

mixture was refluxed for 30 min, the heating was discontinued, and ca. 2.25 g (0.03 mol) of $(\text{CD}_3)_2\text{C}=\text{CCH}_3$ was added to the reaction mixture, during which refluxing occurred. The reaction mixture was further refluxed for 24 h, and the color changed from grey to purple. The products were distilled into the cold trap by increasing the nitrogen flow and draining the cooling water from the reflux condenser. This product was distilled, with the distillate below 75 °C being collected. The deuterated trimethylcyclopropane was analyzed by using gas chromatography, and the fraction having a retention time identical with that of a commercial sample of 1,1,2-trimethylcyclopropane was collected. Further characterization was provided by ^1H NMR analysis.

$[\text{PtCl}_2(1,1\text{-bis(trideuteriomethyl)-2-methylcyclopropane})]_4$. Anhydrous diethyl ether (10 mL), 0.2494 g of Zeise's dimer, and an excess of the hexadeuterated cyclopropane (0.1–0.12 mL) were refluxed in a 10-mL, round-bottomed flask. After 5.5 h, a pale yellow powder was filtered, washed with chloroform and with ether, and dried in vacuo; yield 0.0856 g (28%).

$(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2\text{Pt}(1,1\text{-bis(trideuteriomethyl)-2-methylcyclopropane})$. $[\text{PtCl}_2(1,1\text{-bis(trideuteriomethyl)-2-methylcyclopropane})]_4$ (0.085 g) was suspended in ca. 3 mL of chloroform and cooled in a dry ice/acetone bath. Pyridine (0.04 mL) was added and the mixture allowed to warm slowly. Dissolution took place below -5 °C. The yellow solution was eluted through a short silica gel column by using chloroform as solvent. The effluent was evaporated to dryness and dried in vacuo; yield 0.090 g (73%).

$(N,N,N',N'\text{-Tetramethylethylenediamine})\text{PtCl}_2(\text{methylcyclopropane})$. **IIa** (0.057 g) was suspended in 1–2 mL of chloroform and cooled in a dry ice/acetone bath. $N,N,N',N'\text{-Tetramethylethylenediamine}$ (0.03 mL, Aldrich Chemical Co.) was added and the mixture allowed to warm slowly. Dissolution took place between -40 and -30

°C. The yellow solution was eluted through a short silica gel column, and the solvent was removed from the yellow effluent. The yellow solid was then dried in vacuo; yield 0.0513 g (66%). $N,N,N',N'\text{-Tetramethylethylenediamine}$ adducts of the ethylcyclopropane (72% yield), 1,1-dimethylcyclopropane (55% yield), and 1,1,2-trimethylcyclopropane (97% yield) insertion complexes were prepared in an analogous fashion.

$(\text{C}_5\text{H}_5\text{N})\text{Cl}_2\text{Pt}[\text{C}(\text{H})(\text{C}_5\text{H}_5\text{N})(\text{CH}_2\text{CHMe}_2)]$. **IIc** (ca. 50 mg) was dissolved in 4 mL of benzene- d_6 . The solution was heated in a 50 °C water bath and the formation of the ylide complex monitored by using ^1H NMR. After several days, no platinacyclobutane was detectable in the NMR spectrum, and a yellow precipitate had formed. The yellow solution was filtered and allowed to evaporate to dryness under vacuum (H_2O aspirator), yielding 18 mg (ca. 36%) of **VIc**. **VIb** and **VIe** were prepared in a similar manner.

Registry No. Ia, 77629-62-0; iso-Ia, 77629-63-1; Ib, 68472-65-1; Ic, 68472-64-0; Id, 68508-44-1; Ie, 67235-51-2; I, R = R' = CD_3 , R'' = Me, 77629-64-2; IIa, 68111-87-5; iso-IIa, 68111-86-4; IIb, 68487-93-4; IIc, 68472-68-4; IId, 68111-91-1; IIe, 67605-97-4; IIIf, 36569-03-6; II, R = R' = CD_3 , R'' = Me, 77647-93-9; IIIa, 77629-65-3; iso-IIIa, 77629-66-4; IIIb, 77629-67-5; IIIc, 77629-68-6; IIIe, 77629-69-7; IVa, 68111-89-7; iso-IVa, 68111-88-6; IVb, 77629-70-0; IVc, 77629-71-1; IVd, 75597-46-5; IVe, 77629-72-2; Va, 77629-73-3; Vb, 77629-74-4; Vc, 77629-75-5; Vd, 77629-76-6; Ve, 77661-60-0; VIa, 77629-77-7; VIb, 77629-78-8; VIc, 77629-79-9; VIe, 35327-31-2; $\text{PtCl}_2(\text{C}_5\text{H}_5\text{N})(\text{CH}_2=\text{CMeCHMe}_2)$, 67235-52-3; Zeise's dimer, 12073-36-8; 1,1-bis(trideuteriomethyl)-2-methylcyclopropane, 72195-38-1; $(\text{CD}_3)_2\text{C}=\text{CHCH}_3$, 1787-45-7; $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_2\text{H}_5)\text{Br}$, 1530-32-1; $(\text{CD}_3)_2\text{C}=\text{O}$, 666-52-4; *trans*- $\text{PyCl}_2\text{Pt}(\text{CH}_2=\text{CMeCH}_2\text{Me})$, 77629-80-2.

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Novel Reactions of Metal–Metal Bonds. Reactions of $\text{Pd}_2\{(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Cl}_2$ with Acetylenes, Olefins, and Isothiocyanates

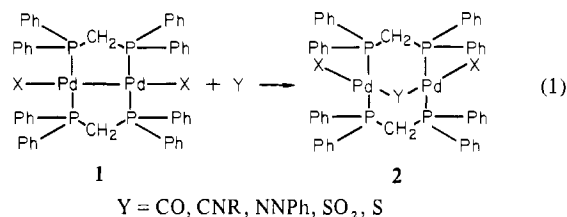
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Acetylenes with electron-withdrawing substituents react with $\text{Pd}_2(\text{dpm})_2\text{X}_2$ ($\text{dpm} = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2$; X = Cl, Br, I) to form $\text{Pd}_2(\text{dpm})_2(\mu\text{-acetylene})\text{X}_2$ (acetylene = $\text{C}_2(\text{CF}_3)_2$, $\text{C}_2(\text{CO}_2\text{CH}_3)_2$, $\text{C}_2(\text{CO}_2\text{C}_2\text{H}_5)_2$, $\text{HC}_2\text{CO}_2\text{H}$, $\text{HC}_2\text{CO}_2\text{CH}_3$) which have been characterized by infrared and $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. These acetylene adducts are resistant to acetylene exchange and to protonation. Reaction with methyl isocyanide yields $[\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)(\text{CNCH}_3)_2][\text{PF}_6]_2$ which is also formed by reaction of $[\text{Pd}_2(\text{dpm})_2(\mu\text{-CNCH}_3)(\text{CNCH}_3)_2][\text{PF}_6]_2$ with dimethyl acetylenedicarboxylate. $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ is a catalyst for the cyclotrimerization of dimethyl acetylenedicarboxylate and $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$ is formed during the reaction. The reaction of $\text{Pd}_2(\text{dpm})_2\text{I}_2$ with maleic anhydride results in the formation of $\text{Pd}(\text{dpm})\text{I}_2$ and two other incompletely characterized products which can also be obtained through the addition of maleic anhydride to $\text{Pd}_2(\text{dpm})_3$. Ethylene, norbornadiene, and chlorotrifluoroethene are unreactive toward $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$. Phenyl and methyl isothiocyanate react with $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ to yield $\text{Pd}_2(\text{dpm})_2(\mu\text{-CNR})\text{Cl}_2$ in 50% isolated yield; some $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$ is formed in the process.

