Lewis Acid Catalysis of the Rearrangement of a Dipalladium Acetylene Adduct to a Vinylidene-Bridged Complex

Constanze Kluwe and Julian A. Davies*

Departments of Chemistry and Medicinal and Biological Chemistry, University of Toledo, Toledo, Ohio 43606

Received February 21, 1995[∞]

The crystallographically characterized vinylidene complex $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C-(SCH_3)_2)]$ (3); dppm = bis(diphenylphosphino)methane) was prepared by the reaction of $[Pd_2-Cl_2(\mu-dppm)_2]$ with CH₃SC=CSCH₃ in the presence of HBF₄·Et₂O as well as through an isomerization of the acetylene adduct $[Pd_2Cl_2(\mu-dppm)_2(\mu-CH_3SCCSCH_3)]$ (1) catalyzed by several Lewis acids. Treatment of the related acetylene adduct $[Pd_2Cl_2(\mu-dppm)_2(\mu-CH_3SCCSCH_3)]$ (2; dmpm = bis(dimethylphosphino)methane) with HBF₄·Et₂O yielded the tetranuclear palladium complex $[Pd_4(\mu-Cl)_2(\mu-dmpm)_2(\mu-SCH_3)_4][BF_4]_2$ (4), which was also characterized crystallographically.

Introduction

The products in the reactions of the metal-metalbonded dipalladium(I) complexes $[Pd_2Cl_2(\mu-dppm)_2]$ and $[Pd_2Cl_2(\mu-dmpm)_2]$ with acetylenes are typically 1,2dimetalated olefins (acetylene adducts) or 1,1-dimetalated olefins (vinylidene complexes).¹ The formation of the former is favored with acetylenes bearing electronwithdrawing groups, while formation of the latter involves an unusual 1,2-shift reaction. Such shift reactions may be observed in cases where heteroatomic groups (Cl, SR, NR₂, etc.) are involved.^{1c,2} It has been shown that coordination of acetylenes, including examples without electron-withdrawing substituents, to form 1,2-dimetalated olefins may be facilitated by acid catalysis.³ We recently reported that the HBF₄·Et₂Ocatalyzed reaction of $[Pd_2Cl_2(\mu-dppm)_2]$ and the unsymmetrically substituted acetylene CH₃SC=CCH₃ gave not an acetylene adduct but rather the vinylidene complex $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(CH_3)(SCH_3))]$, while without acid catalysis no reaction was observed. In contrast, the uncatalyzed reactions of $[Pd_2Cl_2(\mu-dppm)_2]$ and $[Pd_2-dppm]_2$ $Cl_2(\mu$ -dmpm)₂] with the symmetrical sulfur-substituted acetylene $CH_3SC = CSCH_3$ yielded the acetylene adducts $[Pd_2Cl_2(\mu-dppm)_2(\mu-CH_3SCCSCH_3)]$ (1) and $[Pd_2Cl_2(\mu-dppm)_2(\mu-CH_3SCCSCH_3)]$ $dmpm)_2(\mu$ -CH₃SCCSCH₃)] (2).⁴ Our results were opposite to those reported by Miller and Angelici^{2h} for the reactions of the mononuclear ruthenium(II) complex

 $[RuCl(P(CH_3)_3)_2Cp]$ with $CH_3SC \equiv CSCH_3$ and $CH_3-SC \equiv CCH_3$, in which a facile 1,2-migration of SCH_3 and formation of a vinylidene complex was observed only in the reaction with the symmetrical acetylene $CH_3-SC \equiv CSCH_3$.

We now report the synthesis of $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(SCH_3)_2)]$ (3) by reaction of $[Pd_2Cl_2(\mu-dppm)_2]$ and $CH_3SC=CSCH_3$ in the presence of $HBF_4\cdot Et_2O$ and through isomerization of 1 catalyzed by various Lewis acids, as well as the formation of $[Pd_4(\mu-Cl)_2(\mu-dmpm)_2-(\mu-SCH_3)_4][BF_4]_2$ (4) by treatment of 2 with $HBF_4\cdot Et_2O$. These results provide new insight into the role of Lewis acids in these types of reactions.

Experimental Section

General Procedures. All reactions were carried out under argon atmospheres using standard Schlenk techniques unless otherwise noted. The solvents were outgassed and freshly distilled under argon prior to use. Methylene chloride was distilled from calcium carbide. All other chemicals were used as received from commercial sources.

NMR spectra were recorded on Varian VXR-400 or Gemini-200 NMR spectrometers. The chemical shifts for the ¹H NMR spectra were referenced to internal $(CH_3)_4$ Si or to $(CH_3)_4$ Si *via* the signal resulting from the residual protons of the deuterated solvent; for ³¹P{¹H} NMR spectra, the shifts were referenced to external 85% H₃PO₄. The C, H, N analyses were carried out on a PE 2400 elemental analyzer.

