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Reactions of Dimeric Palladium(I) Complexes with Sulfur-Substituted Acetylenes: 1,2-Heteroatomic Shift Reactions versus Adduct Formation. X-ray Crystal Structures of [Pd$_2$Cl$_2$(μ-dppm)$_2$(μ-CH$_3$SCCSCH$_3$)]·CH$_2$Cl$_2$, [Pd$_2$Cl$_2$(μ-dmpm)$_2$(μ-CH$_3$SCCSCH$_3$)], and [Pd$_2$Cl$_2$(μ-dppm)$_2$(μ-σ-C=C(CH$_3$)(SCH$_3$))]

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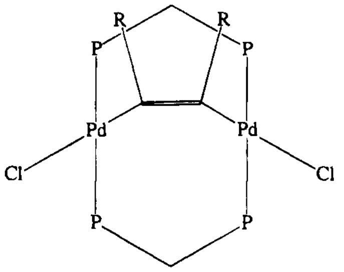
The palladium(I) complexes [Pd$_2$Cl$_2$(μ-dppm)$_2$] (dppm = bis(diphenylphosphino)methane) and [Pd$_2$Cl$_2$(μ-dmpm)$_2$] (dmpm = bis(dimethylphosphino)methane) have been shown to react with the symmetrical sulfur-substituted acetylene CH$_3$SC≡CSCH$_3$ to yield [Pd$_2$Cl$_2$(μ-dppm)$_2$(μ-CH$_3$SCCSCH$_3$)], **1**, and [Pd$_2$Cl$_2$(μ-dmpm)$_2$(μ-CH$_3$SCCSCH$_3$)], **2**. The acid-catalyzed reaction of the unsymmetrically substituted acetylene, CH$_3$SC≡CCH$_3$, with [Pd$_2$Cl$_2$(μ-dppm)$_2$] led to the formation of the bridged vinylidene complex [Pd$_2$Cl$_2$(μ-dppm)$_2$(μ-σ-C=C(CH$_3$)(SCH$_3$))], **3**, *via* a formal 1,2-shift of the heteroatomic group. The structures of complexes **1**·CH$_2$Cl$_2$, **2**, and **3** have been determined by X-ray crystallography.

Introduction

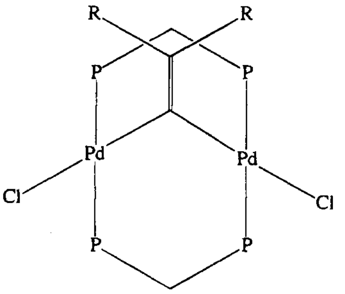
The metal–metal bonded dipalladium(I) complexes [Pd$_2$Cl$_2$(μ-dppm)$_2$] and [Pd$_2$Cl$_2$(μ-dmpm)$_2$] are known to react with acetylenes to form either 1,2-dimetalated olefins (acetylene adducts, type A) by coordination[1] or 1,1-dimetalated olefins (vinylidene complexes, type B) *via* 1,2-shift reactions[2] (Chart 1). Coordination of an acetylene may be facilitated by acid catalysis.[3] While there are many examples of metal-assisted transformations of terminal alkynes into vinylidene ligands,[4] there are only a few cases of 1,2-shifts that involve heteroatomic groups[2,5–9] in general and, to the best of our knowledge, only one example that involves a sulfur group. Miller and Angelici[10] have reported the formation of a vinylidene complex *via* a 1,2-SCH$_3$ shift in the reaction of the mononuclear complex [RuCl(P(CH$_3$)$_3$)$_2$-Cp] with CH$_3$SC≡CSCH$_3$.

In this paper we describe the syntheses of the acetylene adducts [Pd$_2$Cl$_2$(μ-dppm)$_2$(μ-CH$_3$SCCSCH$_3$)], **1**, and [Pd$_2$Cl$_2$(μ-dmpm)$_2$(μ-CH$_3$SCCSCH$_3$)], **2**, and also report the formation of the vinylidene complex [Pd$_2$Cl$_2$(μ-dppm)$_2$(μ-σ-C=C(CH$_3$)(SCH$_3$))], **3**, in an acid-catalyzed reaction of CH$_3$SC≡CCH$_3$ with the dinuclear palladium(I) complex [Pd$_2$Cl$_2$(μ-dppm)$_2$], *via* a formal 1,2-shift of the sulfur group. The X-ray crystal structures of **1**·CH$_2$Cl$_2$, **2**, and **3** are reported.

Chart 1



Type A



Type B

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, and hexane, from sodium metal. All other chemicals were used as received from commercial sources.

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NMR spectra were recorded on Varian VXR-400 or Gemini-200 NMR spectrometers. The chemical shifts for the ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal $(CH_3)_4Si$ or to $(CH_3)_4Si$ *via* the signal resulting from the residual protons of the deuterated solvent and for $^{31}P\{^1H\}$ NMR spectra to external 85% H_3PO_4. The C, H, N analyses were carried out on a PE 2400 elemental analyzer.

The compounds $[Pd_2Cl_2(\mu\text{-dppm})_2]$,[11] $[Pd_2Cl_2(\mu\text{-dmpm})_2]$,[12] $CH_3SC\equiv CCH_3$,[13] and $CH_3SC\equiv CSCH_3$[14] were prepared by following the literature procedures.

$[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]\cdot CH_2Cl_2$. To methylene chloride (20 mL) in a 50-mL Schlenk flask was added $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (119 mg, 0.113 mmol). $CH_3SC\equiv CSCH_3$ (0.05 mL, 0.482 mmol, 4.25-fold excess) was added slowly, dropwise, through a rubber septum with a syringe. The solution was refluxed for 3.5 h. After about 20 min the orange solution started to turn red. After further overnight stirring, a $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed that all $[Pd_2Cl_2(\mu\text{-dppm})_2]$ had reacted. The now dark-red solution proved to be no longer air-sensitive. The product was precipitated by the addition of hexane (20 mL). $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]\cdot CH_2Cl_2$, a brownish solid, was collected by filtration, washed with hexane (10 mL) and diethyl ether (5 mL), and dried for 2 h *in vacuo*. The yield was 121 mg (91%). Anal. Calcd for $Pd_2Cl_2P_4S_2C_{54}H_{50}\cdot CH_2Cl_2$: C, 52.60; H, 4.14; N, 0.00. Found: C, 52.19; H, 4.04; N, 0.07. NMR ($CDCl_3$): (^1H) δ 1.17 (6 H, s, SCH_3)), 6.9–7.8 (40 H, m, C_6H_5), 2.7 (2 H, m, PCH_2P), 3.8 (2 H, m, PCH_2P), 5.3 (2 H, s, CH_2Cl_2); ($^{13}C\{^1H\}$) δ 15.8 (s, SCH_3), 123 (m, $C{=}C$), 127.8–135.8 (m, C_6H_5), 22.3 (m, PCH_2P), 53.4 (s, CH_2Cl_2); ($^{31}P\{^1H\}$) δ 4.3 (s).