Introduction

Continuing studies in this laboratory have focused on the interaction of $\text{Pd}_2(\text{dpm})_2\text{X}_2$ (**1**) ($\text{dpm} = \text{bis}(\text{diphenylphosphino})\text{methane}$, X = halide ion) and $\text{Pd}_2(\text{dam})_2\text{X}_2$ ($\text{dam} = \text{bis}(\text{diphenylarsino})\text{methane}$) with small molecules. These dimeric Pd(I) complexes undergo facile and sometimes reversible insertion of a variety of substances, including carbon monoxide,^{1,2} sulfur dioxide,³ atomic sulfur (from cyclooctasulfur or an episulfide),³ and diazonium ions,⁴ into the metal–metal bond. The products are complexes which have become known as molecular A frames.⁵ This is shown in eq 1.



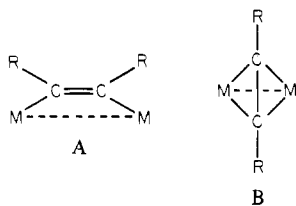
Tin(II) chloride, however, inserts into the Pd–Cl bonds to form $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_2)\text{Cl}$ and $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)_2$.⁶

We have recently reported that acetylenes also add to **1**.⁷ Acetylenes can bind two metal centers in two distinct ways.^{7–9}

- (1) Olmstead, M. M.; Hope, H.; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502–5503.
- (2) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099–6106.
- (3) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996–3003.
- (4) Rattray, A. D.; Sutton, D. *Inorg. Chim. Acta* **1978**, *27*, L85.

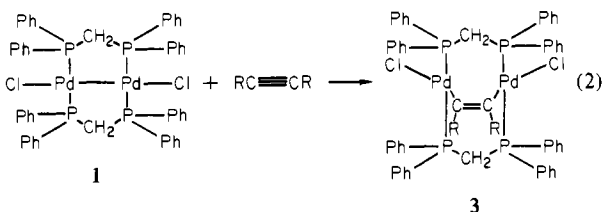
- (5) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 6129–6131.
- (6) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, *32*, 193–198.
- (7) Balch, A. L.; Lee, C.-L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979**, *177*, C22–C26.

One, A, places the two carbon atoms, their substituents, and



the two metal atoms in a plane. In complexes of this type, the portion derived from the acetylene acquires the geometry of a cis-dimetalated olefin. The other arrangement, B, involves a pseudotetrahedral array of the two acetylenic carbon atoms and the two metal atoms. In this situation both of the π bonds of the acetylene are used to donate a total of four electrons to the two metal atoms.

An X-ray crystallographic study of Pd₂(dpm)₂(μ -C₂{CF₃})₂Cl₂ has shown that it belongs to the structural class A.⁷ Thus the acetylene addition reaction occurs according to eq 2. This reaction differs from the insertion reactions described



by eq 1 because acetylene addition involves insertion of a two-atom unit between the palladium atoms. In contrast the substrates involved in reaction 1 insert a single atom between the two palladium ions.

Here we report details of the synthesis and reaction chemistry of these acetylene adducts along with the products obtained from the reaction of **1** with olefins and isothiocyanates.

Experimental Section

Preparation of Compounds. Pd₂(dpm)₃,¹⁰ Pd₂(dpm)₂X₂,² Pd(dpm)X₂¹¹ (X = Cl, Br, I) and dimethyl acetylenedicarboxylate-*d*₆¹² were prepared by established procedures.

Pd₂(dpm)₂(μ -C₂{CO₂CH₃})₂Cl₂. Pd₂(dpm)₂Cl₂ (300 mg, 0.285 mmol) was dissolved in 15 mL of dichloromethane. After the solution was filtered, 1.156 g (8.13 mmol) of dimethyl acetylenedicarboxylate was added, and the solution was allowed to stand for 10 h. Ethyl ether was added dropwise to the solution in order to precipitate the product as yellow crystals. The product was collected by filtration and purified by recrystallization from dichloromethane/ether; yield 292 mg (86%). Anal. Calcd for C₅₆H₅₀O₄Pd₂: C, 56.30; H, 4.22; Cl, 5.94. Found: C, 56.78; H, 4.14; Cl, 5.95.

Acetylene adducts of Pd₂(dpm)₂X₂ and Pd₂(dam)₂X₂ with diethyl acetylenedicarboxylate, methyl propiolate, and propiolic acid were prepared similarly.

Pd₂(dam)₂(μ -C₂{CF₃})₂Cl₂. A solution of Pd₂(dam)₂Cl₂ (200 mg) in 15 mL of dichloromethane was saturated with hexafluoro-2-butyne and stored under 1 atm of hexafluoro-2-butyne for 18 h. The yellow crystals which formed were collected by filtration and purified by recrystallization from dichloromethane/ether; yield 146 mg (65%). Pd₂(dpm)₂(μ -C₂{CF₃})₂Cl₂ was obtained by a similar procedure and has been characterized by X-ray crystallography.

[Pd₂(dpm)₂(μ -C₂{CO₂CH₃})(CNCH₃)₂][PF₆]₂. Methyl isocyanide was added dropwise to a stirred suspension of 200 mg (0.167 mmol)

of Pd₂(dpm)₂(μ -C₂{CO₂CH₃})₂Cl₂ in 15 mL of methanol until all of the yellow solid has dissolved to give a clear pale yellow solution. The solution was filtered, and a solution of 54.6 mg (0.335 mmol) of ammonium hexafluorophosphate in 3 mL of methanol was added. Ethyl ether was added in order to precipitate the product. The pale yellow solid was purified by dissolving it in acetonitrile, filtering, and reprecipitating by addition of a 5:1 v:v mixture of ether and methanol; yield 185 mg (74%). Anal. Calcd for C₆₀H₅₆F₁₂N₂O₄P₆Pd₂: C, 48.18; H, 3.77; N, 1.87. Found: C, 47.88; H, 3.85; N, 1.84.