The compounds $[Pd_2Cl_2(\mu-dppm)_2]$,⁵ $[Pd_2Cl_2(\mu-dmpm)_2]$,⁶ and CH₃SC=CSCH₃⁷ were prepared by following the literature procedures. $[Pd_2Cl_2(\mu-dppm)_2(\mu-CH_3SCCSCH_3)]$ (1) and $[Pd_2-Cl_2(\mu-dmpm)_2(\mu-CH_3SCCSCH_3)]$ (2) were prepared as described previously.⁴

 $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(SCH_3)_2)].$ (a) $[Pd_2Cl_2(\mu-dppm)_2]$ (126 mg, 0.12 mmol) was dissolved in CH₂Cl₂ (15 mL). CH₃-SC=CSCH₃ (22 μ L, 0.17 mmol) was first added slowly, dropwise, through a rubber septum with a syringe. Next, HBF₄Et₂O (1 μ L) was added. The solution was stirred for 48 h. Over this period of time the mixture had turned cloudy. After the

⁸ Abstract published in Advance ACS Abstracts, August 15, 1995. (1) (a) Lee, C.-L.; Hunt, C. T.; Balch, A. L. Inorg. Chem. **1981**, 20, 2498. (b) Balch, A. L.; Lee, C.-L.; Lindsay, C. H.; Olmstead, M. M. J. Organomet. Chem. **1979**, 177, C22. (c) Davies, J. A.; Pinkerton, A. A.; Syed, R.; Vilmer, M. J. Chem. Soc., Chem. Comm. **1988**, 47.

<sup>Organomet. Chem. 1373, 177, 022. (c) Davies, J. A., Finkerolli, A. A.;
Syed, R.; Vilmer, M. J. Chem. Soc., Chem. Comm. 1988, 47.
(2) (a) Horvath, I. T.; Palyi, G.; Marko, L. J. Chem. Soc., Chem.
Commun. 1979, 1054. (b) Horvath, I. T.; Palyi, G.; Marko, L.; Andretti,
G. D. Inorg. Chem. 1983, 22, 1049. (c) Löwe, C.; Hund, H.-U.; Berke,
H. J. Organomet. Chem. 1989, 371, 311. (d) Fogg, D. E.; MacLaughlin,
S. A.; Kwek, K.; Cherkas, A. A.; Taylor, N. J.; Carty, A. J. J. Organomet.
Chem. 1988, 352, C17. (e) Adams, R. D.; Chen, G.; Pompeo, M. P.; Yin,
J. Organometallics 1991, 10, 2541. (f) Adams, R. D.; Chen, G.; Chen,
L.; Yin, J. Organometallics 1993, 12, 2644. (g) Werner, H.; Baum, M.;
Schneider, D.; Windmüller, B. Organometallics 1994, 13, 1089. (h)
Miller, D. C.; Angelici, R. J. Organometallics 1991, 10, 79. (i) Bruce,
M. I. Chem. Rev. 1991, 91, 197.</sup>

⁽³⁾ Higgins, S. J.; Shaw, B. L. J. Chem. Soc., Chem. Commun. 1986, 1629.

⁽⁴⁾ Davies, J. A.; Kirschbaum, K.; Kluwe, C. Organometallics 1994, 13, 3664.

⁽⁵⁾ Balch, A. L.; Benner, L. S. Inorg. Synth. 1982, 21, 47.

⁽⁶⁾ Davies, J. A.; Dutremez, S.; Vilmer, M. J. Prakt. Chem. 1992, 334, 34.

⁽⁷⁾ Brandsma, L. Preparative Acetylene Chemistry; Elsevier: New York, 1971; p 92.

Table 1. X-ray Data for $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(SCH_3)_2)]$ (3) and $[Pd_4(\mu-Cl)_2 \ (\mu-dmpm)_2(\mu-SCH_3)_4][BF_4]_2 \cdot \frac{1}{2}CH_2Cl_2$ $(4 \cdot \frac{1}{2}CH_2Cl_2)$

	3	$4\cdot^{1/2}CH_{2}Cl_{2}$
formula	$Pd_2Cl_2P_4S_2C_{54}H_{50}$	$Pd_4Cl_2P_4S_4C_{14}B_2F_8H_{40}$. $^{1/2}CH_2Cl_2$
fw	1170.73	1173.19
F(000)	2368	1096
cryst dimens, mm	0.11 imes 0.10 imes 0.20	$0.30 \times 0.10 \times 0.03$
radiation (λ, \mathbf{A})	Μο Κα (0.710 73)	Μο Κα (0.710 73)
temp, K	150 ± 1	294 ± 1
space group	tetragonal, $P4_1$	triclinic, PĪ
a, Å	21.115(4)	11.799(2)
b, Å		12.256(3)
c, Å	14.368(2)	15.599(3)
a, deg		72.21(2)
β , deg		83.00(2)
γ, deg		67.29(2)
V, Å ³	6404 (3)	1981 (1)
Z	4	2
$D_{\rm calc},{ m g/cm^3}$	1.21	1.97
μ , cm ⁻¹	8.3	23.1
no. of params	531	336
R	0.049	0.055
$R_{\rm w}$	0.050	0.068
S	1.18	1.64
max resd	0.69	1.17
density, e/Å ³		

stirring was stopped, a light yellow solid settled immediately out of solution. It proved to be air stable and was isolated by filtration and washed with cold CH_2Cl_2 (5 mL). The yield was 92 mg (0.078 mmol, 65%). Anal. Calcd for $Pd_2P_4Cl_2S_2C_{54}H_{50}$: C, 55.42; H, 4.27. Found: C, 54.47; H, 4.15. NMR (CDCl₃): ¹H, δ 1.27 (6H, s, SCH₃), 6.9–8.1 (40H, m, C₆H₅), 2.8 (2H, m, PCH₂P), 3.0 (2H, m, PCH₂P); ${}^{31}P{}^{1}H$ }, δ 10.3 (s). (b) In an alternative synthesis, $[Pd_2Cl_2(\mu-dppm)_2(\mu-CH_3SCCSCH_3)]$ (1; 115 mg, 0.098 mmol) was dissolved in CH_2Cl_2 (10 mL). HBF₄·Et₂O (1 μ L) was added and the solution stirred for 48 h. A light yellow solid precipitated out of solution and was isolated by filtration. The yield was 85 mg (0.073 mmol, 74%). The signals in the recorded ³¹P{¹H} and ¹H NMR spectra of the isolated complex were in agreement with those described above. $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(SCH_3)_2)]$ (3) was also obtained in similar reactions where $[Pd_2Cl_2(\mu-dppm)_2(\mu-CH_3 SCCSCH_3$] (1) was treated with either catalytic amounts of BF₃·Et₂O or 1 equiv of [PtCl₂(cod)].