$[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$. To methylene chloride (20 mL) in a 50-mL Schlenk flash was added $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ (70 mg, 0.126 mmol). To the stirred yellow solution was slowly added $CH_3SC\equiv CSCH_3$ (0.05 mL, 0.482 mmol, 3.8-fold excess. The solution was stirred for 48 h. The color changed from yellow to orange. The product was precipitated by the addition of hexane (45 mL). $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$, an orange solid, was separated by filtration, washed twice with diethyl ether (5 mL), and dried *in vacuo*. $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$ was found to be air-stable. The yield was 58.5 mg (68%). Anal. Calcd for $Pd_2Cl_2P_4S_2C_{14}H_{34}$: C, 24.95; H, 5.05; N, 0.00. Found: C, 25.17; H, 5.20; N, 0.02. NMR ($CDCl_3$): (^1H) δ 2.61 (6 H, s, SCH_3), 1.66 (12 H, s, $P(CH_3)_2$), 1.58 (12 H, s, $P(CH_3)_2$), 1.6 (2 H, m, PCH_2P), 2.26 (2 H, m, PCH_2P); ($^{13}C\{^1H\}$) δ 19.7 (s, SCH_3), 121 (m, $C{=}C$), 14.5 (m, $P(CH_3)_2$), 15.6 (m, $P(CH_3)_2$), 28.7 (m, PCH_2P); ($^{31}P\{^1H\}$) δ −10.2 (s).

$[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}C{=}C(CH_3)(SCH_3))]$. $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (0.233 g, 0.22 mmol) was dissolved in methylene chloride (15 mL). To the stirred solution was added $CH_3SC\equiv CCH_3$ (20 μL, 0.26 mmol, 1.2-fold excess) dropwise through a rubber septum with a syringe. Immediately after this, $HBF_4\cdot(C_2H_5)_2O$ (2 μL) was introduced. The solution was stirred for 24 h. Over this period of time the color changed from orange to yellow. After the stirring was stopped, a light yellow powder slowly precipitated, which was separated by filtration, washed three times with methylene chloride (10 mL), and dried in *vacuo*. The yield was 110 mg (44%). Anal. Calcd for $Pd_2Cl_2P_4SC_{54}H_{50}$: C, 56.94; H, 4.39; N, 0.00. Found: C, 56.43; H, 4.37; N, 0.06. NMR: (^1H) (CD_2Cl_2), δ 1.19 (3 H, s, CCH_3), 1.6 (3 H, s, SCH_3), 6.9–8.1 (40 H, m, C_6H_5), 2.72 (2 H, m, PCH_2P), 3.13 (2 H, m, PCH_2P); ($^{31}P\{^1H\}$) (DMSO-d_6) δ 10–14 (m, AA′BB′).

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 ω-2Θ mode. Data were collected to a maximum 2Θ of 52°. Lorentz and polarization corrections were applied to the data. Absorption effects were corrected by a semiempirical method on the basis of a series of ψ-scans. The structure was refined in full matrix least-squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w was defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from the standard literature.[15] Anomalous dispersion effects were included in F_c. The unweighted and weighted agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. All calculations were performed on a VAX 3100 computer using MolEN.[16]

$[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]\cdot CH_2Cl_2$. Slow vapor diffusion of hexane into a solution of the complex in methylene chloride yielded dark-red single crystals. The monoclinic 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 $11 < \Theta < 14°$. As a check on crystal stability the intensities of three representative reflections were measured every 60 min, indicating a total gain in intensity of 0.1%. A linear decay correction was applied with correction factors on I in the range from 0.999 to 1.000. A total of 11 268 reflections were collected, of which 10 472 were unique. Intensities of equivalent reflections were averaged, the agreement factors were 2.1% based on I and 1.6% based on F_o. A total of 6951 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ 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, $U_{iso} = 1.3U_{eq}$(bonding atom). One disordered methylene chloride molecule was present in the asymmetric unit. It was modeled by setting the occupancies of Cl(3) and Cl(4) to $^2/_3$ and those of Cl(3b) and Cl(4b) to $^1/_3$. All non-hydrogen atoms of the disordered solvent molecule were refined with isotropic thermal parameters. The positions of the hydrogen atoms of methylene chloride were not calculated. All other atoms were refined with anisotropic thermal parameters. The final cycle of refinement included 597 variable parameters and converged with $R = 0.038$ and $R_w = 0.048$. Further details relevant to the data collection and structure refinements are given in Table 1.

$[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$. Slow vapor diffusion of hexane into a solution of the complex in methylene chloride yielded red single crystals. The orthorhombic 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 $11 < \Theta < 14°$. The crystal stability was monitored by measuring the intensities of three representative reflections every 60 min, which indicated a total loss in intensity of 0.2%. An anisotropic decay correction was applied with correction factors on I in the range from 0.951 to 1.000. A total of 2792 unique reflections were collected, and 1962 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ were used in the calculations.

Structure Solution and Refinement. The position of one Pd atom in the asymmetric unit was found by direct methods. The remaining atoms were located by repeated least-squares refinements followed by difference Fourier syntheses. The complex was situated on a crystallographic inversion center. Hydrogen atoms were included in the refinements with isotropic thermal parameters. All non-hydrogen atoms were

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Table 1. X-ray Data for $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]\cdot CH_2Cl_2$ ($1\cdot CH_2Cl_2$), $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$ (2), and $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}C{=}C(CH_3)(SCH_3))]$ (3)

	$1\cdot CH_2Cl_2$	2	3
formula	$C_{55}H_{52}Cl_4Pd_2P_4S_2$	$C_{14}H_{34}Cl_2Pd_2P_4S_2$	$C_{54}H_{50}Cl_2Pd_2P_4S$
fw	1255.66	674.16	1138.67
F(000)	2536	1344	2304
cryst dimens, mm	0.30 × 0.32 × 0.15	0.40 × 0.35 × 0.20	0.30 × 0.17 × 0.12
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	21 ± 1	21 ± 1	21 ± 1
space group	monoclinic, $P2_1/n$	orthorhombic, *Pbcn*	tetragonal, $P4_3$
cell dimens			
a, Å	16.495(2)	14.926(2)	21.484(4)
b, Å	16.019(2)	13.885(2)	
c, Å	20.208(2)	12.079(3)	14.405(1)
β, deg	90.75(1)		
V, $Å^3$	5339(2)	2503(1)	6649(2)
Z	4	4	4
D_{calc}, g/cm^3	1.56	1.79	1.14
μ, cm^{-1}	11.0	20.5	7.9
no. of params	597	177	530
R	0.038	0.031	0.058
R_w	0.048	0.047	0.079
S	1.38	1.55	1.50
max resd density, e/Å^3	0.92	0.64	0.74

refined with anisotropic thermal parameters. The final cycle of refinement included 177 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.031$ and $R_w = 0.047$. Further details are given in Table 1.