Reaction of Pd₂(dpm)₂Cl₂ with Methyl Isothiocyanate. Pd₂(dpm)₂Cl₂ (0.290 g, 0.276 mmol) and methyl isothiocyanate (1.726 g, 23.61 mmol) were dissolved in 25 mL of dichloromethane; the mixture was filtered and allowed to stand for 3 days. The red crystalline product, which slowly separated from solution, was collected by filtration, washed with dichloromethane, and vacuum-dried. The product could be purified by dissolving it in a large volume of dichloromethane. Upon concentration of the dichloromethane, the product crystallized; yield 165 mg (55%). The red solid was identified as Pd₂(dpm)₂(μ -CNCH₃)₂Cl₂ by comparison of spectroscopic properties with those of an authentic sample.²

Reaction of Pd₂(dpm)₂Cl₂ with Phenyl Isothiocyanate. Pd₂(dpm)₂Cl₂ (0.183 g, 0.83 mmol) and phenyl isothiocyanate (0.565 g, 4.18 mmol) were dissolved in 15 mL of dichloromethane. After standing for 18 h the red crystals, which had formed, were collected by filtration and were recrystallized from dichloromethane/ether. The product was identified as Pd₂(dpm)₂(μ -CNC₆H₅)₂Cl₂ by spectroscopic comparison with an authentic sample;² yield 108 mg (51%).

[Pd₂(dpm)₂(μ -S)(CNCH₃)₂][B(C₆H₅)₄]₂. Methyl isocyanide was added dropwise to a stirred slurry of 0.160 g (0.148 mmol) of Pd₂(dpm)₂(μ -S)Cl₂ in 10 mL of methanol until all of the solid had dissolved. The solution was filtered, and a solution of 55.54 mg (0.162 mmol) of sodium tetraphenylborate in methanol was added. The yellow orange crystalline product was collected by filtration and recrystallized from acetonitrile/methanol; yield 150 mg (94%). Anal. Calcd for C₁₀₂H₉₀B₂N₂P₄Pd₂S: C, 70.64; H, 5.23; S, 1.62. Found: C, 71.08; H, 5.34; N, 1.58.

Trimerization of Dimethyl Acetylenedicarboxylate. The catalyst (0.0508 mmol) and dimethyl acetylenedicarboxylate (1.156 g, 8.134 mmol) were heated in a sealed glass tube in an oil bath at 125 \pm 5 $^{\circ}$ C for 1–2 h. After the tube was cooled and opened, the brown-black reaction mixture, which became viscous if extensive conversion to hexamethyl mellitate had occurred, was dissolved in a minimum of dichloromethane and chromatographed on a column of silica gel (30 cm long, 3 cm in diameter) with dichloromethane as the eluant. All of the colorless to pale yellow eluate was collected and taken to dryness by the use of a rotary evaporator. The pale yellow solid was recrystallized from dichloromethane/pentane to give white crystals of hexamethyl mellitate which was identified by comparison of spectral properties with an authentic sample.¹³

Reaction of Dimethyl Acetylenedicarboxylate with Pd₂(dpm)₂(μ -C₂{CO₂CD₃})₂I₂. Pd₂(dpm)₂(μ -C₂{CO₂CD₃})₂I₂ (0.140 g, 0.101 mmol) and dimethyl acetylenedicarboxylate (0.578 g, 4.07 mmol) were mixed and sealed in a glass tube. The mixture was heated at 125 \pm 5 $^{\circ}$ C for 2 h, cooled, and chromatographed on silica gel to yield hexamethyl mellitate. Analysis of the product's isotopic labeling by mass spectrometry revealed the presence of 3.6% hexamethyl mellitate-*d*₆ as the only deuterium-labeled species detectable in the sample. Complete reaction of all materials present would have produced 7.8% of hexamethyl mellitate-*d*₆. However during the reaction Pd₂(dpm)₂(μ -C₂{CO₂CD₃})₂I₂ did not completely dissolve; consequently the theoretical yield of 7.8% hexamethyl mellitate-*d*₆ should not have been produced if the undissolved material did not contribute to the reaction. We did not rerun this experiment with a lower amount of Pd₂(dpm)₂(μ -C₂{CO₂CD₃})₂I₂ because we felt that the ability to detect hexamethyl mellitate-*d*₆ would be jeopardized.

Physical Measurements. 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 acetonitrile solutions. ¹H NMR and proton-decoupled ³¹P NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer at 200 and 81 MHz, respectively. An external 85% phosphoric acid reference was used for ³¹P NMR spectra, and the high-frequency-positive convention, rec-

(8) Muettterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090–2096.

(9) Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* **1979**, 277–278.

(10) Stern, E. W.; Maples, P. K. *J. Catal.* **1972**, *27*, 134–141.

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

(12) Huntress, E. H.; Lesslie, T. E.; Bornstein, J. "Organic Syntheses"; Wiley: New York; Collect. Vol. IV, pp 321–330.

(13) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169–175.

Table I. Characteristic Infrared Spectral Features (cm⁻¹)

compd	$\nu(\text{C}=\text{O})$	$\nu(\text{Pd}-\text{X})$
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{Cl}_2$)	1702, 1690	280
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{Br}_2$)	1702, 1690	224
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{I}_2$)	1695	211
Pd ₂ (dam) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{Cl}_2$)	1702, 1693	275
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_2\text{CH}_3\}_2\text{Cl}_2$)	1702	279
Pd ₂ (dam) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_2\text{CH}_3\}_2\text{Cl}_2$)	1686	276
Pd ₂ (dpm) ₂ ($\mu\text{-HC}_2\{\text{CO}_2\text{CH}_3\}_2\text{Cl}_2$)	1689	277
Pd ₂ (dpm) ₂ ($\mu\text{-HC}_2\{\text{CO}_2\text{H}\}_2\text{Cl}_2$)	1680, 1688, 1651	280
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CF}_3\}_2\text{Cl}_2$)		286, 296
Pd ₂ (dam) ₂ ($\mu\text{-C}_2\{\text{CF}_3\}_2\text{Cl}_2$)		286, 296
[Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2$)- (CNCH ₃) ₂][PF ₆] ₂ ^a	1705	

^a $\nu(\text{CN})$ at 2236 cm⁻¹.

ommended by IUPAC, has been used in reporting chemical shifts.

Simulations of the entire ³¹P spectra were performed with use of 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.

Results

Synthesis of Acetylene Adducts. Dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate react with Pd₂(dpm)₂X₂ (X = Cl, Br, I) in dichloromethane solution over a period of several hours to yield yellow crystalline precipitates of the adducts Pd₂(dpm)₂($\mu\text{-C}_2\text{R}_2$)X₂. Similar adducts are formed by the diarsine complex Pd₂(dam)₂X₂.

Exposure of a dichloromethane solution of Pd₂(dpm)₂Cl₂ to hexafluoro-2-butyne vapor yields Pd₂(dpm)₂($\mu\text{-C}_2\{\text{CF}_3\}_2$)Cl₂.⁷ Other acetylenes including diphenylacetylene, phenylacetylene, 1-phenyl-1-propyne and acetylene itself, which lack electron-withdrawing substituents, are unreactive toward Pd₂(dpm)₂X₂ and Pd₂(dam)₂X₂ under the conditions used to prepare the other acetylene adducts. However acetylenes bearing only a single electron-withdrawing group are reactive.

Both propiolic acid and methyl propiolate react with Pd₂(dpm)₂Cl₂. Despite the presence of other reactive centers (the acetylenic and carboxylic protons) the adducts formed from these latter two acetylenes appear to possess the same structural features as the adducts of symmetric acetylenes.