 $[\mathbf{Pd_4}(\mu-\mathbf{Cl})_2(\mu-\mathbf{dmpm})_2(\mu-\mathbf{SCH_3})_4][\mathbf{BF_4}]_2$. To a solution of $[\mathbf{Pd_2Cl_2}(\mu-\mathrm{dmpm})_2(\mu-\mathbf{CH_3SCCSCH_3})]$ (2) (30 mg, 0.044 mmol) in $\mathbf{CH_2Cl_2}$ (15 mL) was added $\mathbf{HBF_4}\cdot\mathbf{Et_2O}$ (3 μ L). The solution was stirred for 48 h. During this time the color of the solution changed from orange to yellow. Yellow crystals were grown by slow evaporation of $\mathbf{CH_2Cl_2}$. The isolated solid proved to be air stable.

X-ray Structure Determination. General Methods. A single crystal selected for data collection was mounted on a glass fiber in a random orientation. X-ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer in the $w-2\theta$ mode. Data were collected to a maximum 2θ of 52°. Lorentz and polarization corrections and an empirical absorption correction were applied to the data. The structure was refined by full-matrix least-squares methods where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weight w was defined as $4F_o^{2/\sigma^2}(F_o^2)$. Scattering factors were taken from the standard literature.⁸ Anomalous dispersion effects were included in F_c . The unweighted and weighted agreement factors are defined as $R = \Sigma ||F_o| - |F_c||\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma |F_o|^2)^{1/2}$. All calculations were performed on a VAX 3100 computer using MolEN.⁹

 $[\mathbf{Pd_2Cl_2}(\mu - \mathbf{dppm})_2(\mu - \sigma \cdot \mathbf{C} = \mathbf{C}(\mathbf{SCH_3})_2)]$. Yellow single crystals were grown by slow evaporation of the solvent, methylene chloride. The tetragonal unit cell constants and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $7 \le \theta \le 13^{\circ}$. As a check on crystal stability the intensities of three representative reflections were measured every 60 min, indicating a total loss in intensity of 4.0%. An anisotropic decay correction was applied with correction factors on I in the range from 0.954 to 1.187. A total of 6888 reflections were collected, of which 6523 were unique. Intensities of equivalent reflections were averaged; the agreement factors were 5.8% based on I and 4.4% based on F_{\circ} . A total of 3310 reflections with $F_{\circ}^2 \ge 3.0\sigma(F_{\circ}^2)$ were used in the calculations,

Structure Solution and Refinement. The positions of the two Pd atoms in the asymmetric unit were found by direct methods. The remaining atoms were located by repeated least-squares refinements followed by difference Fourier syntheses. The positions of the hydrogen atoms were calculated and included in the least-squares refinement as riding atoms; $U_{\rm iso} = 1.3[U_{\rm eq}({\rm bonding atom})]$. The carbon atoms C(5), C(10), C(15), C(24), C(47), C(50), C(52), C(53), and C(54) were refined with isotropic thermal parameters. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The final cycle of refinement included 531 variable parameters and converged with R = 0.049 and $R_{\rm w} = 0.050$. Further details relevant to the data collection and structure refinements are given in Table 1.

 $[\mathbf{Pd_4}(\mu-\mathbf{Cl})_2(\mu-\mathbf{dmpm})_2(\mu-\mathbf{SCH_3})_4][\mathbf{BF_4}]_2^{1/2}\mathbf{CH_2Cl_2}$. Yellow single crystals were grown by slow evaporation of the solvent, methylene chloride. The triclinic unit cell constants and the orientation matrix for data collection were obtained from leastsquares refinement, using the setting angles of 25 reflections in the range $7 \le \theta \le 15^{\circ}$. As a check on crystal stability the intensities of three representative reflections were measured every 60 min, indicating a total loss in intensity of 3.8%. An anisotropic decay correction was applied with correction factors on I in the range from 0.960 to 1.093. A total of 8158 reflections were collected, of which 7752 were unique. Intensities of equivalent reflections were averaged; the agreement factors were 2.8% based on I and 2.3% based on F_0 . A total of 3158 reflections with $F_0^2 \ge 3.0\sigma(F_0^2)$ were used in the calculations.

Structure Solution and Refinement. The positions of the four Pd atoms in the asymmetric unit were found by direct methods. The remaining atoms were located by repeated leastsquares refinements followed by difference Fourier syntheses. The positions of the hydrogen atoms of the tetranuclear palladium complex were calculated and included in the leastsquares refinement as riding atoms; $U_{iso} = 1.3[U_{eq}(bonding$ atom)]. All non-hydrogen atoms of the tetranuclear palladium complex were refined with anisotropic thermal parameters. For both BF_4^- anions each fluorine was found to be equally disordered over two positions. All atoms of the anions were refined with isotropic thermal parameters. Highly disordered solvent was also found in the asymmetric unit. The model refined contained 1/2 equiv of CH2Cl2 per tetranuclear palladium complex disordered over four positions. The positions of the non-hydrogen atoms were found in the difference Fourier map and fixed during refinements (Cl(a) to Cl(h), C(21) to C(23)). The isotropic thermal parameters were refined; hydrogen positions were not calculated. The final cycle of refinement included 336 variable parameters and converged with R = 0.055 and $R_w = 0.068$. Further details relevant to the data collection and structure refinements are given in Table 1.