$[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}C{=}C(CH_3)(SCH_3))]$. 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 $10 < \Theta < 14°$. As a check on crystal stability the intensities of three representative reflections were measured every 60 min, indicating a total loss in intensity of 21.4%. An anisotropic decay correction was applied with correction factors on *I* in the range from 0.985 to 1.312. A total of 7151 reflections were collected, of which 6780 were unique. Intensities of equivalent reflections were averaged; the agreement factors were 3.4% based on *I* and 2.9% based on F_o. A total of 3108 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ were used in the calculations. The reflections (110) and (220) had an unusually high difference in the magnitudes of F_o and F_c and were therefore rejected.

Structure Solution and Refinement. The positions of the two Pd atoms were found by direct methods. The remaining atoms were located by repeated least-squares refinements followed by difference Fourier syntheses. The substituents on C(2) were found to be disordered over a 2-fold axis. As a result, the atoms S(1), S(1a), C(6), C(6a), C(5), and C(5a) had to be refined with isotropic thermal parameters and a multiplicity set to 0.5. The *x*, *y*, *z* values for C(5) and C(5a) were fixed during the least-squares refinements. One phenyl ring on P(4) showed high thermal parameters, probably due to a disorder which could not be modeled. The coordinates and isotropic temperature factors were refined for C(39). For the carbon atoms C(40), C(41), and C(42) of this particular phenyl ring only the isotropic temperature factors were refined. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated and included in the least-squares refinement as riding atoms, $U_{iso} = 1.3U_{eq}$(bonding atom). The final cycle of refinement included 530 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.058$ and $R_w = 0.079$. Further details are given in Table 1.

Results and Discussion

Reactions of $CH_3SC{\equiv}CSCH_3$ with $[Pd_2Cl_2(\mu\text{-dppm})_2]$ and $[Pd_2Cl_2(\mu\text{-dmpm})_2]$. Refluxing and further stirring of a methylene chloride solution of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ and excess $CH_3SC{\equiv}CSCH_3$ produced $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]$, **1**, a complex whose $^{31}P\{^1H\}$ NMR spectrum as a $CDCl_3$ solution exhibited a single resonance at 4.3 ppm. In the $^{13}C\{^1H\}$ NMR spectrum of **1** the resonance for the sulfur-bound methyl carbon was at 15.8 ppm (the corresponding resonance in the free acetylene was at 20.2 ppm) and for the "olefinic" carbons at 123 ppm (cf. 87.05 ppm for the free acetylene). The ^1H NMR spectrum showed an upfield shift for the protons of the sulfur-bound methyl groups (1.17 ppm compared to 2.37 ppm for the free acetylene). $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]$ was found to be air stable and to exhibit good thermal stability. High temperature NMR studies of **1** in deuterated nitrobenzene showed no change in the $^{31}P\{^1H\}$ NMR spectrum up to 120 °C, at which temperature the complex decomposed.

The X-ray crystal structure determination revealed a symmetrical complex in which the two palladium centers were held together by two mutually *trans* dppm ligands. The 1,2-dimetalated olefin fragment occupied the equatorial plane. The coordination sphere around the two metal centers was completed by one terminal chloride ligand on each palladium atom. Deviations from square planar geometry were found to be most significant in the P—Pd—P angles of 168.27(4) and 167.72(4)° and Cl(1)—Pd(1)—P(1) and Cl(2)—Pd(2)—P(3) angles of 98.41(4) and 99.84(4)°. Bond angles and distances (Table 2) were very similar to those reported by Balch *et al.* for $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CF_3CCCF_3)]$.[1] The C(51)—C(52) distance of 1.330(6) Å and angles around 120° indicated a hybridization close to sp^2 for the two carbons bridging the palladium metal centers in a *cis* mode. The Pd(1)—Pd(2) distance was 3.5618(5) Å and longer than the intraligand P(1)—P(4) (3.124(2) Å) and P(2)—P(3) (3.141(2) Å) distances. This excluded the possibility of a Pd—Pd bonding interaction. There was also no interaction between the sulfur lone pairs and palladium (Pd(1)—S(1) 3.218(2) Å; Pd(2)—S(2) 3.231(2) Å).

Reaction of $CH_3SC{\equiv}CSCH_3$ with $[Pd_2Cl_2(\mu\text{-dmpm})_2]$, which contains the stronger σ-donor ligand, dmpm, in place of dppm, in methylene chloride yielded $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$, **2**. The $^{31}P\{^1H\}$ NMR spec-

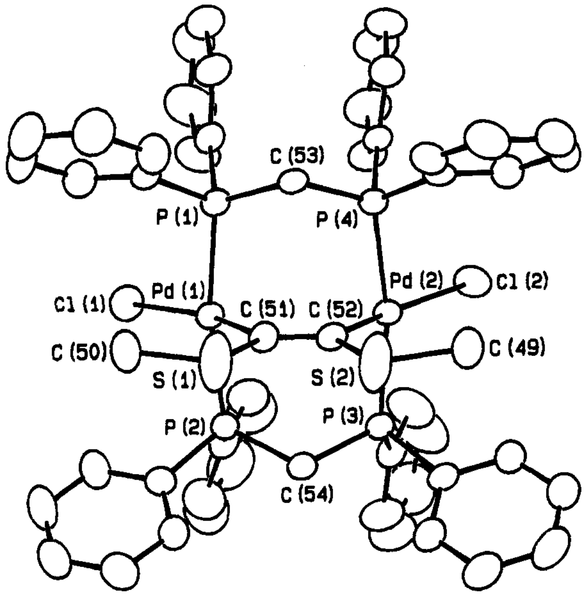

Figure 1. ORTEP diagram of $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]$ (**1**), showing 50% probability thermal ellipsoids.