These acetylene adducts are all yellow crystalline solids which have some solubility in dichloromethane and chloroform but otherwise have negligible solubility in common organic solvents. Changing the halide from chloride to bromide to iodide results in increasing solubility of the adducts. The spectroscopic properties of these compounds and the response of these spectral features to substitutional changes within the molecules indicates that they all possess the basic A-frame structure which has been established for Pd₂(dpm)₂($\mu\text{-C}_2\{\text{CF}_3\}_2$)Cl₂. The structure of Pd₂(dpm)₂($\mu\text{-C}_2\{\text{CF}_3\}_2$)Cl₂ is shown in Figure 1.⁷ The infrared spectra of these adducts are dominated by the relatively uninformative spectral bands due to the dpm ligands. Table I records infrared spectral features that are characteristic of these adducts: the carbonyl stretching vibration of the coordinated acetylenic esters and acid and the palladium halide stretching bands. An unambiguous assignment of a perturbed acetylenic C-C stretching vibration in these molecules has not been made.

¹H and ³¹P{¹H} NMR spectral characteristics are recorded in Table II. In the ¹H NMR spectra, the methylene protons of the dpm and dam ligands show their unusual sensitivity to structure.³ Because of the A-frame structure, the two protons of a methylene group are inequivalent although both methylene groups in a molecule are equivalent. Consequently, the methylene resonances of these adducts appear as a basic AB quartet with a ca. 12-Hz coupling between the geminal protons. For the dpm complexes further splitting occurs due to P-H coupling. Since the phosphine ligands lie trans to one another, virtual coupling occurs and each proton resonance in the AB quartet is further split into a 1:4:6:4:1 quintet due to P-H coupling. Since there are two inequivalent dpm methylene protons in these molecules, there are two P-H coupling constants in these molecules, one in the range 3-4 Hz and the

Table II. ¹H and ³¹P Nuclear Magnetic Resonance Parameters

compd	¹ H ^a					³¹ P ^a δ
	dpm methylene			acetylene (or MeNC)		
	δ^b	$J(\text{P-H}), J(\text{H-H}),$ Hz	Hz	δ^b	δ	
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{Cl}_2$)	3.0 (2)	3.74	12.5			
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{Br}_2$)	3.56 (2)	5.26		2.47 (6)		4.07
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{I}_2$)	2.95 (2)	3.78	12.4			
	3.62 (2)	5.49		2.50 (6)		4.51
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{I}_2$)	2.97 (2)	3.72	12.5			
	3.72 (2)	5.40		2.53 (6)		5.47
Pd ₂ (dam) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2\text{Cl}_2$)	2.72 (2)		12.0			
	3.18 (2)			2.516 (6)		
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_2\text{CH}_3\}_2\text{Cl}_2$)	3.09 (2)	3.75	16.1			
	3.58 (2)	5.15		0.405 (6)	2.93 (4)	4.50
Pd ₂ (dam) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_2\text{CH}_3\}_2\text{Cl}_2$)	2.91 (2)		10.7			
	3.14 (2)			0.42 (6)	3.00 (4)	
Pd ₂ (dpm) ₂ ($\mu\text{-HC}_2\{\text{CO}_2\text{CH}_3\}_2\text{Cl}_2$)	2.86 (2)	3.52	12.7			5.59 ^c
	3.21 (2)	5.27		2.55 (3)		8.88 ^c
Pd ₂ (dpm) ₂ ($\mu\text{-HC}_2\{\text{CO}_2\text{H}\}_2\text{Cl}_2$)	2.94 (2)	3.60	12.7			4.47 ^d
	3.25 (2)	5.25				8.32 ^d
Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CF}_3\}_2\text{Cl}_2$)	2.90 (2)	3.03	11.9			
	3.51 (2)	4.66				1.87
Pd ₂ (dam) ₂ ($\mu\text{-C}_2\{\text{CF}_3\}_2\text{Cl}_2$)	2.80 (2)		11.0			
	3.01 (2)					
[Pd ₂ (dpm) ₂ ($\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2$)(CNCH ₃) ₂][PF ₆] ₂	3.34 (2)	6.07	13.4			
	4.13 (2)	3.87		2.369 (6)	3.03 (6) (MeNC)	16.48
[Pd ₂ (dpm) ₂ ($\mu\text{-S}$)(CNCH ₃) ₂][PF ₆] ₂	3.35 (2)	3.62	13.8			
	4.75 (2)	6.40		2.154 (6) (MeNC)		13.30

^a In dichloromethane-d₂ solution. ^b Relative intensities in parentheses. ^c AA'BB' multiplet with $J(\text{A},\text{B}') = 1.00$, $J(\text{A},\text{B}) = 48.54$, and $|J(\text{A},\text{A}') - J(\text{B},\text{B}')| = 26.50$ Hz. ^d AA'BB' multiplet with $J(\text{A},\text{B}') = 0.79$, $J(\text{A},\text{B}) = 44.68$, and $|J(\text{A},\text{A}') - J(\text{B},\text{B}')| = 31.03$ Hz.

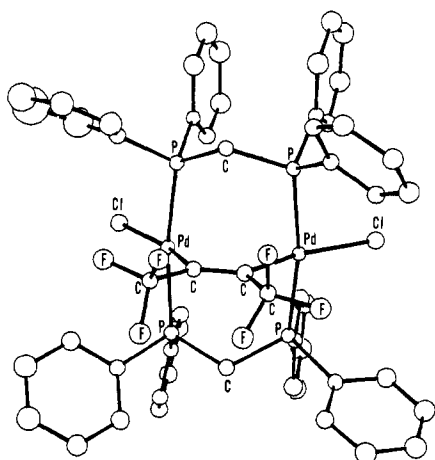


Figure 1. ORTEP drawing of $\text{Pd}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-C}_4\text{F}_6)\text{Cl}_2$ showing 50% thermal ellipsoids. Some bond lengths are Pd–C = 1.994 (12) and 2.014 (12), Pd–Cl = 2.378 (3) and 2.389 (3), C–C = 1.338 (16), and Pd–P = 2.332 (3), 2.313 (3), 2.317 (3), and 2.338 (3) Å. Significant bond angles include Pd–C–C = 123.5 (9) and 121.5 (9), Pd–C–CF₃ = 113.7 (8) and 113.8 (8), C–C–CF₃ = 122.8 (1.1) and 124.7 (1.1), and P–Pd–P = 170.4 (1) and 169.8 (1)°.

