bridged

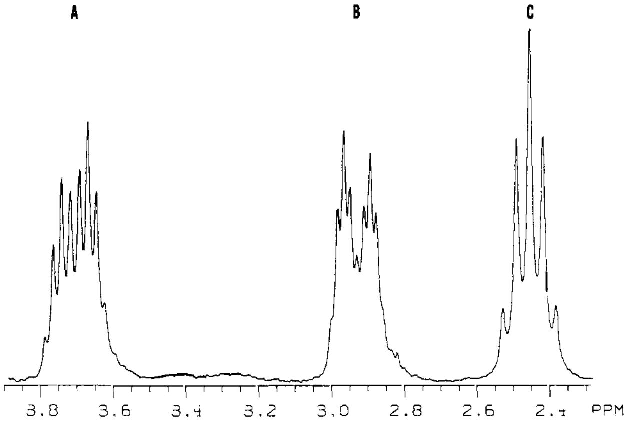
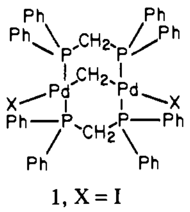


Figure 1. The methylene region of the 200-MHz ^{1}H NMR spectrum of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$ in dichloromethane-d_2. A and B are the methylene protons of dpm, and C denotes the protons of the Pd-CH$_2$-Pd unit.



1, X = I
2, X = Br
3, X = Cl

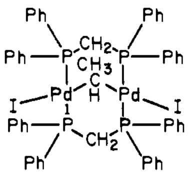
Table III. Electronic Spectral Data for New Compounds

compd	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}) at 25 °C[a]
$Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$	400 (10 700), 348 (8800)
$Pd_2(dpm)_2(\mu\text{-}CHCH_3)I_2$	428 (10 800), 363 (7400)
$Pd_2dpm_2(CH_3)_2Br_2$	325 (4 100), 288 (17 000) 255 (39 800), 232 (49 800)
$Pd_2dpm_2(CH_3)_2I_2$	330 (4020), 290 (12 000) 262 (37 800), 238 (53 400)
$[Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)_2]PF_6$	320 (4690), 288 (18 100) 255 (40 800), 230 (52 600)
$[Pd_2dpm_2(\mu\text{-}I)(CH_3)_2]PF_6$	400 (439), 340 (4610) 264 (43 000), 233 (55 400)
$[Pd_2dpm_2(\mu\text{-}I)I(CH_3)]BF_4$	498 (1510), 410 (4180) 337 (13 400), 263 (39 100), 237 (50 000)

[a] In dichloromethane solution.

complexes are dominated by absorptions due to the dpm ligands. For **2** the Pd–Br stretch occurs at 196 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra show simple singlets. These and other NMR characteristics are presented in Table I. The ^1H NMR spectral data for these and other new molecules are presented in Table I, which contains data on the phosphine methylene protons, and Table II, which contains information about the bridging methylene ligands. Figure 1 shows the 200-MHz ^1H NMR spectrum of the methylene region for **1**. The phenyl regions of these new compounds are generally uninformative and therefore are not shown. The protons of the $Pd–CH_2–Pd$ group appear as a 1:4:6:4:1 quintet due to coupling of the C–H protons to the four equivalent palladium-bound phosphorus atoms. Due to the A-frame structure, the two methylene protons of each dpm ligand are inequivalent so that they appear as a basic AB quartet. Each line of this quartet is further split into a 1:4:6:4:1 quintet due to coupling to the phosphorus atoms. Because of virtual coupling of the trans phosphines the four phosphorus atoms appear equivalent. These features have been observed for other molecular A-frames.[12] Electronic spectra for these and other new complexes are summarized in Table III.

Addition of 1,1-diiodoethane to $Pd_2(dpm)_3$ yields **4** as orange-brown crystals. Its stability and solubility are similar to those of **1**. The $^{31}P\{^1H\}$ NMR spectrum is shown in Figure 2 along with a computed simulation based on analysis as an AA′BB′ spin system. The observation of a large AB(P–P) coupling constant of 364 Hz is wholly consistent with structure **4** which makes the trans phosphorus atoms inequivalent. The ^1H NMR spectrum of this complex is also completely in accord with structure **4**. Each of the four dpm methylene protons appears as a distinct multiplet showing coupling to the other proton on its carbon in addition to coupling to the four phosphorus atoms. The methyl group of the bridging methylmethylene appears as a multiplet with coupling to the C–H protons and to the four phosphorus atoms. The C–H proton likewise is coupled to the four phosphorus atoms and the protons of the attached methyl group. Although there are two chemically inequivalent phosphorus atoms in **4**, the difference in the proton–phosphorus coupling constants to the two types of phosphorus has not been resolved.