Results and Discussion

Syntheses of $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(SCH_3)_2)]$ (3). Stirring a solution of $[Pd_2Cl_2(\mu-dppm)_2]$ in CH_2Cl_2

⁽⁸⁾ Cromer, D. T.; Waber, J. T. International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(9) Fair, C. K.; MolEN: An Interactive Intelligent System for Crystal Structure Analysis; User Manual; Enraf-Nonius: Delft, The Netherlands, 1990.



Figure 1. ORTEP diagram of $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C-(SCH_3)_2)]$ (3), showing 50% probability thermal ellipsoids.

with excess CH₃SC=CSCH₃ in the presence of a small amount of HBF₄·Et₂O under an inert atmosphere over a period of 48 h yielded a light yellow solid which settled from solution and proved to be air stable. The ³¹P{¹H} NMR spectrum of the complex in CDCl₃ showed a singlet at 10.3 ppm. The ¹H NMR spectrum (CDCl₃) included a singlet for the methyl protons at 1.27 ppm. This chemical shift was very similar to that of 1.17 ppm found for the methyl protons in [Pd₂Cl₂(μ -dppm)₂(μ -CH₃SCCSCH₃)] (1) (cf. 2.37 ppm for the free acetylene).

The same complex, **3**, could also be obtained from the reaction of **1** with HBF₄·Et₂O in CH₂Cl₂. If very small (catalytic) amounts of acid were used, only one product, **3**, was formed and the reaction was slow. When the amount of acid was increased, the reaction proceeded faster, but the formation of side products, including the mononuclear complex [PdCl₂(dppm)], was observed.

Single crystals suitable for X-ray analysis were grown by slow evaporation of the solvent CH_2Cl_2 . The X-ray crystal structure determination revealed that a symmetrical vinylidene complex (3; Figure 1) had been formed by rearrangement of the acetylene adduct, 1. The two palladium atoms in **3** were held together by two mutually *trans* dppm ligands. The vinylidene moiety lay in the equatorial plane. Palladium exhibited an approximate square-planar coordination geometry which was completed by two terminal chloride ligands. The α -carbon (C(1)) of the vinylidene moiety symmetrically bridged the two palladium atoms. The β -carbon (C(2)) was disubstituted with two SCH₃ groups (for significant bond lengths and bond angles refer to Table 2).

The rearrangement of 1 to 3 was also observed in the presence of other Lewis acids $(BF_3 \cdot Et_2O \text{ and } [PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene)) under similar conditions (Scheme 1). These results show that Lewis acids not only facilitate the insertion of acetylenes into palladium-palladium bonds as reported previously³ but also catalyze the rearrangement of heteroatom-substituted acetylene adducts to the vinylidene isomers. This catalytic rearrangement has, to our knowledge, not been observed previously.

In terms of mechanism, it seemed possible that the Lewis acid (e.g. H^+) coordinates to sulfur in the initiating step. The possibility of a subsequent carbon-sulfur bond cleavage, elimination of CH₃SH, and formation of

Table 2. Selected Bond Angles and Distances for $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(SCH_3)_2)]$ (3)

(a) Bond Angles (deg)				
Cl(1) - Pd(1) - P(1)	92.5(1)	Cl(2) - Pd(2) - P(3)	95.0 (1)	
Cl(1) - Pd(1) - P(2)	95.3(1)	Cl(2) - Pd(2) - P(4)	92.4(1)	
Cl(1) - Pd(1) - C(1)	178.4(4)	Cl(2) - Pd(2) - C(1)	177.7(4)	
P(1) - Pd(1) - P(2)	172.1(1)	P(3) - Pd(2) - P(4)	171.8(2)	
P(1) - Pd(1) - C(1)	88.8(4)	P(3) - Pd(2) - C(1)	86.2(4)	
P(2) - Pd(1) - C(1)	83.5(4)	P(4) - Pd(2) - C(1)	86.3(4)	
Pd(1)-C(1)-Pd(2)	110.2(7)	S(1)-C(2)-S(2)	119.9(8)	
Pd(1) - C(1) - C(2)	122(1)	S(1)-C(2)-C(1)	118(1)	
Pd(2) - C(1) - C(2)	127(1)	S(2)-C(2)-C(1)	122(1)	
(h) Distances (Å)				
(D) Distances (A)				
Pd(I) - Cl(I)	2.412(3)	Pd(2) - Cl(2)	2.401(4)	
Pd(1) - P(1)	2.308(4)	Pd(2) - P(3)	2.330(4)	
Pd(1) - P(2)	2.333(4)	Pd(2) - P(4)	2.302(4)	
Pd(1) - C(1)	2.00(1)	Pd(2) - C(1)	1.96(1)	
S(1)-C(2)	1.79(2)	S(2) - C(2)	1.76(1)	
C(1) - C(2)	1.35(2)	$Pd(1) \cdot \cdot \cdot Pd(2)$	3.245(1)	