other in the range 5–6 Hz. The resonances in the phenyl region of these adducts are usually complex and uninformative. In the adducts of dimethyl acetylenedicarboxylate and methyl propiolate the methyl resonances experience a shift to lower frequency from the free acetylenes. (The methyl resonances of dimethyl acetylenedicarboxylate and methyl propiolate occur at 3.86 and 3.83 ppm, respectively.) For the diethyl acetylenedicarboxylate adducts, the methylene resonance of the ethyl group experiences a similar shift to lower frequency. (The free ligand exhibits a methyl and methylene resonance at 1.33 and 4.29 ppm, respectively, with $J(\text{H},\text{H}) = 7.0$ Hz.) For $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}\text{H})\text{Cl}_2$ no resonance assignable to the unique proton of the coordinated acetylenic moiety could be found. Presumably it occurs in the region of the complex phenyl absorption. Similarly for $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{H}\}\text{H})\text{Cl}_2$, no resonances due to either of the protons of the acetylene-derived ligand could be observed.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the adducts formed by symmetric acetylenes (dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, hexafluoro-2-butyne) consist of a single resonance. For the adducts of methyl propiolate and propiolic acid the ^{31}P spectrum shows an AA'BB' spectral pattern. The spectrum of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{H}\}\text{H})\text{Cl}_2$ is shown in Figure 2 along with a computer-generated simulation of the spectrum. That analysis of the spectrum produces the following spectral parameters: $\delta_A = 4.47$, $\delta_B = 8.32$, $J(\text{P}_A,\text{P}_B) = 0.79$ Hz, $J(\text{P}_A,\text{P}_B) = 44.68$ Hz. As is frequently the case in this spin system $J(\text{P}_A,\text{P}_A')$ and $J(\text{P}_B,\text{P}_B')$ are not determined. However the difference $|J(\text{P}_A,\text{P}_A') - J(\text{P}_B,\text{P}_B')|$ is measurable and is found to be 31.0 Hz. The relatively small (<100 Hz) values of $J(\text{P}_A,\text{P}_B)$ and $J(\text{P}_A,\text{P}_B')$ are of particular structural significance. Had the adduct assumed the geometry of structure B, then one of the AB coupling constants would have been a trans P–M–P coupling where a coupling constant in excess of 300 Hz would be expected.¹⁴ Since $J(\text{P}_A,\text{P}_B)$ and $J(\text{P}_A,\text{P}_B')$ are less than 100 Hz, the adduct cannot possess a structure of type B. On the other hand the magnitudes of the coupling constants are fully compatible with structure A. P–P coupling constants in binuclear dpm-bridged complexes of platinum^{15,16}

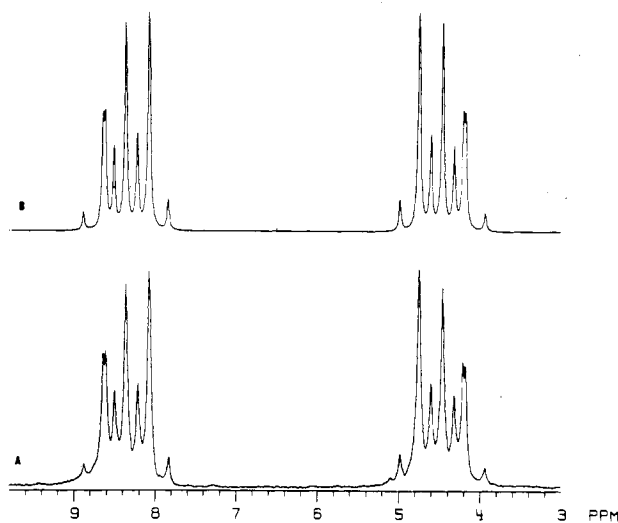


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Pd}_2(\text{dpm})_2(\mu\text{-HC}_2\{\text{CO}_2\text{H}\})\text{Cl}_2$ in dichloromethane solution: A, observed spectrum; B, simulated spectrum with parameters $\delta_B = 8.32$, $\delta_A = 4.47$, $|J(\text{A},\text{A}') - J(\text{B},\text{B}')| = 31.03$ Hz (with $J(\text{A},\text{A}')$, $J(\text{B},\text{B}')$ in the region of 200–600 Hz), $J(\text{A},\text{B}') = 0.79$ Hz, and $J(\text{A},\text{B}) = 44.68$ Hz.

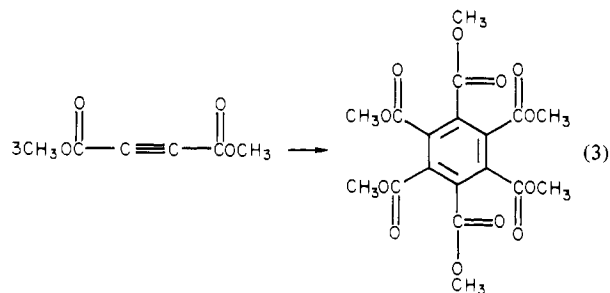
Table III. Catalysis of Dimethyl Acetylenedicarboxylate Acetylenedicarboxylate Trimerization

catalyst precursor	% isolated yield of hexamethyl mellitate ^a
$\text{Pd}_2(\text{dpm})_2\text{Cl}_2$	40 ^b
$\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$	33 ^b
$\text{Pd}(\text{dpm})\text{Cl}_2$	0 ^b
$\text{Pd}_2(\text{dpm})_2\text{I}_2$	68
$\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\})\text{I}_2$	51
$\text{Pd}(\text{dpm})\text{I}_2$	27
$\text{Pd}_2(\text{dpm})_3$	8

^a Conditions: 160:1 mole ratio of dimethyl acetylenedicarboxylate to catalyst precursor; temperature, 125 ± 5 °C; reaction time, 2 h. ^b Reaction time 1.5 h.

and rhodium¹⁷ are of similar magnitude to the values reported here. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}\text{H})\text{Cl}_2$ shows similar features. Its spectral parameters are recorded in Table II.

Catalysis of Dimethyl Acetylenedicarboxylate Cyclo-trimerization. $\text{Pd}_2(\text{dpm})_2\text{X}_2$ is an active catalyst for the trimerization of dimethyl acetylenedicarboxylate to hexamethyl mellitate (eq 3). This reaction has been conducted in neat



dimethyl acetylenedicarboxylate at 125 °C. The efficiency of a variety of palladium complexes as catalysts for this reaction are compared in Table III. Both $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2\text{I}_2$ are catalysts. During this reaction, the palladium

(14) Pregosin, P. S.; Kunz, R. W. *³¹P and ¹³C NMR of Transition Metal Phosphine Complexes*, NMR16⁺; Springer-Verlag: New York, 1979; p 46.

(15) Brown, M. P.; Franklin, S. J.; Puddephatt, R. J.; Thomason, M. A.; Seddon, K. R. *J. Organomet. Chem.* **1979**, 178, 281–290.

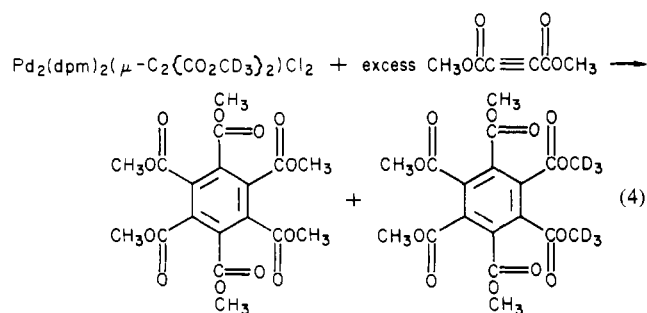
(16) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, 18, 2808–2813.