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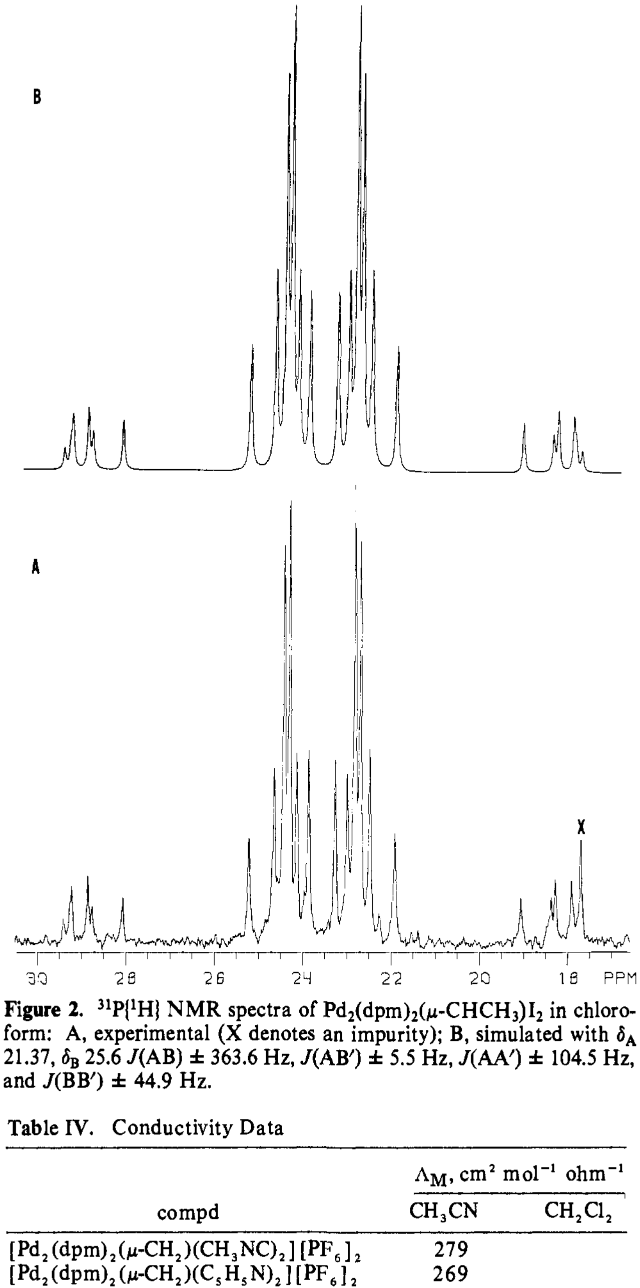


Figure 2. $^{31}P\{^1H\}$ NMR spectra of $Pd_2(dpm)_2(\mu\text{-}CHCH_3)I_2$ in chloroform: A, experimental (X denotes an impurity); B, simulated with δ_A 21.37, δ_B 25.6 $J(AB)$ ± 363.6 Hz, $J(AB')$ ± 5.5 Hz, $J(AA')$ ± 104.5 Hz, and $J(BB')$ ± 44.9 Hz.

Table IV. Conductivity Data

compd	Λ_M, cm^2 mol^{-1} ohm^{-1}	
	CH_3CN	CH_2Cl_2
$[Pd_2(dpm)_2(\mu\text{-}CH_2)(CH_3NC)_2][PF_6]_2$	279	
$[Pd_2(dpm)_2(\mu\text{-}CH_2)(C_5H_5N)_2][PF_6]_2$	269	
$[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2][PF_6]$	103	
$[Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)_2][PF_6]$	114	62
$[Pd_2(dpm)_2(\mu\text{-}I)I(CH_3)][BF_4]$	126	59
$Pd_2(dpm)_2(CH_3)_2I_2$		53
$Pd_2(dpm)_2(CH_3)_2Br_2$		57

The reaction chemistry of these methylene-bridged complexes indicates that substitution of the terminal halides is a facile process. Compound **1** dissolves in pyridine to form the cation $Pd_2(dpm)_2(\mu\text{-}CH_2)(NC_5H_5)_2^{2+}$ which has been isolated as the hexafluorophosphate salt $[Pd_2(dpm)_2(\mu\text{-}CH_2)(NC_5H_5)_2][PF_6]_2$ (**5**). The conductivity data for this salt and other salts are presented in Table IV. It indicates that **5** is a 1:2 electrolyte. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet due to the cation in addition to the septet due to the hexafluorophosphate ion. The methylene region of the ^1H NMR spectrum is similar to those of **1**, **2**, and **3**. Addition of methyl isocyanide to **1**, followed by precipitation with ammonium hexafluorophosphate, yields $[Pd_2(dpm)_2(\mu\text{-}CH_2)(CNCH_3)_2][PF_6]_2$ (**6**). The infrared spectrum of **6** shows a terminal isocyanide stretching vibration at 2217 cm^{-1}. The conductivity and nuclear magnetic resonance features of **6** are similar to those of **5** except for the addition of isocyanide methyl group protons in the ^1H NMR spectrum of **6**. The data clearly show that the isocyanide ligands have substituted for the terminal iodide ligands.

Insertion of small molecules into the Pd–C bonds has not been observed. There is no evidence for insertion of the isocyanide into the Pd–C bonds. Attempts to insert carbon monoxide or sulfur dioxide into the Pd–C bonds of **1** and **2** have been unsuccessful. Storing a solution of **1** in dichloromethane for 2 days under 4 atm of carbon monoxide yields only starting material after precipitation

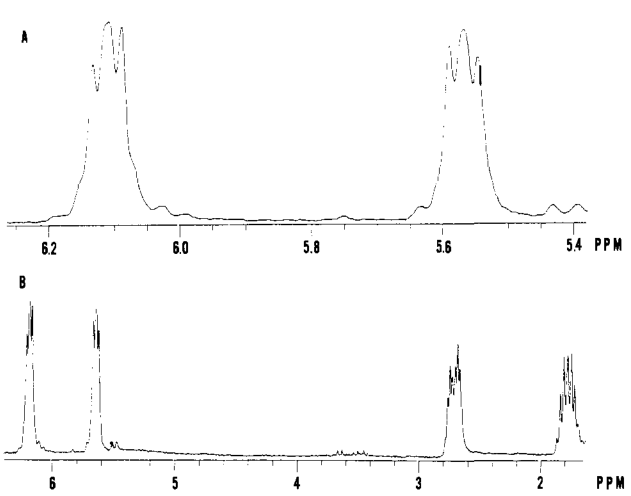
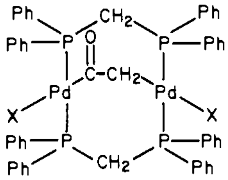


Figure 3. ^1H NMR spectrum of $Pd_2(dpm)_2(\mu\text{-}C_6H_4)I_2$ in dichloromethane-d_2. A represents the expanded phenylene region, and B shows both the phenylene and methylene protons.