Table 2. Selected Bond Angles and Distances for $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_3SCCSCH_3)]\cdot CH_2Cl_2$ (1)

	(a) Bond Angles (deg)		
Cl(1)—Pd(1)—P(1)	98.41(4)	C(50)—S(1)—C(51)	107.2(2)
Cl(1)—Pd(1)—P(2)	92.73(4)	C(49)—S(2)—C(52)	108.4(2)
Cl(1)—Pd(1)—C(51)	165.3(1)	Pd(1)—C(51)—S(1)	116.9(2)
P(1)—Pd(1)—P(2)	168.27(4)	Pd(1)—C(51)—C(52)	124.1(3)
P(1)—Pd(1)—C(51)	85.6(1)	S(1)—C(51)—C(52)	118.9(3)
P(2)—Pd(1)—C(51)	84.5(1)	Pd(2)—C(52)—S(2)	118.2(2)
Cl(2)—Pd(2)—P(3)	99.84(4)	Pd(2)—C(52)—C(51)	123.6(3)
Cl(2)—Pd(2)—P(4)	92.24(4)	S(2)—C(52)—C(51)	118.2(3)
Cl(2)—Pd(2)—C(52)	165.6(1)	P(3)—Pd(2)—C(52)	84.4(1)
P(3)—Pd(2)—P(4)	167.72(4)	P(4)—Pd(2)—C(52)	84.4(1)
	(b) Distances (Å)		
Pd(1)—Cl(1)	2.418(1)	S(1)—C(50)	1.765(5)
Pd(1)—P(1)	2.345(1)	S(1)—C(51)	1.769(5)
Pd(1)—P(2)	2.312(1)	S(2)—C(49)	1.788(5)
Pd(1)—C(51)	2.004(4)	S(2)—C(52)	1.757(5)
Pd(2)—Cl(2)	2.419(1)	C(51)—C(52)	1.330(6)
Pd(2)—P(3)	2.345(1)	Pd(2)—C(52)	2.004(4)
Pd(2)—P(4)	2.319(1)	Pd(1)⋯Pd(2)	3.5618(5)
P(1)⋯P(4)	3.124(2)	P(2)⋯P(3)	3.141(2)
Pd(1)⋯S(1)	3.218(2)	Pd(2)⋯S(2)	3.231(2)

trum of the complex in $CDCl_3$ showed a single resonance at −10.2 ppm. In the ^1H NMR spectrum the resonance for the sulfur-bound methyl groups was found at 2.61 ppm (cf. 2.37 ppm for the free acetylene) and in the $^{13}C\{^1H\}$ NMR spectrum the resonance for the carbon atom of the sulfur-bound methyl group was found at 19.7 ppm (cf. 20.2 ppm for the free acetylene). The complex exhibited thermal stability comparable to that of **1**, which was determined by high temperature $^{31}P\{^1H\}$ NMR studies of **2** in deuterated nitrobenzene. The appearance of the spectrum did not change until decomposition occurred at 130 °C.

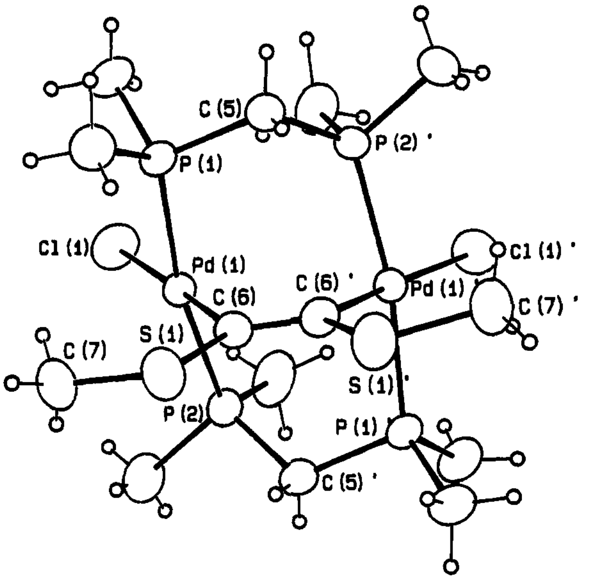

Figure 2. ORTEP diagram of $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$ (**2**), showing 50% probability thermal ellipsoids.

Table 3. Selected Bond Angles and Distances for $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$ (2)

	(a) Bond Angles (deg)		
Cl(1)—Pd(1)—P(1)	94.64(4)	Pd(1)—C(6)—C(6)′	119.3(3)
Cl(1)—Pd(1)—P(2)	89.34(4)	S(1)—C(6)—C(6)′	120.3(3)
Cl(1)—Pd(1)—C(6)	177.1(1)	Pd(1)—C(6)—S(1)	120.1(2)
P(1)—Pd(1)—P(2)	169.86(4)	P(2)—Pd(1)—C(6)	91.7(1)
P(1)—Pd(1)—C(6)	84.8(1)	C(6)—S(1)—C(7)	104.0(2)
	(b) Distances (Å)		
Pd(1)—Cl(1)	2.390(1)	C(6)—C(6)′	1.326(5)
Pd(1)—P(1)	2.318(1)	S(1)—C(7)	1.795(5)
Pd(1)—P(2)	2.309(1)	P(1)⋯P(2)′	3.083(1)
Pd(1)—C(6)	2.019(3)	Pd(1)⋯S(1)	3.295(1)
S(1)—C(6)	1.780(4)	Pd(1)⋯Pd(1)′	3.3267(4)

The molecular structure of **2**, determined by X-ray crystallography, is very similar to that of **1**. $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$ was found to be another example of a *cis* dimetalated "olefinic" complex of the A-frame type. As expected, the distortion from the square planar coordination geometry of the palladium centers was less severe than in **1**, which contained the more bulky phenyl groups of the dppm ligand. The C(6)—C(6)′ distance of 1.326(5) Å and angles of about 120° support a change of hybridization from sp to sp^2 for C(6) and C(6)′ after coordination to palladium. The Pd(1)—Pd(1)′ separation of 3.3267(4) Å was smaller than that in **1** (3.5618(5) Å) but too long for any Pd(1)—Pd(1)′ bonding interactions. The intraligand P(1)—P(2)′ distance was 3.083(1) Å. The observed Pd(1)—S(1) distance of 3.295(1) Å excluded any possibility of Pd—S interactions within the complex. All significant bond angles and lengths are listed in Table 3.