(17) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1980**, 19, 3743.

complexes turn from orange or red to the yellow color characteristic of the acetylene adducts. When $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ is used as the catalyst, a yellow solid forms. This solid has been identified as $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$. The acetylene adducts also serve as catalysts for reaction 3. The yield of hexamethyl mellitate using the acetylene adducts is lower than that using $\text{Pd}_2(\text{dpm})_2\text{X}_2$ under comparable conditions. The reduced yield probably results from our inefficiency in dissolving these isolated complexes in dimethyl acetylenedicarboxylate, rather than a true difference in catalytic activity. This lack of solubility of the acetylene adducts has hampered studies of the mechanism of catalysis.

It appears unlikely that the catalysis proceeds by means of disproportionation of the Pd(I) dimers into Pd(II) and Pd(0) species. The catalytic activities of $\text{Pd}(\text{dpm})\text{I}_2$ and $\text{Pd}_2(\text{dpm})_3$ are lower than those of the Pd(I) dimers, $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2\text{I}_2$, and all of these have comparable solubility in dimethyl acetylenedicarboxylate. $\text{Pd}(\text{dpm})\text{Cl}_2$ shows no activity as a catalyst for reaction 3.

The acetylene-derived moiety in $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{I}_2$ can be converted into hexamethyl mellitate. This has been ascertained by isotopic labeling of the acetylene adduct. The reaction of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CD}_3\}_2)\text{I}_2$ with excess unlabeled dimethyl acetylenedicarboxylate yields both hexamethyl mellitate- d_0 and hexamethyl mellitate- d_6 , via eq 4. This observation could simply mean that exchange occurs

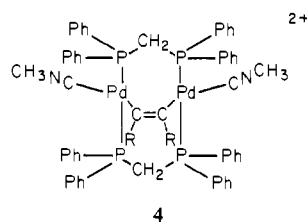


between free and coordinated acetylene. Alternately it could be interpreted to indicate catalysis proceeds by addition of acetylene to the acetylenic moiety of the adducts. Further interpretation of this observation is clouded by the difficulty with catalyst solubility. During this experiment, the catalyst did not completely dissolve.

We have probed the possibility of acetylene exchange between $\text{Pd}_2(\text{dpm})_2(\mu\text{-acetylene})\text{Cl}_2$ and free acetylene. However, the conditions used were milder than those employed in the catalytic acetylene trimerizations. A mixture of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{I}_2$ and excess propiolic acid in dichloromethane solution showed no evidence of acetylene exchange after standing for 12 h at 25 °C. Similarly no exchange was observed between $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{H}\}_2)\text{Cl}_2$ and dimethyl acetylenedicarboxylate or between $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CD}_3\}_2)\text{Cl}_2$ and dimethyl acetylenedicarboxylate in dichloromethane solution at 25 °C.

Reactions of the Acetylene Adducts. The acetylenic portion of these adducts appears to be firmly bound to the two palladium atoms. We have found no evidence for the thermal dissociation of these adducts, and they resist substitution of the acetylenic portion as well.

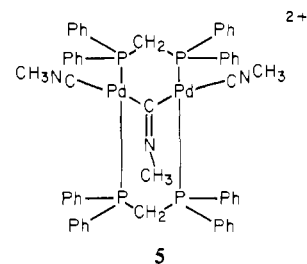
Methyl isocyanide reacts with $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$ to produce the cation $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)(\text{CNCH}_3)_2^{2+}$ (4), which has been isolated as the hexafluorophosphate salt. The electrical conductivity of this salt is $278 \text{ cm}^2 \text{ equiv}^{-1} \Omega^{-1}$ in acetonitrile solution, and it is consistent with its formulation as a 1:2 electrolyte. The infrared spectrum of the salt shows absorptions at 2235 cm^{-1} due to the terminal isocyanide ligands and at 830 cm^{-1} due



to the P-F stretching of the hexafluorophosphate salts along with bands characteristic of the acetylenic ligand and dpm. The ^1H NMR spectrum is similar to that of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$ except that an additional resonance at 3.03 ppm due to the isocyanide ligands is present.

No evidence has been found for the insertion of an isocyanide into the Pd-C bonds of these acetylene adducts.

An alternate route to the preparation of cation 4 is available. Treatment of $\text{Pd}_2(\text{dpm})_2(\mu\text{-CNCH}_3)(\text{CNCH}_3)_2(\text{PF}_6)_2$ (5)^{1,2}

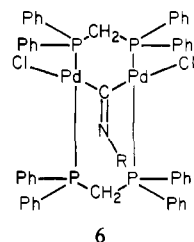


with dimethyl acetylenedicarboxylate produces 4 in 70% yield. This reaction involves the replacement of a bridging isocyanide ligand with a bridging acetylene. The reverse reaction does not appear to occur. The acetylene-bridge in 3 is unaffected by the addition of excess isocyanide.

Although these acetylene adducts are stable to thermal dissociation, acetylene dissociation can be effected photolytically. Exposure of a dichloromethane solution of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{I}_2$ to light from a mercury vapor lamp produces dimethyl acetylenedicarboxylate and $\text{Pd}_2(\text{dpm})_2\text{I}_2$. The reaction has been monitored by ^1H NMR spectroscopy and proceeds to 21% dissociation before reaching an apparent photostationary state.

These acetylene adducts show considerable stability to protic acids. The successful preparation of the propiolic acid adduct offers evidence for this stability. These adducts are also stable to more acidic solutions. Treatment of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{I}_2$ with a sixfold molar excess of trifluoroacetic acid in chloroform solution results in a loss of less than 10% of the original acetylene adduct after 5 days.

Reaction of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ with Isothiocyanates. Addition of methyl isothiocyanate or phenyl isothiocyanate to $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ in dichloromethane solution results in the gradual precipitation of the slightly soluble isocyanide adducts 6,



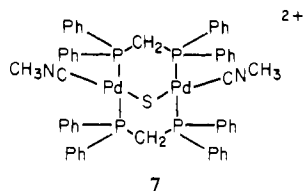
$\text{Pd}_2(\text{dpm})_2(\mu\text{-CNCH}_3)\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2(\mu\text{-CNC}_6\text{H}_5)\text{Cl}_2$, respectively. These isocyanide adducts have previously been characterized as the products resulting from the addition of isocyanides to $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$.² The yields of 6 from the isothiocyanates are about 50% on the basis of the starting palladium complex. In this reaction it is important to allow the product to crystallize slowly from solution. If the product is

Table IV. Structural Parameters of Acetylene Adducts of Structural Type A

compd	M...M, Å	C=C, Å	M–C, Å	M–C–C, deg	ref
Fe ₂ (CO) ₆ (μ-SR) ₂ (μ-C ₂ {CF ₃ }) ₂	3.266 (1)	1.34	2.24		22
Rh ₂ (η ⁵ -C ₅ H ₅) ₂ (CO) ₂ (μ-C ₂ {CF ₃ }) ₂	2.682 (1)	1.27	2.03	110	23
Ir ₂ (PPh ₃) ₂ (NO) ₂ (μ-C ₂ {CF ₃ }) ₂	2.838 (1)	1.26 (5)	2.05 (7)	113 (4)	24
Pd ₂ (dpm) ₂ Cl ₂ (μ-C ₂ {CF ₃ }) ₂	3.492 (1)	1.338 (16)	2.00	122	7
Pt ₂ (COD) ₂ (μ-C ₂ {CF ₃ }) ₂	3.129 (2)	1.32	2.06 (1)	116	25
Au ₂ (Ph ₃ P) ₂ (μ-C ₂ {CF ₃ }) ₂	3.343 (8)		2.05 (6)		26
(COD)Pt(μ-C ₂ {CF ₃ }) ₂ (μ-C ₄ {CF ₃ }) ₂ Pt(μ-C ₂ {CF ₃ }) ₂ Pt(COD)	2.841 (2)				25
	2.630 (3)				

forced from solution by the addition ether or methanol, impure material precipitates since other palladium complexes are present in the reaction mixture. ¹H NMR analysis of a reaction mixture containing Pd₂(dpm)₂Cl₂ and an isothiocyanate reveals the presence of both Pd₂(dpm)₂(μ-CNR)Cl₂² and Pd₂(dpm)₂(μ-S)Cl₂³ in an 8:1 molar ratio along with smaller quantities of an unidentified species which has a dpm methylene resonance characteristic of an A frame.