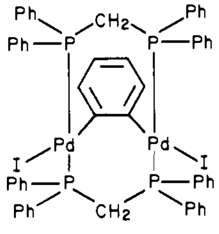
of the complexes present by the addition of ether. Thus under these relatively mild conditions, the insertion product **7** does not form.



7 (hypothetical)

Other routes to **7** have also been explored without success. Ketene does not react with $Pd_2(dpm)_2X_2$ (X = Br, I) in dichloromethane solution at 25 °C, while bromoacetyl bromide produces only a mixture of $Pd(dpm)Br_2$ and $Pd_2(dpm)_2Br_2$ and no trace of **7**. Complex **1** has been dissolved in liquid sulfur dioxide and held in a sealed tube at room temperature for 4 h. Evaporation of the sulfur dioxide resulted in the recovery of unreacted **1**.

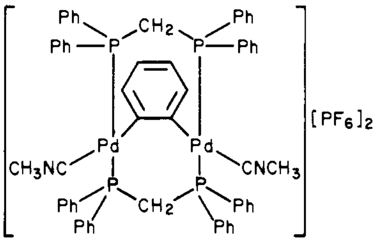
Addition of 1,2-Diiodobenzene. When 1,2-diiodobenzene is added to a refluxing benzene solution of $Pd_2(dpm)_3$, the phenylene-bridged A-frame **8** forms in 79% yield. It is soluble in dichloromethane and chloroform to form air-stable nonconducting solutions.



8

The infrared spectrum shows a band due to the phenylene ligand at 1547 cm^{-1}. The $^{31}P\{^1H\}$ spectrum is a singlet. The ^1H NMR spectrum shows the pattern indicative of an A-frame structure for the methylene protons of the dpm ligands and a fairly well-resolved AA′BB′ multiplet due to the phenylene protons as shown in Figure 3. The phenylene multiplet appears upfield of the phenyl protons. The upfield shift of these protons may result from ring current effects due to a stacking and interweaving of the phenylene groups between phenyl groups of the phosphine ligands. A similar upfield shift of the phenyl protons of the isocyanide ligand in $Mn_2(dpm)_2(CO)_4(\mu\text{-}p\text{-}CNC_6H_4CH_3)$ has been observed,[15] and the stacking of two phenyl rings about the isocyanide ligand has been confirmed by the X-ray structural study.[16]

Treatment of **8** with methyl isocyanide in methanol followed by precipitation with ammonium hexafluorophosphate results in the replacement of the iodo ligands by methyl isocyanide ligands and the formation of **9**. The presence of infrared vibrations at 2282 and 2264 cm^{-1} indicate that the complex contains terminal isocyanides.

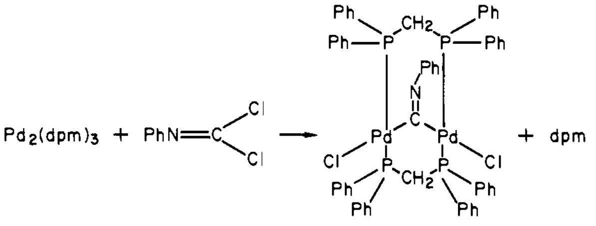


9

The absence of any other new infrared absorptions in the region 2100–1500 ensures then no insertion of isocyanide into the Pd–C bonds has occurred.

The possibility of obtaining a bridging phenylene ligand from a mononuclear palladium complex has been briefly examined without success. The reaction of the Pd(0) complex $Pd(PPh_3)_4$ with 1,2-diiodobenzene yields only a mononuclear complex *trans*-$(Ph_3P)_2Pd(o\text{-}C_6H_4I)I$.

Addition of Other Dihalides. Reaction of $Pd_2(dpm)_3$ with phenyl isocyanide dihalide yields the bridging isocyanide complex **10** via eq 3. This complex has previously been prepared by the insertion of phenyl isocyanide into the Pd–Pd bond of $Pd_2(dpm)_2Cl_2$.[10]



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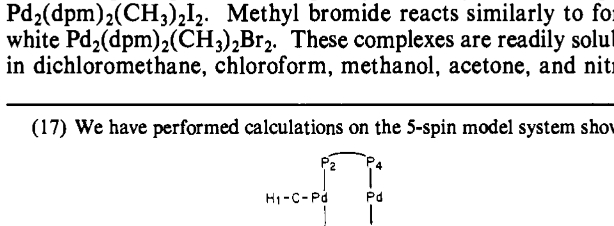
10

Similarly the addition of oxalyl chloride to $Pd_2(dpm)_3$ produces $Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$ via reaction 4. The carbonyl adduct has also been prepared via the addition of carbon monoxide to $Pd_2(dpm)_2Cl_2$.[10]



(4)

Addition of Alkyl Halides. The reaction between methyl iodide and $Ph_2(dpm)_3$ produces the pale yellow, crystalline complex $Pd_2(dpm)_2(CH_3)_2I_2$. Methyl bromide reacts similarly to form white $Pd_2(dpm)_2(CH_3)_2Br_2$. These complexes are readily soluble in dichloromethane, chloroform, methanol, acetone, and nitro-

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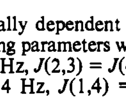
[15] Balch, A. L.; Benner, L. S. *J. Organomet. Chem.* **1977**, *135*, 339–343.

[16] Benner, L. S.; Olmstead, M. M.; Balch, A. L. *Organomet. Chem.* **1978**, *159*, 289–298.

[17] We have performed calculations on the 5-spin model system shown.