a σ,π -acetylide intermediate was considered. To test this possibility, the rearrangement of 1 to 3 was performed in the presence of excess EtSH and, in other experiments, excess PhSH and CH₃OH in order to attempt trapping of a σ, π -acetylide intermediate by external nucleophiles. Such a process would generate an unsymmetrical vinylidene complex by addition to the β -carbon, while readdition of CH₃SH would generate the symmetrical vinylidene complex 3. In all cases 3 was the only reaction product. In low-temperature ${}^{31}P{}^{1}H{}$ NMR studies (CD_2Cl_2), performed at -60 °C, no evidence of a σ,π -acetylide intermediate could be found and it was not possible to characterize any other intermediate. The experimental results thus did not support the possibility of a rearrangement via a σ,π -acetylide formed by elimination of CH₃SH. However, for the uncatalyzed reactions of the terminal alkynes acetylene and phenylacetylene with $[Ir_2I_2(CO)(\mu-CO)(\mu-dppm)_2]$ Xiao and Cowie¹⁰ suggested that the rearrangement of the acetylene adduct to the vinylidene complex proceeded via a hydrido-acetylide intermediate. Previous theoretical calculations by Hoffmann and Silvestre¹¹ had shown that a concerted mechanism for a 1,2-hydride shift was unlikely for a binuclear complex, while the isomerization via an acetylide-hydride intermediate was feasible. In the present case an analogous mechanism would involve initial transfer of the SCH₃ group, presumably following protonation, from carbon to palladium. Indeed, formation of free CH₃SH is unlikely on the basis of results of experiments in the presence of added nucleophiles and the fact that the boiling point of CH₃SH is so low that free CH₃SH would be lost from solution. We note, however, that no intermediate analogous to that proposed by Xiao and Cowie was observed in low-temperature NMR studies (see above).

A CH₂Cl₂ solution of **3** was treated with HBF₄·Et₂O, and a bright orange solution was obtained. The ³¹P-{¹H} NMR spectrum of the reaction solution in CDCl₃ exhibited a signal at 8.3 ppm (cf. **3**: 10.3 ppm). The ¹H NMR spectrum included a resonance at 1.88 ppm which was assigned to the methyl protons (cf. **3**: 1.27 ppm). The magnitude of the downfield shift was in agreement with that observed after protonation of (CH₃)₂S with HBF₄·Et₂O (from 2.04 to 2.69 ppm). These data suggested that protonation occurred on the sulfur atoms

⁽¹⁰⁾ Xiao, J.; Cowie, M. Organometallics 1993, 12, 463.

⁽¹¹⁾ Hoffmann, R.; Silvestre, J. Helv. Chim. Acta 1985, 68, 1461.



of the vinylidene moiety. Attempts to obtain crystals suitable for X-ray diffraction have thus far been unsuccessful.

Reaction of [Pd₂Cl₂(\mu-dmpm)₂(\mu-CH₃SCCSCH₃)] (2) with HBF₄·Et₂O. Addition of catalytic amounts of acid led only to the recovery of 2. However, addition of about ¹/₂ equiv of HBF₄·Et₂O to 2 in CH₂Cl₂ followed by stirring for 48 h led to a change in the color of the solution from orange to yellow. The ³¹P{¹H} NMR spectrum (CDCl₃) of the reaction solution showed a complex set of multiplets. Slow evaporation of the solvent CH₂Cl₂ from the reaction mixture yielded yellow crystals suitable for X-ray analysis. The isolated crystals proved to be a tetranuclear palladium complex (4; Figure 2). The four palladium atoms occupied a plane. Two long and two short palladium–palladium distances were found. These short metal–metal distances (Pd-



Figure 2. ORTEP diagram of $[Pd_4(\mu-Cl)_2(\mu-dmpm)_2(\mu-SCH_3)_4][BF_4]_2$ (4), showing 50% probability thermal ellipsoids.

Table 3. Selected Bond Angles and Distances for $[Pd_4(\mu-Cl)_2(\mu-dmpm)_2(\mu-SCH_3)_4][BF_4]_2 \cdot 1/_2CH_2Cl_2 (4 \cdot 1/_2CH_2Cl_2)$