In order to explore the remote possibility that the ratio of Pd₂(dpm)₂(μ-CNR)Cl₂ to Pd₂(dpm)₂(μ-S)Cl₂ formed in the reaction between Pd₂(dpm)₂Cl₂ and isothiocyanates might result from displacement of the bridging sulfur by an isocyanide, we examined the reaction between Pd₂(dpm)₂(μ-S)Cl₂ and methyl isocyanide. Treatment of Pd₂(dpm)₂(μ-S)Cl₂³ as a slurry in methanol with methyl isocyanide produces an orange-red solution from which cation **7** may be isolated as the



tetraphenylborate salt. The conductivity of this salt, the occurrence of terminal but not bridging isocyanide stretching vibrations in the infrared spectrum, and the ¹H NMR and ³¹P{¹H} NMR spectrum are all in accord with substitution of the terminal chloride ions by isocyanide ligands. This reaction then parallels that of the acetylene adduct Pd₂(dpm)₂(μ-C₂{CO₂CH₃})₂Cl₂ with methyl isocyanide.

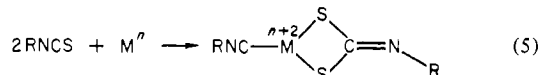
Pd₂(dpm)₂Cl₂ does not react with carbon disulfide or carbonyl sulfide under the conditions used for the reaction with isothiocyanates.

Reactions of Pd₂(dpm)₂Cl₂ with Olefins. Simple adduct formation between olefins and Pd₂(dpm)₂Cl₂ does not appear to occur. We have not detected any reaction between Pd₂(dpm)₂Cl₂ and ethylene, norbornadiene, or chlorotrifluoroethylene under the conditions used for the synthesis of acetylene adducts. However, maleic anhydride does react with Pd₂(dpm)₂I₂ under these conditions. The reaction has been monitored by ³¹P{¹H} NMR spectroscopy. Addition of 2 molar equiv of maleic anhydride to Pd₂(dpm)₂I₂ in dichloromethane results in the loss of the ³¹P NMR resonance at -9.9 ppm due to Pd₂(dpm)₂I₂ and the appearance of three new resonances at 12.4, 11.9, and -61.3 ppm. The resonance at -61.3 ppm is readily identified as Pd(dpm)I₂ by comparison with an authentic sample.¹⁸ The presence of Pd(dpm)I₂ has been confirmed by the ¹H NMR of this mixture which shows a triplet at 4.55 ppm (*J*(P,H) = 10.0 Hz) due to the Pd(II) monomer. The ³¹P resonances at 12.4 and 11.9 ppm are associated with the presence of other palladium complexes. Addition of maleic anhydride to the palladium(0) complex Pd₂(dpm)₃ also produces two resonances at 12.4 and 11.9 ppm as the only ³¹P resonances observed. Unfortunately we have

not as yet been able to isolate the material responsible for these two resonances. We suspect that the compound or compounds responsible for these resonances are Pd(0)-dpm-olefin complexes although we cannot rule out the possibility of oxidative addition of maleic anhydride to Pd₂(dpm)₃.

Discussion

While the addition of electronegatively substituted acetylenes to Pd₂(dpm)₂Cl₂ involves straightforward insertion into the Pd–Pd bond, a well-characterized mode of behavior for these phosphine-bridged Pd(I) compounds, the interactions of maleic anhydride and isothiocyanates show two new types of behavior. The reaction of maleic anhydride with Pd₂(dpm)₂I₂ represents a novel fragmentation of Pd₂(dpm)₂I₂, while the reaction of Pd₂(dpm)₂Cl₂ with isothiocyanates represents a novel fragmentation of the organic substrate. Other cases are known in which reaction of an isothiocyanate with a transition-metal complex forms an isocyanide ligand. Generally a redox disproportionation of 2 mol of isothiocyanate is involved (eq 5), so that both isocyanide and dithiocarbamate



ligands are formed.^{19–21} Thus the behavior of isothiocyanates with these binuclear palladium complexes appears distinct. At present, mechanistic speculation with relatively little information available is not appropriate.

From the present work it is clear that only electronegatively substituted acetylenes will form adducts of structural type A by reaction with Pd₂(dpm)₂Cl₂. This requirement for electron-withdrawing substituents on acetylene-bridged binuclear complexes of type A may be a general requirement. Table IV contains some structural parameters for acetylene-derived compounds with structure A.^{7,22–26} All structurally characterized molecules were prepared from hexafluoro-2-butyne, although in many cases analogues of these compounds derived from dimethyl acetylenedicarboxylate have also been made. It remains to be seen if molecules of structural class A can be constructed from more electron-rich acetylene. On the other hand, binuclear acetylene complexes of structural type B tolerate a much wider variety of acetylenic substituents.

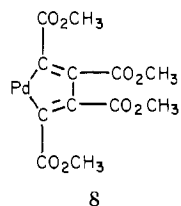
Inspection of Table IV reveals that these bridged acetylene complexes can accommodate a wide variety of metal–metal separations. (η⁵-C₅H₅)₂(CO)₂Rh₂(μ-C₂{CF₃})₂ clearly possesses

(18) Lindsay, C. H.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1980**, *19*, 3503.