The proton spectrum is critically dependent on the chemical shifts of the phosphorus atoms. The following parameters were used to simulate the proton spectrum: $J(1,2) = J(1,3) = 5$ Hz, $J(2,3) = J(4,5) = 300$ Hz, $J(2,4) = J(3,5) = 30$ Hz, $J(2,5) = J(3,4) = 4$ Hz, $J(1,4) = J(1,5) = 0$. When all four phosphorus atoms were given the same chemical shift, the ^1H NMR spectrum appeared as a 1:4:6:4:1 quintet although no direct coupling between H_1 and P_4 or P_5 was introduced. When the chemical shifts of P_2 and P_3 differed from the chemical shifts of P_4 and P_5 by 1 ppm or more, the ^1H NMR spectrum appeared as a 1:2:1 triplet.

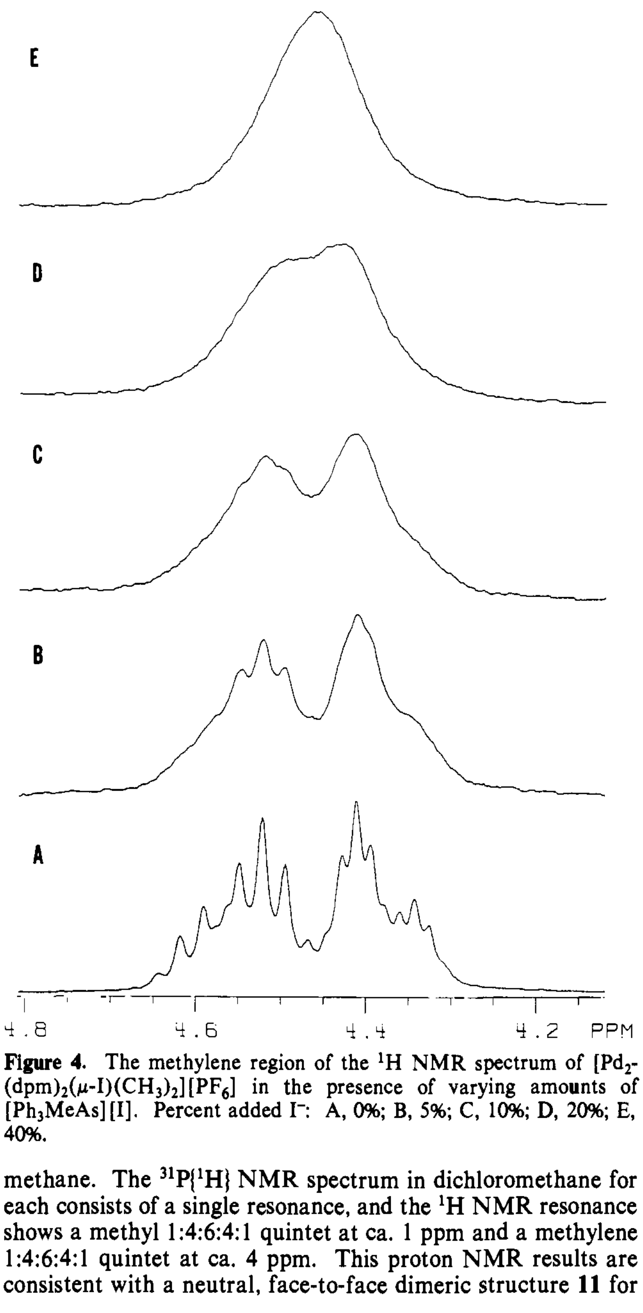
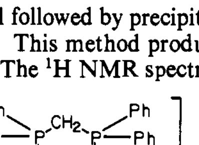


Figure 4. The methylene region of the ^1H NMR spectrum of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2][PF_6]$ in the presence of varying amounts of $[Ph_3MeAs][I]$. Percent added I^-: A, 0%; B, 5%; C, 10%; D, 20%; E, 40%.

methane. The $^{31}P\{^1H\}$ NMR spectrum in dichloromethane for each consists of a single resonance, and the ^1H NMR resonance shows a methyl 1:4:6:4:1 quintet at ca. 1 ppm and a methylene 1:4:6:4:1 quintet at ca. 4 ppm. This proton NMR results are consistent with a neutral, face-to-face dimeric structure **11** for $Pd_2(dpm)_2(CH_3)_2X_2$. In such a structure, all of the methylene protons are equivalent, as are the methyl protons and the phosphorus atoms. However, conductivity measurements indicate that $Pd_2(dpm)_2(CH_3)_2X_2$ behaves as a 1:1 electrolyte in solution (Table IV). The cation involved has been isolated by dissolving these complexes in methanol followed by precipitation with ammonium hexafluorophosphate. This method produces white salts which possess structure **12**. The ^1H NMR spectra clearly indicate that an A-frame structure is present in these salts. The phosphine methylene protons appear as the characteristic AB quartet with superimposed P–H coupling. This portion of the ^1H NMR spectrum is shown in Figure 4, trace A. The other spectral features and the conductivity of the salt are in accord with structure **12**.



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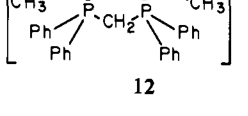


12

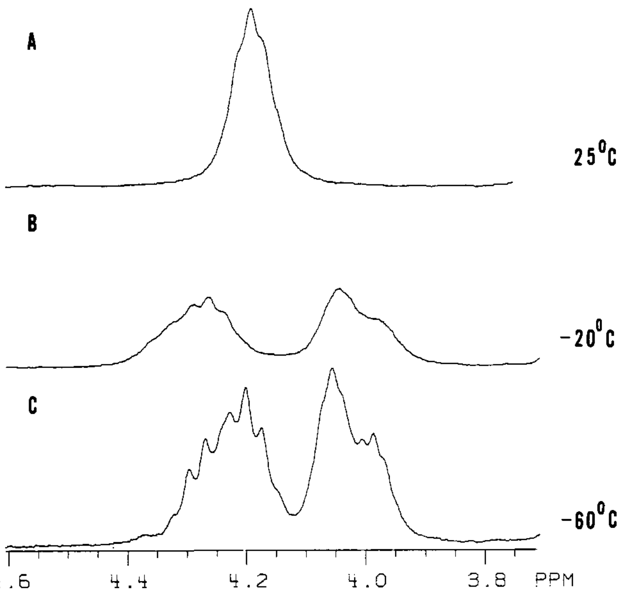
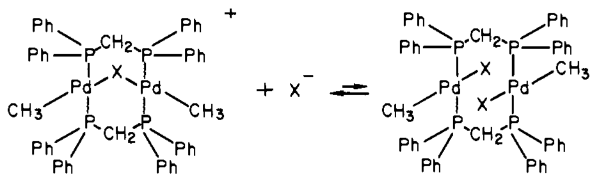