1,2-Dimetalated olefins have been postulated as possible intermediates in the formation of vinylidene complexes.[17] However, in the reactions of the symmetrical acetylene $CH_3SC{\equiv}CSCH_3$ with both $[Pd_2Cl_2(\mu\text{-dppm})_2]$ and $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ no evidence of any transformation into a 1,1-dimetalated olefin (type B) could be found. This observation is in agreement with mechanistic proposals provided through the theoretical work of Hoffmann and Silvestre,[18] whose calculations suggested that 1,2-shift reactions are energetically disfavored on dinuclear frameworks.[19,20]

Reaction of $CH_3SC{\equiv}CCH_3$ with $[Pd_2Cl_2(\mu\text{-dppm})_2]$. The unsymmetrical acetylene $CH_3SC{\equiv}CCH_3$ did not react with $[Pd_2Cl_2(\mu\text{-dppm})_2]$ in methylene chloride without acid catalysis. Stirring of the

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(17) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

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

(19) Recent work by Xiao and Cowie,[20] however, suggested acetylene adducts as the initial intermediates in the reaction of $[Ir_2I_2(CO)(\mu\text{-}CO)(\mu\text{-dppm})_2]$ with acetylene or phenylacetylene. The transformation of the acetylene adducts into vinylidene complexes was proposed to proceed *via* hydrido–acetylide intermediates.

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

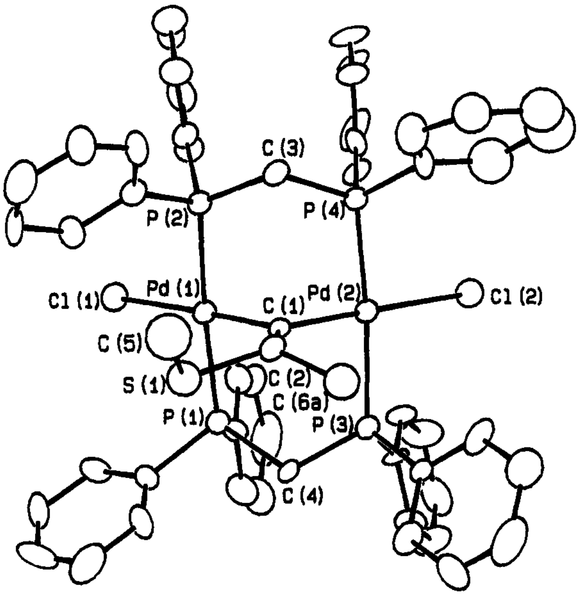


Figure 3. ORTEP diagram of $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-C=C(CH}_3)(SCH_3))]$ (**3**). The substituents on C(2) {S(1), C(5), C(6a)} and four carbon atoms of one of the phenyl rings on P(4) are represented with isotropic thermal parameters.

Table 4. Selected Bond Angles and Distances for $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-C=C(CH}_3)(SCH_3))]$ (3)

	(a) Bond Angles (deg)		
Cl(1)—Pd(1)—P(1)	92.4(2)	Pd(1)—C(1)—Pd(2)	109.2(8)
Cl(1)—Pd(1)—P(2)	95.5(2)	Pd(1)—C(1)—C(2)	125(1)
Cl(1)—Pd(1)—C(1)	177.2(5)	Pd(2)—C(1)—C(2)	126(1)
P(1)—Pd(1)—P(2)	171.6(2)	S(1)—C(2)—C(1)	116(1)
P(1)—Pd(1)—C(1)	86.7(5)	S(1)—C(2)—C(6a)	119(2)
P(2)—Pd(1)—C(1)	85.3(5)	C(1)—C(2)—C(6a)	119(2)
Cl(2)—Pd(2)—P(3)	94.4(2)	C(2)—S(1)—C(5)	102.3(9)
Cl(2)—Pd(2)—P(4)	93.7(2)	P(3)—Pd(2)—C(1)	85.2(5)
Cl(2)—Pd(2)—C(1)	178.5(5)	P(4)—Pd(2)—C(1)	86.6(5)
P(3)—Pd(2)—P(4)	170.7(2)		
	(b) Distances (Å)		
Pd(1)—Cl(1)	2.413(5)	Pd(2)—C(1)	2.00(2)
Pd(2)—Cl(2)	2.407(6)	Pd(1)—C(1)	1.97(2)
Pd(1)—P(1)	2.323(5)	S(1)—C(2)	1.82(2)
Pd(1)—P(2)	2.329(5)	S(1)—C(5)	1.91(1)
Pd(2)—P(3)	2.340(5)	C(1)—C(2)	1.33(3)
Pd(2)—P(4)	2.298(5)	C(2)—C(6a)	1.64(5)
Pd(1)⋯Pd(2)	3.239(2)	P(1)⋯P(3)	3.067(7)
P(2)⋯P(4)	3.072(7)		

Table 5. Positional Parameters and B_{eq} for $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-CH}_3SCCSCH_3)]\cdot CH_2Cl_2$ (1·CH$_2$Cl$_2$)

