The reactions of $[Pd_2Cl_2(\mu\text{-}PP)_2]$ (PP = dppm, dmpm) with $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution: X-ray crystal structures of $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ and hexakis(diethylamino)benzene, $C_6(NEt_2)_6$

Sean R. Klopfenstein, Constanze Kluwe, Kristin Kirschbaum, and Julian A. Davies

Abstract: The binuclear palladium(I) complex, $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ (dppm = bis(diphenylphosphino)methane), has been shown to react with bis(diethylamino)acetylene, $Et_2NC{\equiv}CNEt_2$, in methylene chloride solution to yield two isolable products, the known methylene-bridged complex, $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$, and hexakis(diethylamino)benzene, $C_6(NEt_2)_6$, both of which have been characterized crystallographically. The source of the bridging methylene group in $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ has been shown to be the methylene chloride solvent. A mechanism that accounts for the formation of the two isolable products is proposed. The complex, $[Pd_2Cl_2(\mu\text{-}dmpm)_2]$ (dmpm = bis(dimethylphosphino)methane), was similarly found to react with $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution to yield $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dmpm)_2]$, which was identified spectroscopically.

Key words: acetylene, palladium, cyclooligomerization, aminoacetylene, hexakis(diethylamino)benzene.

Résumé : On montre que le complexe binucléaire de palladium(I), $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ (dppm = bis(diphénylphosphino)-méthane, réagit avec le bis(diéthylamino)acétylène, $Et_2NC{\equiv}CNEt_2$, dans une solution de chlorure de méthylène pour donner deux produits que l'on peut isoler : un complexe avec un méthylène ponté $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ qui est connu, et l'hexakis(diéthylamino)benzène, $C_6(NEt_2)_6$; ces deux complexes sont caractérisés par cristallographie. On montre que le groupe méthylène en position de pont dans le complexe $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ vient du solvant. On propose un mécanisme qui tient compte des deux produits que l'on peut isoler. De façon similaire, on a trouvé que le complexe $[Pd_2Cl_2(\mu\text{-}dmpm)_2]$ (dmpm = bis(diméthylphosphino)méthane) réagit avec $Et_2NC{\equiv}CNEt_2$ en solution dans le chlorure de méthylène pour conduire au complexe $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dmpm)_2]$ que l'on a identifié par spectroscopie.

Mots clés : acétylène, palladium, cyclooligomérisation, aminoacétylène, hexakis(diéthylamino)benzène.

[Traduit par la rédaction]

Introduction

Binuclear palladium(I) complexes of the type $[Pd_2X_2(\mu\text{-}PP)_2]$ (X = anionic ligand, PP = dppm, dmpm, etc.) are known (1) to react with simple acetylenes bearing electron-withdrawing substituents (e.g., $\text{-}CF_3$, $\text{-}CO_2Me$) to yield the acetylene complexes, $[Pd_2X_2(\mu\text{-}RC{\equiv}CR)(\mu\text{-}PP)_2]$. Acid catalysis (2, 3) facilitates acetylene addition to the metal-metal bond of $[Pd_2X_2(\mu\text{-}PP)_2]$ and allows generation of $[Pd_2X_2(\mu\text{-}RC{\equiv}CR)(\mu\text{-}PP)_2]$ complexes from acetylenes *without* electron-withdrawing substituents (e.g., -H, -Ph), Fig. 1. We have shown (4, 5) that the heteroatom-substituted acetylene, $MeSC{\equiv}CSMe$, reacts with $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ to yield the acetylene complex, $[Pd_2Cl_2(\mu\text{-}MeSC{\equiv}CSMe)(\mu\text{-}dppm)_2]$, which undergoes a Lewis-acid-promoted rearrangement to the vinylidene isomer, $[Pd_2Cl_2(\mu\text{-}C{=}C\{SMe\}_2)(\mu\text{-}dppm)_2]$, Fig. 2. Vinylidene complexes, formed via 1,2-heteroatom shift reactions, have similarly been isolated from the reactions of haloacetylenes (6) with $[Pd_2Cl_2(\mu\text{-}dppm)_2]$.

Amino-substituted acetylenes and alkoxyacetylenes, $MeC{\equiv}CY$ (Y = NMe_2, OEt) have been shown (7) to undergo 1,2-heteroatom shifts in reactions with $[Mn_2(CO)_9(NCMe)]$. In these cases the 1,2-heteroatom shift reactions are accompanied by CO insertion into the C—Y bond of the newly formed vinylidene, Fig. 3. Such processes are not typical of the reactions of manganese carbonyls with heteroatom-substituted acetylenes. For example, $[Mn_2(CO)_{10}]$ reacts with $PhC{\equiv}CNEt_2$ to yield the expected acetylene complex, $[Mn_2(CO)_8(PhC{\equiv}CNEt_2)]$ (8). Other nitrogen-containing acetylenes have been shown (8) to react with metal carbonyl

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This paper is dedicated to Professor Howard C. Clark in recognition of his contributions to Canadian chemistry.