Figure 5. The 200-MHz, ^1H NMR spectrum of the methylene region of $Pd_2(dpm)_2(CH_3)_2Br_2$ in CD_2Cl_2 as a function of temperature: A, 25 °C shows that the dpm protons are equivalent; B, –20 °C begins to freeze out the A-frame structure; C, –60 °C shows the $[Pd_2dpm_2(\mu\text{-}Br)CH_3]^+$ cation.

It appears that solutions of $Pd_2(dpm)_2(CH_3)_2X_2$ also contain the cation of **12**. However a dynamic process, which we believe is the equilibrium in eq 5, renders the protons within each methylene group equivalent. The data shown in Figure 4 support the idea that an associative process between $Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2^+$ and halide ion causes the dpm methylene protons to become equivalent. As can be seen in the figure, addition of increasing quantities of halide ion to a solution of $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2][PF_6]$ causes the methylene resonances to broaden and eventually coalesce into a 1:4:6:4:1 quintet. The spectra indicate that the rate depends on the concentration of halide ion and that less than a stoichiometric amount of halide is enough to cause coalescence. The temperature dependence of the ^1H NMR spectrum of $Pd_2(dpm)_2(CH_3)_2Br_2$, shown in Figure 5, is also consistent with the rapid occurrence of reaction 5. The similarity of the electronic spectra of $Pd_2(dpm)_2(CH_3)_2X_2$ and $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2][PF_6]$ in dichloromethane also indicates that both compounds dissolve to give the same cation in solution. Although these results indicate that $Pd_2(dpm)_2(CH_3)_2X_2$ exists as the salt $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2][X]$ in solution, it is not certain at this point whether the solid state exists as the salt or the molecular form **11**.



(5)

These methyl complexes show good thermal and air stability. As solids both $Pd_2(dpm)_2(CH_3)_2X_2$ and $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]PF_6$ are air stable although the iodide-containing complexes do decompose after several days exposure to the atmosphere. The iodide complexes are also light sensitive. Solutions of these complexes can be handled in air for periods of 1–2 h with little sign of decomposition. No doubt the distance between the two methyl groups contributes to their resistance to reductive elimination.

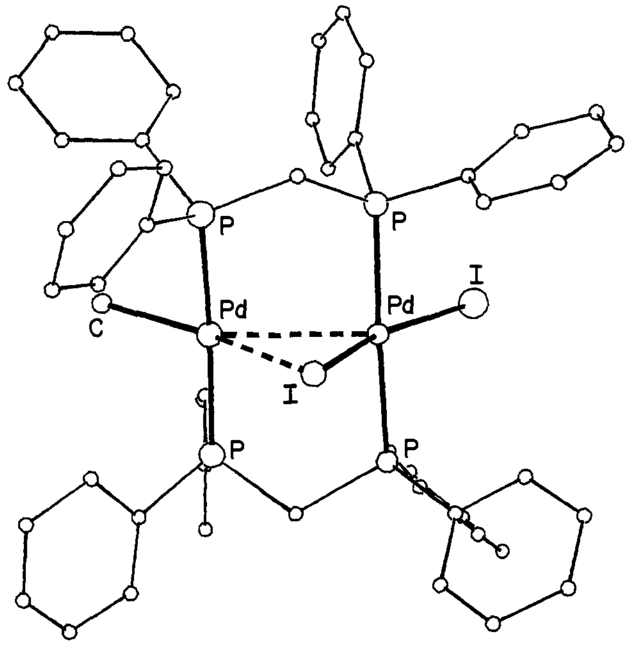
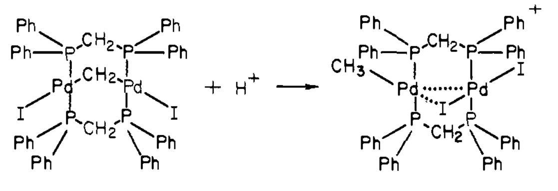


Figure 6. Perspective drawing of the cation in $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$.

Protonation of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$. Treatment of **1** with trifluoroacetic acid or fluoroboric acid converts it into the cation **13** via eq 6. Protonation with trifluoroacetic acid in dichloromethane solution, as monitored by NMR, requires about 1 h. The synthetic procedure which involves protonation with aqueous fluoroboric acid in a methanol/dichloromethane mixture and uses partial evaporation to isolate the brown crystalline fluoroborate salt requires at least 12 h to produce a respectable yield. In both reactions an excess of acid is employed, and the product **13** appears to have considerable stability toward acid.



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The structure of **13** has been confirmed by an X-ray crystal structure of $[Pd_2(dpm)_2(\mu\text{-}I)I(CH_3)]BF_4$.[18] A perspective drawing of the cation is shown in Figure 6. The basic structure is that of a molecular A-frame. However the Pd···Pd distance of 2.976 (6) Å is intermediate between that found for dimers such as $Pd_2(dpm)_2Br_2$ with a direct Pd–Pd bond and a Pd–Pd distance of about 2.7 Å and for A-frames which lack a direct Pd–Pd bond and exhibit Pd···Pd separations in the range 3.2–3.5 Å. The Pd···Pd separation in **13** is indicative of a stronger Pd–Pd interaction in this complex than in other previously characterized palladium A-frames.[19-22] This is further indicated in other properties of the cation.