atom	*x*	*y*	*z*	B^a (Å^2)
Pd(1)	0.46578(2)	0.10241(2)	0.77638(1)	2.223(6)
Pd(2)	0.64695(2)	0.19753(2)	0.83761(2)	2.251(6)
Cl(1)	0.37567(8)	0.11487(9)	0.68154(6)	3.76(3)
Cl(2)	0.72770(8)	0.31948(7)	0.81319(7)	3.91(3)
Cl(3)	0.9307(2)	0.1626(2)	0.0715(2)	8.62(8)*
Cl(3b)	0.9561(4)	0.1722(5)	0.0581(4)	8.8(2)*
Cl(4b)	0.9319(4)	0.2764(5)	−0.0412(4)	8.7(2)*
Cl(4)	0.8841(2)	0.2776(2)	−0.0351(2)	6.73(6)*
S(1)	0.48713(9)	−0.0243(1)	0.89893(8)	5.35(3)
S(2)	0.64264(9)	0.0533(1)	0.94929(7)	5.27(3)
P(1)	0.39870(7)	0.19390(7)	0.84781(6)	2.37(2)
P(2)	0.55412(7)	0.01620(8)	0.72060(6)	2.44(2)
P(3)	0.71521(7)	0.09756(7)	0.77443(6)	2.32(2)
P(4)	0.55880(7)	0.27407(7)	0.90232(6)	2.33(2)
C(1)	0.3535(3)	0.2915(3)	0.8170(3)	3.1(1)
C(2)	0.3540(4)	0.3103(4)	0.7502(3)	4.9(1)
C(3)	0.3149(4)	0.3824(4)	0.7287(3)	6.3(2)
C(4)	0.2771(4)	0.4343(4)	0.7706(4)	5.7(2)
C(5)	0.2765(4)	0.4158(4)	0.8375(4)	5.1(1)
C(6)	0.3140(3)	0.3443(3)	0.8610(3)	4.0(1)
C(7)	0.3028(3)	0.1316(3)	0.9529(3)	3.8(1)
C(8)	0.3095(3)	0.1472(3)	0.8864(2)	2.78(9)
C(9)	0.2461(3)	0.1245(3)	0.8439(3)	3.8(1)
C(10)	0.1766(3)	0.0888(4)	0.8686(3)	4.7(1)
C(11)	0.1692(3)	0.0754(3)	0.9346(3)	5.2(1)
C(12)	0.2319(4)	0.0968(4)	0.9775(3)	5.2(1)
C(13)	0.5182(3)	−0.0916(3)	0.7159(2)	3.0(1)
C(14)	0.4453(3)	−0.1079(4)	0.6850(3)	4.4(1)
C(15)	0.4131(4)	−0.1870(4)	0.6829(3)	5.3(1)
C(16)	0.4534(3)	−0.2515(4)	0.7136(3)	4.8(1)
C(17)	0.5251(4)	−0.2370(4)	0.7449(3)	4.7(1)
C(18)	0.5586(3)	−0.1579(3)	0.7465(3)	3.8(1)
C(19)	0.5738(3)	0.0467(3)	0.6356(2)	3.2(1)
C(20)	0.5745(4)	0.1302(4)	0.6189(3)	4.9(1)
C(21)	0.5949(4)	0.1548(5)	0.5560(3)	6.8(2)
C(22)	0.6111(4)	0.0974(5)	0.5090(3)	7.2(2)
C(23)	0.6090(5)	0.0157(6)	0.5229(3)	7.7(2)
C(24)	0.5922(3)	−0.0108(4)	0.5880(3)	5.5(2)
C(25)	0.8032(3)	0.0558(3)	0.8189(2)	2.58(9)
C(26)	0.8163(3)	−0.0285(3)	0.8307(3)	3.4(1)
C(27)	0.8826(3)	−0.0553(4)	0.8677(3)	4.1(1)
C(28)	0.9379(3)	0.0036(4)	0.8917(3)	4.8(1)
C(29)	0.9262(3)	0.0873(4)	0.8788(3)	4.6(1)
C(30)	0.8595(3)	0.1130(3)	0.8428(3)	3.8(1)
C(31)	0.7589(3)	0.1260(3)	0.6944(2)	2.9(1)
C(32)	0.7591(4)	0.2084(4)	0.6741(3)	5.5(2)
C(33)	0.7956(5)	0.2286(5)	0.6157(3)	7.9(2)
C(34)	0.8283(4)	0.1690(5)	0.5767(3)	7.0(2)
C(35)	0.8274(4)	0.0874(5)	0.5961(3)	6.0(2)
C(36)	0.7931(3)	0.0660(4)	0.6549(3)	4.6(1)
C(37)	0.5292(3)	0.3774(3)	0.8748(2)	2.68(9)
C(38)	0.5359(3)	0.4003(3)	0.8091(3)	3.8(1)
C(39)	0.5089(4)	0.4786(4)	0.7885(3)	5.1(1)
C(40)	0.4749(4)	0.5328(3)	0.8314(3)	4.8(1)
C(41)	0.4670(4)	0.5107(3)	0.8966(3)	4.3(1)
C(42)	0.4946(3)	0.4333(3)	0.9184(3)	3.3(1)
C(43)	0.5715(3)	0.2585(3)	1.0424(2)	3.4(1)
C(44)	0.6102(4)	0.2735(4)	1.1030(3)	4.4(1)
C(45)	0.6773(3)	0.3230(4)	1.1055(3)	4.8(1)
C(46)	0.7062(3)	0.3602(4)	1.0492(3)	4.8(1)
C(47)	0.6689(3)	0.3453(3)	0.9887(3)	3.8(1)
C(48)	0.6007(3)	0.2941(3)	0.9846(2)	2.73(9)
C(49)	0.7252(3)	0.1184(3)	0.9735(3)	3.7(1)
C(50)	0.3945(3)	−0.0508(3)	0.8595(3)	4.0(1)
C(51)	0.5262(3)	0.0638(3)	0.8574(2)	2.30(8)
C(52)	0.5947(3)	0.0983(3)	0.8798(2)	2.34(8)
C(53)	0.4609(2)	0.2253(3)	0.9200(2)	2.36(8)
C(54)	0.6563(3)	0.0037(3)	0.7569(2)	2.47(9)
C(55)	0.8893(5)	0.2573(5)	0.0462(4)	7.2(2)*

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

reaction solution for several days and under reflux led only to the recovery of starting material. The course of the acid-catalyzed reaction was found to be dependent on the amount of acetylene added to the reaction mixture. Several attempts using a 6−10-fold excess of $CH_3SC{\equiv}CCH_3$ yielded an orange product whose $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ exhibited only a single resonance at −31 ppm. Attempts to crystallize and identify this orange material failed. Decreasing the concentration of the acetylene in the reaction mixture resulted in an AA′BB′ pattern in the $^{31}P\{^1H\}$ NMR spectrum. The vinylidene complex, $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-C=C(CH}_3)(SCH_3))]$, **3**, and, as a side product, the mononuclear complex, $[PdCl_2(dppm)]$, were obtained in the $HBF_4{\cdot}(C_2H_5)_2O$-catalyzed reaction of $CH_3SC{\equiv}CCH_3$ with $[Pd_2Cl_2(\mu\text{-dppm})_2]$ in methylene chloride. The $^{31}P\{^1H\}$ NMR spectrum of **3** in DMSO-d_6 showed an AA′BB′ splitting pattern centered at 12 ppm that is typical for unsymmetrical A-frame complexes. In the ^1H NMR spectrum of a solution of **3** in DMSO-d_6 a single resonance at 1.2 ppm was assigned to the protons of the carbon-bound methyl group and one at 1.6 ppm to the protons of the sulfur-bound methyl group.