Vinylidene Complex

(a) Bond Angles (deg)			
Cl(2) - Pd(1) - S(2)	96.5(2)	Cl(1) - Pd(3) - S(1)	84.3(2)
Cl(2) - Pd(1) - S(3)	84.1(2)	Cl(1) - Pd(3) - S(2)	97.5(2)
Cl(2) - Pd(1) - P(3)	173.9(1)	Cl(1) - Pd(3) - P(2)	174.5(2)
S(2) - Pd(1) - S(3)	171.0(2)	S(1) - Pd(3) - S(2)	175.1(2)
S(2) - Pd(1) - P(3)	86.2(2)	S(1) - Pd(3) - P(2)	90.4(2)
S(3) - Pd(1)P(3)	94.2(2)	S(2) - Pd(3) - P(2)	87.9(2)
Cl(1) - Pd(2) - S(1)	84.2(2)	Cl(2) - Pd(4) - S(3)	84.2(2)
Cl(1) - Pd(2) - S(4)	96.6(2)	Cl(2) - Pd(4) - S(4)	96.5(2)
Cl(1) - Pd(2) - P(1)	175.3(1)	Cl(2) - Pd(4) - P(4)	174.4(1)
S(1) - Pd(2) - S(4)	171.2(1)	S(3) - Pd(4) - S(4)	173.4(2)
S(1) - Pd(2) - P(1)	92.5(2)	S(3) - Pd(4) - P(4)	92.3(2)
S(4) - Pd(2) - P(1)	87.2(2)	S(4) - Pd(4) - P(4)	87.5(2)
Pd(2) - Cl(1) - Pd(3)	77.5(1)	Pd(1)-S(2)-Pd(3)	85.4(2)
Pd(1)-Cl(2)-Pd(4)	78.7(1)	Pd(1)-S(3)-Pd(4)	81.9(1)
Pd(2) - S(1) - Pd(3)	80.6(1)	Pd(2)-S(4)-Pd(4)	86.2(2)
	(b) Dista	nces (Å)	
$Pd(1) \cdot \cdot \cdot Pd(4)$	3.053(2)	Pd(3)-Cl(1)	2.416(5)
Pd(1)-Cl(2)	2.407(5)	Pd(3) - S(1)	2.338(5)
Pd(1) - S(2)	2.326(5)	Pd(3) - S(2)	2.333(5)
Pd(1) - S(3)	2.333(5)	Pd(3) - P(2)	2.220(5)
Pd(1) - P(3)	2.230(5)	Pd(4)-Cl(2)	2.408(5)
$Pd(2) \cdot \cdot \cdot Pd(3)$	3.027(2)	Pd(4) - S(3)	2.326(5)
Pd(2)-Cl(1)	2.418(5)	Pd(4) - S(4)	2.344(4)
Pd(2) - S(1)	2.340(6)	Pd(4) - P(4)	2.231(6)
Pd(2) - S(4)	2.326(5)	$Pd(1) \cdot \cdot \cdot Pd(3)$	3.161(1)
Pd(2) - P(1)	2.244(5)	$Pd(2) \cdot \cdot \cdot Pd(4)$	3.192(2)

(1) $\cdot \cdot \cdot Pd(4) = 3.053(2) \text{ Å}, Pd(2) \cdot \cdot \cdot Pd(3) = 3.027(2) \text{ Å})$ were supported by two bridging chloride ligands, while the long distances (Pd(1) $\cdot \cdot \cdot Pd(3) = 3.161(1) \text{ Å}, Pd (2) \cdot \cdot \cdot Pd(4) = 3.192(2) \text{ Å})$ result from bridging by two dmpm ligands. The metal-metal distances for the chloro-/mercapto-bridged moieties {Pd₂X₄(μ -Cl)(μ -SMe)} were unusually short compared with palladium-palladium separations in analogous dinuclear palladium-(II) complexes (e.g. cis-[Pd₂Cl₂(μ -Cl)(μ -SEt)(PMe₂Ph)₂],¹² 3.234(1) Å; cis-[Pd₂Cl₂(μ -Cl)(μ -SMe)(PMe₃)₂],¹³ 3.294(4)

⁽¹²⁾ Jain, V. K.; Patel, R. P.; Muralidharan, K. V.; Bohra, R. Polyhedron 1989, 8, 2151.

Table 4. Positional Parameters and B_{eq} Values for $[Pd_2Cl_2(\mu-dppm)_2(\mu-\sigma-C=C(SCH_3)_2)] (3)$