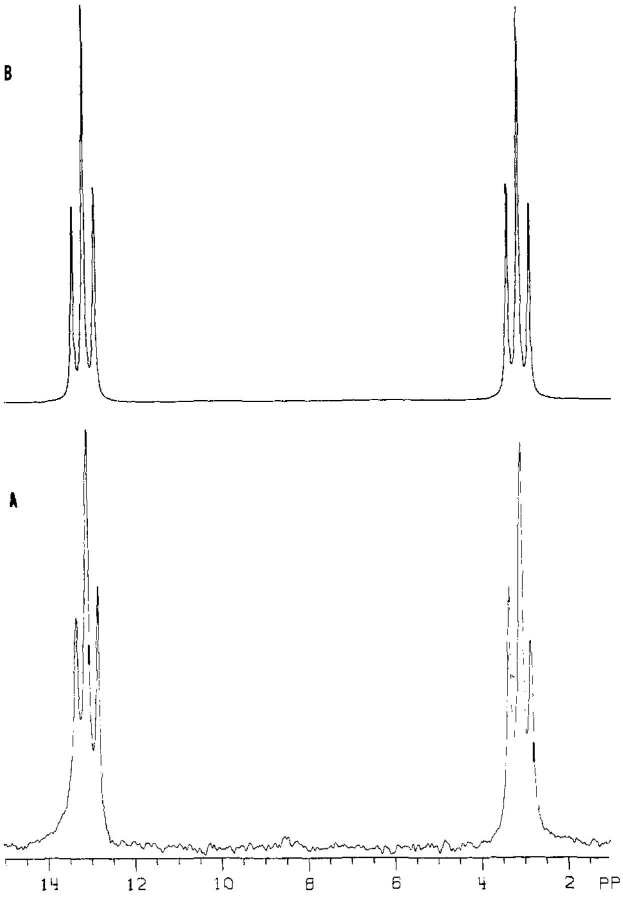

Figure 7. The $^{31}P\{^1H\}$ NMR spectra of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$: A, experimental; B, simulated.

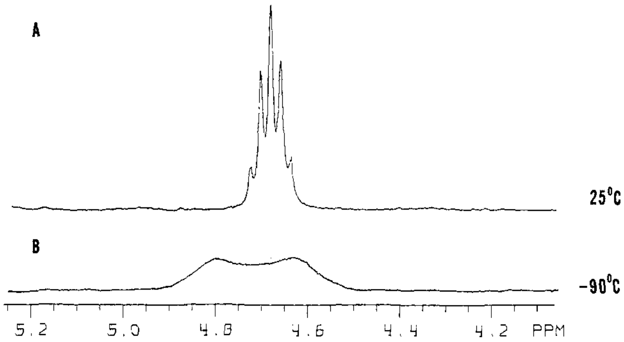

Figure 8. The methylene region of the 200-MHz ^1H NMR spectra of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$ at 25 and −90 °C in dichloromethane-d_2.

The $^{31}P\{^1H\}$ NMR spectrum of the cation is shown in 7. The spectrum has been analyzed as an AA′BB′ spin system, and the simulation is also shown in Figure 7. The magnitude of the AB and AB′ coupling constants indicate that the chemically dissimilar phosphorus atoms are not trans to one another. The ^1H NMR spectrum of **13** is temperature dependent. At room temperature, the methyl group appears as a 1:2:1 triplet[17] due to coupling of the methyl protons to the two adjacent phosphorus atoms. The methylene protons appear as a single 1:4:6:4:1 quintet. The magnitude of the proton coupling to the two different phosphorus

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[18] Olmstead, M. M.; Farr, J. P.; Balch, A. L., *Inorg. Chim. Acta*, in press.

[19] Balch, A. L. *Adv. Chem. Ser.*, in press.

[20] We propose the following electron-counting scheme for **13**. Each palladium atom is considered as d^8 Pd(II). The palladium on the right achieves a 16-electron count by accepting two electrons from each of the two phosphorus donors and each of the two iodide ligands. The methyl-bound palladium achieves a 14-electron count via accepting two electrons from the methyl group and four electrons from the two phosphine ligands. This palladium can increase its electron count to 16 by either accepting two more electrons from the bridging iodide ligand or by accepting two electrons from the other palladium (a dative Pd–Pd bond). Alternately, this palladium achieves an 18-electron count if both the iodide and the other palladium act as two electron donors toward it.

[21] A full dative Pd–Pd bond and the absence of Pd–I (bridging) bonding for the left side palladium in **13** should cause a shortening of the Pd–Pd distance and lengthening of the Pd–I (bridging) distance. For example consider the structure of the related $Pt_2(dpm)_2(CH_3)_3^+$. This cation lacks the bridging halide ligands of **13** and exhibits a Pt–Pt distance of 2.769 (1) Å, a value consistent with a dative Pt–Pt single bond.

[22] Frew, A. A.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1980**, 624–625.