Table 6. Positional Parameters and B_{eq} for $[Pd_2Cl_2(\mu\text{-dmpm})_2(\mu\text{-}CH_3SCCSCH_3)]$ (2)

atom	x	y	z	B^a (Å^2)
Pd(1)	0.58551(2)	0.25512(2)	0.16169(2)	2.075(7)
Cl(1)	0.65644(8)	0.11053(8)	0.0996(1)	4.08(2)
S(1)	0.56976(9)	0.49172(8)	0.1535(1)	3.64(2)
P(1)	0.69148(6)	0.28729(7)	0.29707(8)	2.46(2)
P(2)	0.46293(7)	0.21875(9)	0.05283(9)	2.76(2)
C(1)	0.7565(3)	0.3973(3)	0.2949(4)	3.69(9)
C(2)	0.7771(3)	0.1959(4)	0.3153(4)	3.79(9)
C(3)	0.4234(3)	0.0972(3)	0.0793(5)	4.4(1)
C(4)	0.4826(3)	0.2222(5)	−0.0962(4)	5.6(1)
C(5)	0.6358(3)	0.2944(3)	0.4323(3)	3.06(8)
C(6)	0.5302(3)	0.3811(2)	0.2097(3)	2.35(7)
C(7)	0.6423(3)	0.4552(4)	0.0427(4)	3.9(1)
H(1a)	0.797(3)	0.403(3)	0.235(4)	6(1)*
H(1c)	0.721(3)	0.451(3)	0.287(3)	5(1)*
H(1b)	0.798(4)	0.398(4)	0.362(4)	6(1)*
H(2a)	0.820(3)	0.212(3)	0.260(4)	4(1)*
H(2c)	0.810(4)	0.207(4)	0.374(4)	6(1)*
H(2b)	0.751(4)	0.141(5)	0.310(5)	9(2)*
H(3c)	0.395(3)	0.091(4)	0.154(4)	6(1)*
H(3a)	0.473(4)	0.060(5)	0.059(5)	7(1)*
H(3b)	0.370(4)	0.078(4)	0.018(4)	7(1)*
H(4a)	0.528(3)	0.174(3)	−0.113(3)	4(1)*
H(4b)	0.437(3)	0.196(4)	−0.128(4)	5(1)*
H(4c)	0.504(5)	0.273(5)	−0.110(8)	12(2)*
H(5a)	0.671(3)	0.277(4)	0.490(4)	6(1)*
H(5b)	0.618(3)	0.349(3)	0.445(4)	4(1)*
H(7b)	0.682(3)	0.492(3)	0.533(3)	3(1)*
H(7c)	0.615(4)	0.569(4)	0.489(4)	7(1)*
H(7a)	0.680(4)	0.405(4)	0.061(5)	6(1)*

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

Table 7. Positional Parameters and B_{eq} for $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}C{=}C(CH_3)(SCH_3))]$ (3)

atom	x	y	z	B^a (Å^2)
Pd(1)	0.48360(6)	0.22168(6)	0.998	3.91(3)
Pd(2)	0.56202(7)	0.11534(6)	0.8899(1)	4.12(3)
Cl(1)	0.3894(2)	0.2827(2)	1.0047(4)	5.9(1)
Cl(2)	0.5655(3)	0.0451(2)	0.7598(4)	6.5(1)
S(1)	0.5845(6)	0.2197(6)	1.168(1)	7.7(3)*
S(1a)	0.6805(7)	0.1429(7)	1.038(1)	8.4(3)*
P(1)	0.4383(2)	0.1396(2)	1.0785(4)	4.3(1)
P(2)	0.5429(2)	0.2977(2)	0.9243(3)	3.9(1)
P(3)	0.5238(2)	0.0406(2)	0.9934(4)	4.5(1)
P(4)	0.6069(2)	0.1959(2)	0.8090(4)	4.2(1)
C(1)	0.5611(8)	0.1726(7)	1.000(1)	3.9(4)
C(2)	0.6052(9)	0.1767(8)	1.064(1)	4.9(5)
C(3)	0.6154(7)	0.2711(7)	0.872(1)	4.1(4)
C(4)	0.4885(9)	0.0695(7)	1.099(1)	4.4(4)
C(5)	0.658	0.267	1.191	13(2)*
C(5a)	0.687	0.095	1.143	17(3)*
C(6a)	0.656(2)	0.120(2)	1.072(4)	8(1)*
C(6)	0.611(1)	0.225(1)	1.144(3)	3.7(7)*
C(7)	0.5731(8)	0.3555(8)	1.005(1)	4.7(4)
C(8)	0.534(1)	0.3718(9)	1.081(1)	5.6(5)
C(9)	0.6302(8)	0.3849(8)	0.999(2)	6.1(5)
C(10)	0.556(1)	0.4172(8)	1.146(1)	7.0(5)
C(11)	0.650(1)	0.426(1)	1.067(2)	6.9(6)
C(12)	0.614(1)	0.443(1)	1.136(2)	8.1(6)
C(13)	0.4107(8)	0.1573(8)	1.196(1)	4.5(4)
C(14)	0.445(1)	0.114(1)	1.273(1)	6.5(5)
C(15)	0.424(1)	0.157(1)	1.358(2)	9.8(8)
C(16)	0.3550(9)	0.190(1)	1.203(1)	6.4(6)
C(17)	0.333(1)	0.206(1)	1.293(2)	8.0(6)
C(18)	0.371(1)	1.189(1)	1.367(1)	10.3(8)
C(19)	0.5870(8)	−0.0063(8)	1.037(1)	4.5(4)
C(20)	0.5851(9)	−0.0316(9)	1.124(2)	6.9(5)
C(21)	0.632(1)	−0.068(1)	1.152(2)	9.1(7)
C(22)	0.680(1)	−0.055(1)	1.005(2)	10.5(9)
C(23)	0.635(1)	−0.0183(9)	0.978(2)	8.7(7)
C(24)	0.679(1)	−0.080(1)	1.100(2)	10.5(8)
C(25)	0.4638(9)	−0.0157(7)	0.952(1)	4.7(4)
C(26)	0.451(1)	−0.0683(9)	1.003(2)	7.3(6)
C(27)	0.4325(9)	−0.0062(8)	0.870(1)	5.3(5)
C(28)	0.409(1)	−0.1102(9)	0.971(2)	8.3(7)
C(29)	0.380(1)	−0.098(1)	0.889(2)	8.5(7)
C(30)	0.390(1)	−0.047(1)	0.836(2)	9.4(7)
C(31)	0.556(1)	0.2838(9)	0.573(2)	8.0(6)
C(32)	0.5658(9)	0.2189(8)	0.704(1)	4.6(4)
C(33)	0.508(1)	0.1896(9)	0.687(2)	6.8(6)
C(34)	0.475(1)	0.2091(9)	0.605(2)	9.3(7)
C(35)	0.502(1)	0.2558(9)	0.549(2)	9.6(8)
C(36)	0.585(1)	0.2645(8)	0.645(1)	5.7(5)
C(37)	0.686(1)	0.1823(9)	0.768(2)	7.8(6)
C(38)	0.738(1)	0.218(1)	0.799(2)	8.2(7)
C(39)	0.793(1)	0.199(1)	0.767(2)	9.6(7)*
C(40)	0.810	0.153	0.707	11.9(9)*
C(41)	0.754	0.124	0.659	17(1)*
C(42)	0.691	0.135	0.699	14(1)*
C(43)	0.3720(9)	0.1059(8)	1.023(1)	4.8(5)
C(44)	0.3520(9)	0.129(1)	0.942(1)	5.7(5)
C(45)	0.305(1)	0.1059(9)	0.893(2)	7.9(7)
C(46)	0.275(1)	0.052(1)	0.930(2)	12.5(9)
C(47)	0.289(1)	0.028(1)	1.020(2)	9.9(8)
C(48)	0.340(1)	0.058(1)	1.064(2)	7.2(6)
C(49)	0.539(1)	0.3899(9)	0.794(1)	6.0(5)
C(50)	0.461(1)	0.407(1)	0.685(2)	8.9(7)
C(51)	0.517(1)	0.422(1)	0.719(2)	8.0(7)
C(52)	0.430(1)	0.359(1)	0.720(2)	7.3(6)
C(53)	0.4533(9)	0.3234(9)	0.797(1)	5.4(5)
C(54)	0.5067(8)	0.3415(8)	0.831(1)	4.5(4)