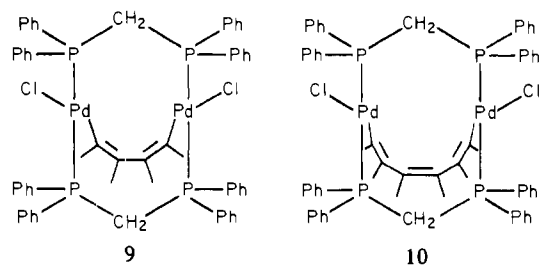
- (19) Thewissen, D. H. M. W.; Van Gaal, H. L. M. *J. Organomet. Chem.* **1979**, *172*, 69–79.
 (20) Harris, R. O.; Powell, J.; Walker, A.; Yanoff, P. V. *J. Organomet. Chem.* **1977**, *141*, 217–229.
 (21) Bowden, F. L.; Giles, R.; Haszeldine, R. N. *J. Chem. Soc., Chem. Commun.* **1974**, 578.
 (22) Davison, J. L.; Harrison, W.; Sharp, D. W. A.; Sion, G. A. *J. Organomet. Chem.* **1972**, *46*, C47–C49.
 (23) Dickson, R. S.; Mok, C.; Pain, G. *J. Organomet. Chem.* **1979**, *166*, 385–402.
 (24) Clemens, J.; Green, M.; Kuo, M.-C.; Fritchies, C. J., Jr.; Mague, J. T.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 53–54.
 (25) Smart, L. E.; Browning, J.; Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1777–1785. Kuo, M. C. Ph.D. Thesis, Tulane University, 1976.
 (26) Gilmore, C. J.; Woodward, P. *Chem. Commun.* **1971**, 1233–1234.

a metal-metal bond whereas molecules such as $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{COCH}_3\}_2)\text{Cl}_2$ and $(\text{Ph}_3\text{P})_2\text{Au}(\mu\text{-C}_2\{\text{CF}_3\}_2)$, which contain d^8 and d^{10} metal atoms, respectively, lack formal metal-metal bonds.

A number of different palladium compounds are known to catalyze the cyclotrimerization of acetylenes, and at least two distinct mechanisms have been demonstrated to be involved.²⁷ Catalysis by Pd(0) in the form of $\text{Pd}_2(\text{dba})_3$ (dba = dibenzylideneacetone) proceeds via the formation of a metal-locycle (8).¹³ On the other hand catalysis by palladium-



(II)-chloro complexes, particularly $(\text{PhCN})_2\text{PdCl}_2$, proceeds via initial insertion of the acetylenes into the Pd-Cl bond. This is followed by successive insertions of acetylenes into the vinylic Pd-C bonds. The mechanism of catalysis in the presence of $\text{Pd}_2(\text{dpm})_2\text{X}_2$ appears to proceed by a different route involving initial insertion into the Pd-Pd bond to give the acetylene adduct 3. Since we have demonstrated that this inserted acetylene may be incorporated into the final product of catalysis, it is possible that catalysis proceeds via successive insertions into the Pd-C bonds to give 9 and 10 as intermediates. A mechanism of this type would be akin to the acetylene addition products obtained from $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4$ (M = Cr, Mo) where stepwise addition of three acetylenes



across the metal-metal bond has been demonstrated.²⁸

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Registry No. 1, X = Cl, 64345-29-5; 1, X = Br, 60482-68-0; 1, X = I, 67477-87-6; 2, Y = S, X = Cl, 71171-39-6; 3, R = CO_2CH_3 , 71957-42-1; 3, R = $\text{CO}_2\text{CH}_2\text{CH}_3$, 77590-21-7; 3, R = CF_3 , 71957-44-3; 4, R = CO_2CH_3 , PF_6 salt, 77590-23-9; 5, 68228-56-8; 6, R = CH_3 , 64345-34-2; 6, R = C_6H_5 , 64345-38-6; 7, BPh_4 salt, 77590-25-1; 7, PF_6 salt, 77590-26-2; $\text{Pd}_2(\text{dam})_2(\mu\text{-C}_2\{\text{CF}_3\}_2)\text{Cl}_2$, 77590-27-3; $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Br}_2$, 77590-28-4; $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{I}_2$, 77590-29-5; $\text{Pd}_2(\text{dam})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$, 71957-43-2; $\text{Pd}_2(\text{dam})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_2\text{CH}_3\}_2)\text{Cl}_2$, 77590-30-8; $\text{Pd}_2(\text{dpm})_2(\mu\text{-HC}_2\{\text{CO}_2\text{CH}_3\})\text{Cl}_2$, 77590-31-9; $\text{Pd}_2(\text{dpm})_2(\mu\text{-HC}_2\{\text{CO}_2\text{H}\})\text{Cl}_2$, 77590-32-0; $\text{Pd}_2(\text{dam})_2\text{Cl}_2$, 67415-28-5; $\text{Pd}(\text{dpm})\text{I}_2$, 77462-40-9; $\text{Pd}_2(\text{dpm})_3$, 37266-95-8; dimethyl acetylenedicarboxylate, 762-42-5; hexamethyl mellitate, 6237-59-8; maleic anhydride, 108-31-6.

(27) Maitlis, P. M. *Acc. Chem. Res.* 1976, 9, 93-99.

(28) Know, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. J. *Chem. Soc., Chem. Commun.* 1978, 221-223.

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Ruthenium(II) Azophenol and Azonaphthol Complexes

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Bis(2,2'-bipyridine)(azophenol)- and bis(2,2'-bipyridine)(azonaphthol)ruthenium(II) complexes have been synthesized and characterized by their chromatographic behavior, conductivity, and visible-ultraviolet spectra. These Ru(II) azo ligand derivatives are of particular interest for the characterization of metal-azo protein complexes currently under investigation. A ligand-localized, bathochromically shifted absorption band at $18\,000\text{ cm}^{-1}$ (550 nm) is observed upon Ru(II) complexation of the azo ligands. Analogous behavior has been observed on complexation of azo dyes and azo proteins by Co(III), Co(II), and Zn(II).

Introduction

Methods for incorporating substitution-inert metal ions into proteins and peptides through azotyrosine and azohistidine derivatives are currently under investigation.²⁻⁵ Of primary interest have been metal ions with the low-spin d^6 configuration, in particular cobalt(III). Ruthenium(II) offers several potential advantages over cobalt(III) for the biological studies. Because Ru(II) forms particularly stable complexes with π -acid ligands, it is anticipated that Ru(II) will be more

specific than Co(III) for the azotyrosines and azohistidines present in the modified proteins. Ruthenium(II) complexes also offer the advantage of having significantly higher molar absorptivities than cobalt(III) complexes and thus should be detected more readily at the low concentrations generally encountered in biological studies. Finally, isomorphous replacement with heavy metals to establish the sign of real structure factors has been extensively applied in protein crystallography.⁶ The method that we have developed offers the possibility of systematizing the approach to isomorphous replacement, and Ru(II) has a distinct advantage over Co(III) due to its greater atomic number.

Model cobalt(III) azophenol complexes have provided essential information³⁻⁵ for the synthesis and characterization of the corresponding protein complexes.² This study reports

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(2) M. S. Urdea and J. I. Legg, *Biochemistry*, 18, 4984 (1979); M. S. Urdea and J. I. Legg, *J. Biol. Chem.*, 254, 11868 (1979); J. I. Legg, *Coord. Chem. Rev.*, 25, 103 (1978).

(3) J. I. Legg, K. Igi, G. J. Pielak, B. D. Warner, and M. S. Urdea, *ACS Symp. Ser.*, No. 119, 195 (1980); W. I. White and J. I. Legg, *J. Chromatogr.*, 124, 134 (1976).

(4) W. I. White and J. I. Legg, *J. Am. Chem. Soc.*, 97, 3937 (1975).

(5) W. I. White and J. I. Legg, *Bioinorg. Chem.*, 6, 163 (1976).

(6) D. C. Phillips, *Adv. Struct. Res. Diffr. Methods*, 2, 75 (1966).