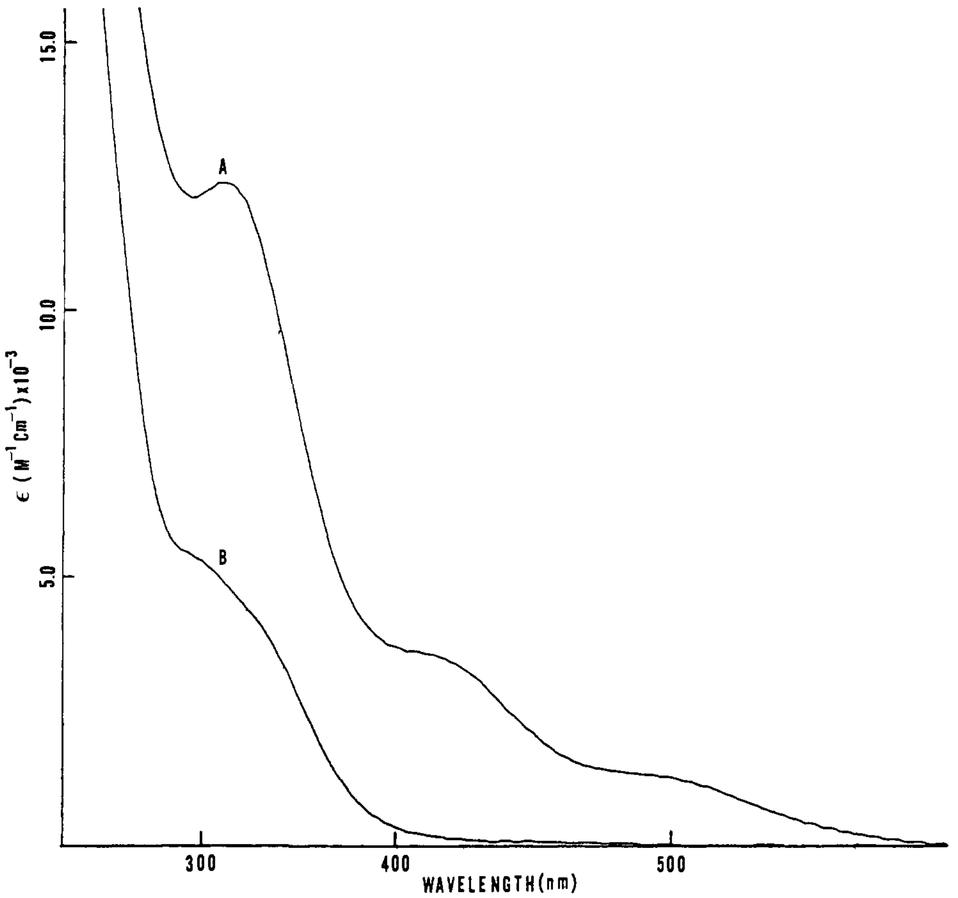
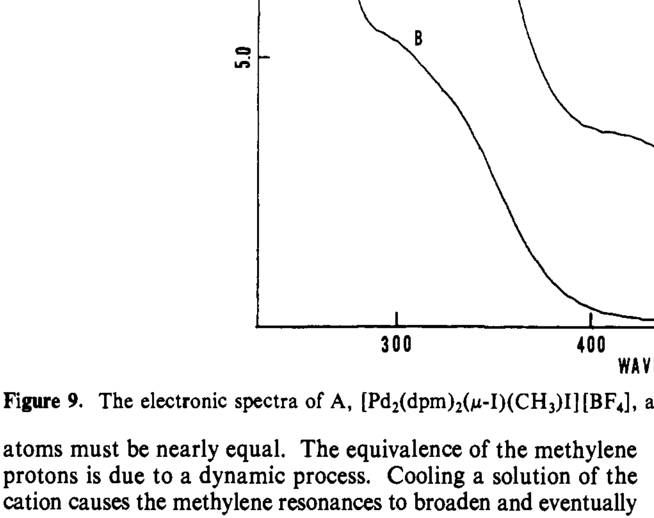


Figure 9. The electronic spectra of A, $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I][BF_4]$, and B, $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2][PF_6]$, in dichloromethane solution.

atoms must be nearly equal. The equivalence of the methylene protons is due to a dynamic process. Cooling a solution of the cation causes the methylene resonances to broaden and eventually separate as shown in Figure 7. Although the spectrum is not completely resolved at the lowest temperature accessible, it has the general shape associated with an A-frame structure. To account for the dynamic behavior indicated by ^1H NMR spectrum, we propose that this complex undergoes rocking about the Pd–Pd vector as illustrated in eq 7, which shows the in-plane ligands and



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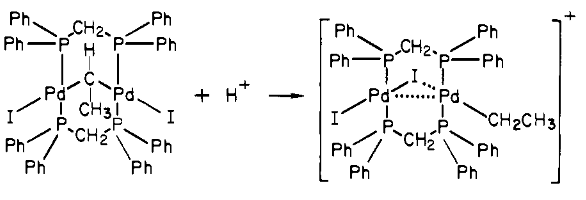
(7)

omits the dpm ligands that lie above and below the plane of the drawing. The rocking process is facilitated by the proximity of the two metal atoms and by the ability of one palladium to donate electrons to the other to form a full, dative Pd–Pd bond in the proposed intermediate **14**. This novel behavior, we believe, is caused in part by the asymmetry of the complex. In almost all of the dpm-bridged, binuclear complexes investigated to date, the two metal atoms sit in chemically equivalent environments. In this methyl derivative, however, the two palladium ions are clearly different. The asymmetry allows one palladium to become a donor toward the other while the presence of two identical and potentially bridging ligands on that donor palladium allows for the rapid transfer of the bridging halide from one side of the molecule to the other.

Additional evidence for significant metal–metal interaction in **13** comes from its electronic spectrum. In Figure 9 the spectra of $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)_2]^+$ (**12**) and $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]^+$ (**13**) are compared. These complexes are related by substitution of methyl and iodo ligands. The electronic spectrum of the asymmetric **13** shows two low-energy features which are absent from the spectrum of **12**. We suspect that these transitions involve the three-centered Pd_2I unit and result from the close proximity of the two palladium ions.