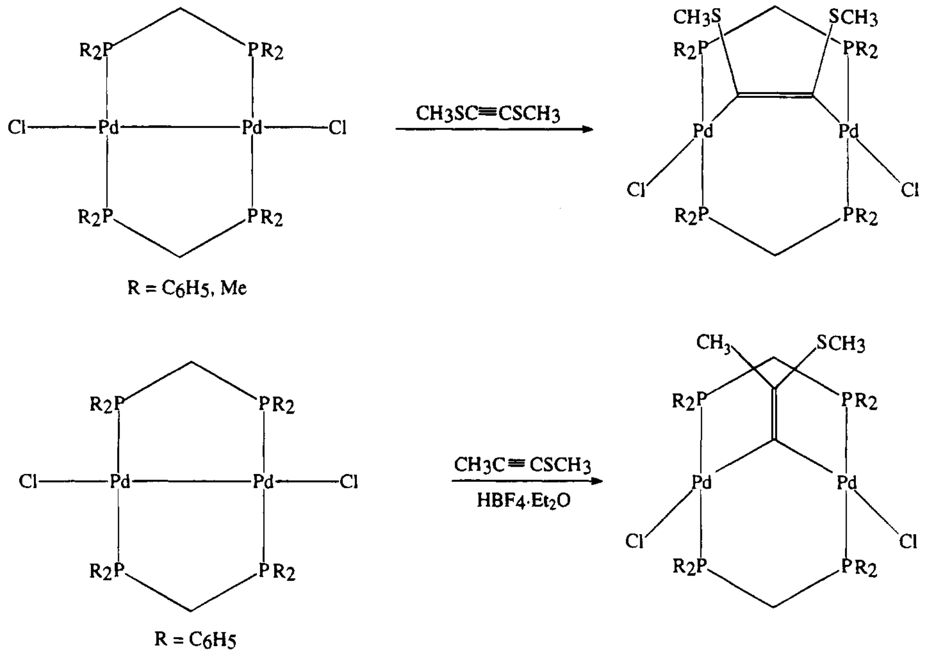
[a] Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The X-ray structure of **3** exhibited two palladium metal centers held together by two mutually *trans* dppm ligands. The α-carbon (C(1)) of the vinylidene moiety symmetrically bridged the palladium atoms. *Trans* to the vinylidene moiety were two terminal chloride ligands, completing the coordination spheres around the metal centers. Palladium exhibited an approximate square planar coordination geometry in this A-frame complex. The most significant deviations occurred in the P(3)—Pd(2)—P(4) (170.7(2)°) and Cl(1)—Pd(1)—P(2) (95.5(2)°) angles. These values (Table 4) were in agreement with those reported for the related complex $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}C{=}CCl_2)]$.[2] The vinylidene moiety of **3** was unsymmetrical, with two different substituents (CH_3 and SCH_3) on C(2), the β-carbon, and bridged the metal centers. A distance of 1.33(3) Å between C(1) and C(2) suggested a hybridization close to sp^2. Significant deviations from the ideal value (120°) for some angles about the vinylidene ligand (Pd(1)—C(1)—Pd(2) 109.2(8)°; Pd(2)—C(1)—C(2) 126(1)°) were probably due to steric hindrance; the listed angles were almost identical to the comparable ones in $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}C{=}CCl_2)]$. The bridging of the metal centers by the vinylidene was not supported by Pd—Pd bonding interactions (Pd—Pd separation 3.239(2) Å).

Low temperature $^{31}P\{^1H\}$ NMR spectra recorded at various temperature between −40 and −90 °C showed broadening of one half of the signals representing the AA′BB′ splitting pattern, while the other half of the signals remained sharp. This effect is attributed to dynamic processes (inversion) that involve the SCH_3 group.

Conclusions. Our results contrast with those reported by Miller and Angelici[10] for the reactions of the mononuclear ruthenium(II) complex $[RuCl(P(CH_3)_3)_2Cp]$ with $CH_3SC{\equiv}CSCH_3$ and $CH_3SC{\equiv}CCH_3$. These authors observed a facile 1,2-migration of SCH_3 and formation of a vinylidene complex only in the reaction

Scheme 1



with the symmetrical acetylene, $CH_3SC{\equiv}CSCH_3$, and suggested that, for a rearrangement to occur, both SCH_3 groups were necessary. The results of our studies on the dinuclear palladium(I) systems, $[Pd_2Cl_2(\mu\text{-dppm})_2]$ and $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ (Scheme 1), are the opposite. Reactions that involved the symmetrical acetylene, $CH_3SC{\equiv}CSCH_3$, lead to stable acetylene adducts. No evidence for a 1,2-shift of the SCH_3 group could be obtained. While $CH_3SC{\equiv}CSCH_3$ reacted with the palladium(I) complexes in uncatalyzed reactions, in the case of $CH_3SC{\equiv}CCH_3$ the presence of $HBF_4{\cdot}(C_2H_5)_2O$ was necessary. The reaction that involved the unsymmetrical acetylene $CH_3SC{\equiv}CCH_3$ led to the formation of the vinylidene complex, $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}C{=}C(CH_3)(SCH_3))]$, *via* a formal 1,2-$SCH_3$ shift. While vinylidene formation *via* a 1,2-shift of the SCH_3 group seems thermodynamically more likely than the alternative, a 1,2-CH_3 shift, the possibility of the latter cannot be excluded until appropriate labeling experiments are performed.

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Supplementary Material Available: Tables of bond distances and angles and thermal parameters (28 pages). Ordering information is given on any current masthead page.

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