atom	x	У	Z	B (Å ²) ^a
Pd(1)	0.48591(5)	0.22249(5)	0.983	1.28(2)
Pd(2)	0.56674(5)	0.11507(5)	1.09281(9)	1.39(2)
Cl (1)	0.3898(2)	0.2841(2)	0.9781(3)	2.20(7)
Cl(2)	0.5710(2)	0.0439(2)	1.2229(3)	2.49(8)
S(1)	0.6889(2)	0.1496(2)	0.9447(3)	2.09(8)
S(2)	0.5960(2)	0.2168(2)	0.8136(3)	2.15(8)
$\mathbf{P}(1)$	0.4404(2)	0.1395(2)	0.9032(3)	1.44(8)
$\mathbf{P}(2)$	0.5453(2)	0.2994(2)	1.0607(3)	1.30(7)
$\mathbf{P}(3)$	0.5281(2)	0.0399(2)	0.9885(3)	1.49(7)
$\mathbf{P}(4)$	0.6108(2)	0.1965(2)	1.1774(3)	1.69(8)
$\mathbf{C}(1)$	0.5669(6)	0.1737(6)	0.987(1)	1.7(3)
$\mathbf{C}(2)$	0.6110(7)	0.1779(6)	0.919(1)	1.9(3)
C(3)	0.7086(7)	0.1043(7)	0.842(1)	3.2(4)
C(4)	0.6607(7)	0.2717(7)	0.794(1)	3.3(4)
C(5)	0.4930(6)	0.0718(6)	0.8822(9)	1.3(3)*
C(6)	0.6178(6)	0.2700(6)	1.1123(9)	1.5(3)
$\mathbf{C}(7)$	0.3712(6)	0.1055(6)	0.962(1)	1.6(3)
C(8)	0.3506(6)	0.1282(7)	1.045(1)	2.1(3)
C(9)	0.2987(7)	0.1021(8)	1.088(1)	3.5(4)
C(10)	0.2685(7)	0.0508(7)	1.049(1)	3.1(3)*
$\mathbf{C}(11)$	0.2906(7)	0.0258(7)	0.967(1)	3.3(4)
C(12)	0.3413(7)	0.0522(7)	0.920(1)	2.9(4)
C(13)	0.4105(6)	0.1583(6)	0.787(1)	1.7(3)
C(14)	0.3540(6)	0.1894(6)	0.779(1)	21(3)
C(15)	0.3276(7)	0.2049(7)	0.696(1)	$2.2(3)^{*}$
C(16)	0.3614(7)	0.1907(7)	0.615(1)	3.3(4)
C(17)	0.4174(7)	0.1604(7)	0.625(1)	2.9(4)
C(18)	0.4426(7)	0.1452(6)	0.707(1)	1.8(3)
C(19)	0.5067(6)	0.3433(6)	1.154(1)	1.6(3)
C(20)	0.5376(7)	0.3937(6)	1.194(1)	21(3)
C(21)	0.5124(7)	0.4254(6)	1.271(1)	2.6(4)
$\tilde{C}(22)$	0.4553(7)	0.4035(7)	1.307(1)	2.6(3)
C(23)	0.4268(7)	0.3539(7)	1.268(1)	2.7(4)
C(24)	0.4494(6)	0.3218(6)	1,1907(9)	1.3(3)*
C(25)	0.5741(6)	0.3604(6)	0.981(1)	1.8(3)
C(26)	0.5395(6)	0.3744(6)	0.900(1)	2.0(3)
C(27)	0.5591(7)	0.4177(7)	0.837(1)	2.9(3)
C(28)	0.6160(7)	0.4486(6)	0.852(1)	2.8(4)
C(29)	0.6522(7)	0.4356(7)	0.926(1)	2.3(3)
C(30)	0.6315(6)	0.3925(6)	0.991(1)	1.7(3)
C(31)	0.5906(7)	-0.0111(6)	0.945(1)	1.9(3)
C(32)	0.6436(6)	-0.0206(7)	1.002(1)	2.4(3)
C(33)	0.5906(7)	-0.0374(6)	0.856(1)	2.9(4)
C(34)	0.6389(6)	-0.0757(6)	0.827(1)	2.4(3)
C(35)	0.6905(7)	-0.0861(8)	0.884(1)	3.7(4)
C(36)	0.6931(6)	-0.0584(7)	0.970(1)	2.7(3)
C(37)	0.4693(6)	-0.0176(6)	1.0287(9)	1.4(3)
C(38)	0.4378(7)	-0.0071(7)	1.114(1)	2.3(3)
C(39)	0.4552(6)	-0.0723(6)	0.979(1)	2.1(3)
C(40)	0.4109(7)	-0.1135(7)	1.011(1)	2.9(4)
C(41)	0.3805(7)	-0.1017(7)	1.092(1)	3.1(4)
C(42)	0.3934(7)	-0.0483(7)	1.144(1)	2.4(3)
C(43)	0.5671(7)	0.2180(7)	1.280(1)	2.0(3)
C(44)	0.5105(7)	0.1894(7)	1.300(1)	2.6(3)
C(45)	0.4744(7)	0.2062(7)	1.379(1)	3.1(4)
C(46)	0.4963(7)	0.2535(7)	1.436(1)	2.9(4)
C(47)	0.5529(7)	0.2838(8)	1.417(1)	3.1(4)*
C(48)	0.5881(7)	0.2660(6)	1.341(1)	2.3(3)
C(49)	0.6914(6)	0.1829(6)	1.217(1)	2.3(3)
C(50)	0.7438(7)	0.2092(7)	1.180(1)	2.3(3)*
C(51)	0.8026(7)	0.1963(7)	1.209(1)	3.3(4)
C(52)	0.814(1)	0.1563(9)	1.275(1)	5.6(5)*
C(53)	0.762(1)	0.131(1)	1.327(2)	10.2(8)*
C(54)	0.700(1)	0.142(1)	1.291(2)	7.2(6)*

^a Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\frac{4}{3}[a^2B(1,1)] +$ $b^2 B(2,2) + c^2 B(3,3) + ab(\cos \gamma) B(1,2) + ac(\cos \beta) B(1,3) + bc(\cos \beta) B(1,3)$ $\alpha)B(2,3)].$

A) but too long for palladium-palladium bonding interactions. The metal-metal distances for the dmpm-/mercapto-bridged moieties $\{Pd_2X_4(\mu-dmpm)(\mu-SMe)\}$ were in the range observed for related A-frame complexes containing dmpm ligands (e.g. $[Pd_2Cl_2(\mu-CO)(\mu-CO)]$

Table 5. Positional Parameters and B_{eq} Values for $[Pd_4(\mu-Cl)_2(\mu-dmpm)_2(\mu-SCH_3)_4][BF_4]_2^{,1/2}CH_2Cl_2$