Protonation of **2** with trifluoroacetic acid in dichloromethane produces a mixture of $Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)Br^+$, $Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)_2^+$, and $Pd(dpm)Br_2$. $Pd_2(dpm)_2(\mu\text{-}Br)(CH_3)Br^+$ has been identified by its ^1H NMR spectrum and by comparison of this with the spectrum of **13**. Further work is in progress on the mechanism of apparent methyl transfer involved in this reaction. Similarly protonation of **4** with trifluoroacetic acid in dichloromethane produces the ethyl complex **15** by reaction 8. Complex



(8)

15

15 is the sole product of this reaction. It has been identified via its ^1H NMR spectrum which is reported in Table I.

Discussion

The two-center, three-fragment oxidative addition offers a new route to the preparation of methylene- and phenylene-bridged complexes. Most other methylene-bridged complexes have been obtained by the reaction of diazo compounds with organometallics.[23] For example the reaction between diazomethane and $Pt_2(dpm)_2Cl_2$ produces $Pt_2(dpm)_2(\mu\text{-}CH_2)Cl_2$,[24] the platinum

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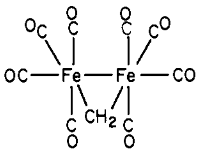
[23] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–812.

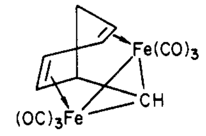
[24] Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808–2813.

analogue of **3**. However, diiodomethane has been used by Pettit and coworkers to form **16** from $Fe_2(CO)_8^{2-}$.[25] This reaction closely resembles the synthesis reported here. The reaction between $(Ph_3P)_4Pt$ and iodochloromethane follows a somewhat different course. This reaction produces the ylide complex *cis*-$[(Ph_3P)_2Pt(CH_2PPh_3)Cl]I$ which may be viewed as containing a methylene group bridging a platinum atom and a phosphorus atom.[26]



16

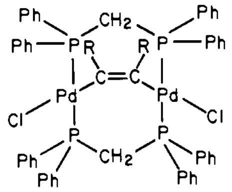
Most previously characterized examples of methylene bridges spanning two transition metals have involved compounds containing metal–metal bonds. Examples include $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CH_2)$,[27] $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2(\mu\text{-}CHCO_2C_2H_5)$,[28,29] $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(CO)_4(\mu\text{-}CH_2)$,[30] $Ru_2\{P(CH_3)_3\}_6(\mu\text{-}CH_2)_3$,[31] $W_2(CO)_8(\mu\text{-}CHCH{=}CMe_2)$,[32] and **17**.[33] However both $Pd_2(dpm)_2(\mu\text{-}CHR)Y_2$ and $Pt_2(dpm)_2(\mu\text{-}CH_2)X_2$ are exceptions to this. These A-frame molecules are isoelectronic and presumably isostructural with $Pd_2(dpm)_2(\mu\text{-}S)Cl_2$[12] whose Pd···Pd separation of 3.258 (2) Å clearly places these metals outside of the metal–metal bonded range.



17

Electrophilic attack on bridging methylene groups has been noted in a few cases. At present each example appears to follow a distinct mode of reaction. Compound **17** undergoes hydrogen/deuterium exchange when treated with trifluoroacetic acid-*d*.[33] Protonation of $Ru_3(\mu\text{-}CH_2)_3[P(CH_3)_3]_6$ with 1 equiv of fluoroboric acid yields $Ru_3(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)[P(CH_3)_3]_6^+$.[31] In this process a bridging methylene is converted into a bridging methyl group and the Ru–Ru bond remains intact. The complex $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CH_2)$ undergoes addition of HCl or HBr to form $(\eta^5\text{-}C_5H_5)Rh(CH_3)(\mu\text{-}CO)_2Rh(X)(\eta^5\text{-}C_5H_5)$.[34] This opening of the three-membered Rh_2C ring proceeds through the initial protonation of the Rh–Rh bond, which remains intact in the final product. In the case of **1** and **2** there is no metal–metal bond to be protonated. Whatever metal–metal interaction is present is certainly strengthened in the protonated product. In the process of protonation, the conversion of a terminal halide to a bridging halide allows the two palladium ions to retain their 16-electron configuration as one of the Pd–C bonds is lost.

The structures of the phenylene-bridged complexes **8** and **9** are anticipated to resemble closely **18** which has a Pd···Pd separation of 3.492 Å.[11] Compound **18** is formed by the addition of hexafluoro-2-butyne to $Pd_2(dpm)_2Cl_2$, and it demonstrates the flexibility of the bridging dpm ligands that allow a two-atom unit to bridge the two palladium ions. A number of other phenylene (benzyne)-bridged complexes are known. These include both cases where there is a metal–metal bond, $HOs_3(CO)_7(PPh_2)(PPh_3)(\mu\text{-}C_6H_4)$,[35] $Os_3(CO)_7(PPh_2)_2(\mu\text{-}C_6H_4)$,[36] $H_3Os_3(CO)_8(\mu\text{-}HC{=}NPh)(\mu\text{-}C_6H_4)$,[37] $(\eta^5\text{-}C_5H_5)_2Ir_2(CO)_2(\mu\text{-}C_6H_4)$,[38] and $Fe_2(CO)_8(\mu\text{-}C_6F_4)$,[39] and a case where there is no metal–metal bond, $Pt_4(\mu\text{-}C_6H_4)_2Cl_{14}^{2-}$.[40] Compounds **8** and **9** join the latter class.



18, R = CF_3

Most previous preparations of bridging phenylene complexes have produced very small yields.[35-43] Frequently the phenylene group has been formed from another ligand such as triphenylphosphine or a phenyl isocyanide. In these cases complex reaction mixtures are obtained. In contrast, the formation of **8** proceeds in high yield, and there is no problem involved in isolating a pure product. Consequently **8** is the most readily available phenylene-bridged complex now known.

Further studies of these binuclear hydrocarbon complexes and of the reactivity of $Pd_2(dpm)_3$ toward organic halides are in progress.

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