		$(4\cdot 1/2CH_2CI)$.2)	
atom	X	У	z	$B~({ m \AA}^2)^a$
Pd(1)	0.0464(1)	0.2007(1)	0.74289(8)	3.04(3)
Pd(2)	0.4305(1)	0.0818(1)	0.83574(9)	3.32(3)
Pd(3)	0.2946(1)	-0.0295(1)	0.75654(9)	3.17(3)
Pd(4)	0.1818(1)	0.3170(1)	0.82026(9)	3.25(3)
Cl(a)	0.219	0.453	0.045	14(3)*
Cl(b)	0.002	0.589	-0.045	9(2)*
Cl(d)	0.142	0.549	-0.002	16(3)*
Cl(c)	-0.138	0.537	-0.021	7(1)*
Cl(e)	0.562	0.404	1.003	7(1)*
CI(f)	0.314	0.639	1.038	8(1)*
Cl(g)	-0.051	0.488	-0.020	12(2)*
	0.187	0.469	0.020	$10(2)^{*}$
Cl(1)	0.3404(4)	-0.0693(4)	0.9125(3)	4.1(1)
Cl(2)	0.0522(4)	0.2050(4)	0.8955(3)	41(1)
$\mathbf{S}(1)$	0.4947(4)	-0.0313(4)	0.7304(3)	4.0(1)
$\mathbf{S}(2)$	0.0891(4)	-0.0096(4)	0.7764(3)	3.6(1)
$\tilde{S}(3)$	0.0368(4)	0.4034(4)	0.7061(3)	3.9(1)
S(4)	0.3413(4)	0.2137(4)	0.9258(3)	3.8(1)
$\mathbf{P}(1)$	0.5282(4)	0.2101(4)	0.7632(3)	3.7(1)
P(2)	0.2716(4)	0.0023(5)	0.6107(3)	4.2(1)
P(3)	0.0197(4)	0.2095(4)	0.60107(3)	32(1)
P(4)	0.2856(5)	0.4372(5)	0.7483(4)	5.0(1)
F(1)	0.017(2)	0.809(2)	0.649(2)	7.0(6)*
F(2)	-0.188(2)	0.830(2)	0.643(1)	6.0(5)*
F(3)	-0.071(2)	0.768(2)	0.770(2)	6 6(6)*
F(4)	-0.166(3)	0.957(3)	0.705(2)	12(1)*
F(5)	-0.115(2)	0.850(2)	0.774(2)	9.5(8)*
F(6)	-0.165(3)	0.965(3)	0.643(2)	10.4(9)*
F(7)	-0.005(2)	0.864(2)	0.633(2)	6.3(6)*
F(8)	-0.141(2)	0.769(2)	0.663(2)	7.0(6)*
F(9)	0.361(3)	0.333(3)	0.434(2)	10.8(9)*
F(10)	0.501(4)	0.399(4)	0.411(3)	16(1)*
F(11)	0.331(3)	0.548(3)	0.369(2)	9.6(8)*
F(12)	0.443(2)	0.394(2)	0.309(2)	7.0(6)*
F(13)	0.285(2)	0.424(2)	0.443(2)	8.7(7)*
F(14)	0.477(2)	0.429(2)	0.437(1)	6.0(5)*
F(15)	0.326(2)	0.549(2)	0.326(2)	8.6(7)*
F(16)	0.387(3)	0.346(3)	0.347(2)	9.8(8)*
C(1)	0.115(1)	0.071(1)	0.572(1)	3.1(4)
C(2)	0.057(1)	-0.069(2)	0.894(1)	4.9(5)
C(3)	0.552(2)	0.226(1)	0.645(1)	5.1(5)
C(4)	0.590(2)	-0.185(2)	0.786(1)	5.6(6)
C(5)	0.451(1)	0.365(1)	0.771(1)	4.6(5)
C(6)	0.674(1)	0.165(2)	0.811(1)	5.3(5)
C(7)	-0.134(1)	0.221(2)	0.584(1)	6.2(6)
C(8)	0.046(2)	0.333(2)	0.514(1)	5.9(6)
C(9)	0.289(2)	0.128(2)	1.030(1)	5.1(6)
C(10)	-0.104(2)	0.485(2)	0.756(1)	7.2(7)
C(11)	0.245(2)	0.574(2)	0.782(2)	9(1)
C(12)	0.276(2)	0.493(2)	0.631(1)	10.1(9)
U(13)	0.333(2)	-0.136(2)	0.579(2)	10.1(9)
U(14)	0.343(2)	0.104(2)	0.538(1)	8.8(8)
\cup (21)	0.441	0.496	1.083	$0(2)^{*}$
$\cup(22)$	0.066	0.453	0.045	$3(1)^{*}$
U(23)	0.018	0.487	0.019	7(5)*
B(1)	-0.102(2)	0.842(2)	0.685(2)	5.5(6)*
Б (2)	0.390(2)	0.428(2)	0.388(2)	7.0(7)*

^a Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\frac{4}{3}[a^2B(1,1) +$ $b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \beta)B(1,3)$ $\alpha)B(2,3)].$

 $dmpm)_2$],¹⁴ 3.171(1) Å) and also excluded support by palladium-palladium bonding. The nearly squareplanar coordination environment around each palladium center was completed by four bridging SCH₃ groups. The tetranuclear palladium complex was found to be a dication. Two BF_4^- counterions were found in

⁽¹³⁾ Padilla, E. M.; Golen, J. A.; Richmann, P. N.; Jensen, C. M. Polyhedron 1991, 10, 1343.
(14) Kullberg, M. L.; Kubiak, C. P. Inorg. Chem. 1986, 25, 26.



the asymmetric unit. A vinylidene complex could not be isolated from this reaction (refer to Scheme 2). **Conclusions.** Our results indicated that Lewis acids not only facilitate the formation of acetylene adducts by protonation of the metal-metal bond, as described earlier,³ but also catalyze certain 1,2-heteroatom shift reactions and the formation of vinylidene complexes. The mechanism of the isomerization is the subject of further investigation. Formation of the tetranuclear palladium complex upon treatment of **2** with HBF₄·Et₂O supports the proposal that an early step in the reaction of dipalladium adducts of sulfur-substituted acetylenes with Lewis acids is C-S bond cleavage.

Acknowledgment. We are grateful to Dr. Bruce Cheesman for his assistance in the low-temperature NMR studies. The financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged. X-ray facilities were provided by the College of Arts and Sciences Instrumentation Center.

Supporting Information Available: Tables of crystal data and intensity measurement and structure solution details, thermal parameters, and all bond distances and angles for **3** and **4** (16 pages). Ordering information is given on any current masthead page.

OM950135R