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Fig. 1. Acetylene addition to the metal–metal bond of $[Pd_2X_2(\mu\text{-}PP)_2]$.

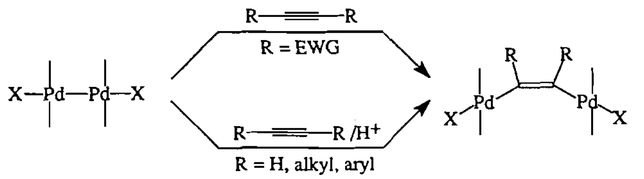


Fig. 2. Reactions of MeSC≡CSMe with $[Pd_2Cl_2(\mu\text{-dppm})_2]$.

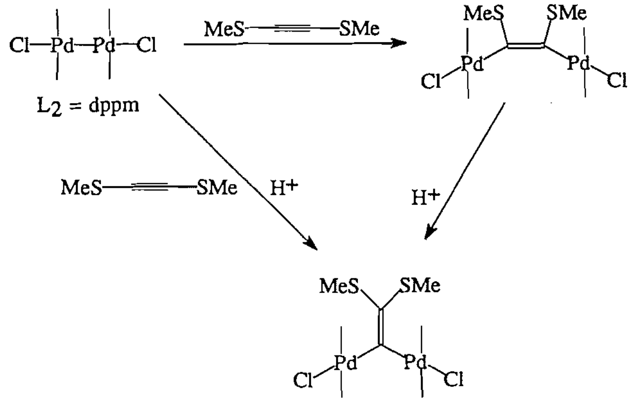


Fig. 3. Reactions of MeC≡CY (Y = NMe_2, OEt) with $[Mn_2(CO)_9(NCMe)]$.

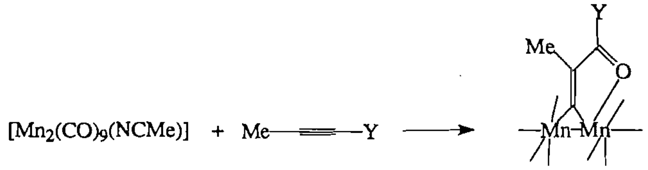
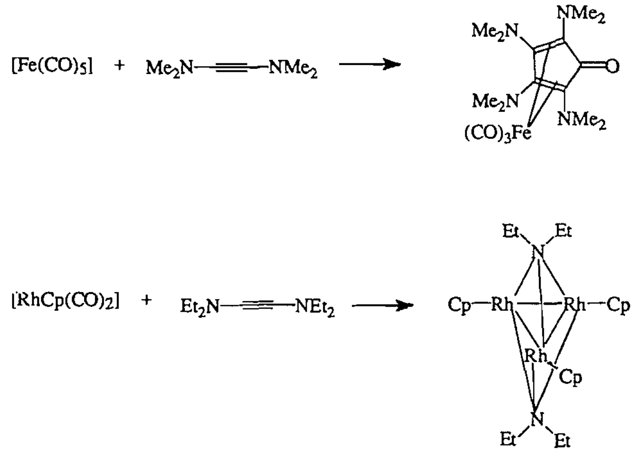


Fig. 4. Reactions of nitrogen-containing acetylenes with metal carbonyl complexes.



complexes to yield products that arise either from acetylene oligomerization or from C-N bond cleavage, Fig. 4.

In this paper, the reactions between the palladium(I) complexes, $[Pd_2Cl_2(\mu\text{-}PP)_2]$ (PP = dppm, dmpm), and bis(diethylamino)acetylene, $Et_2NC{\equiv}CNEt_2$, in methylene chloride solution are described. Neither acetylene complexes nor the vinylidene isomers could be identified among the reaction products. Two compounds were isolated from the reaction of $Et_2NC{\equiv}CNEt_2$ with $[Pd_2Cl_2(\mu\text{-dppm})_2]$ in CH_2Cl_2, the known methylene-bridged complex, $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$, **1**, and hexakis(diethylamino)benzene, $C_6(NEt_2)_6$, **2**, both of which were characterized crystallographically ($\mathbf{1}\cdot 2CH_2Cl_2$ and **2**). From the reaction of $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ with $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution the analogous methylene-bridged complex, $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dmpm})_2]$, was isolated and characterized spectroscopically.

Experimental

Materials

All solvents were deoxygenated prior to use. Reactions were performed under argon or nitrogen using standard Schlenck techniques. Methylene chloride was distilled from calcium carbide under nitrogen. Diethyl ether was distilled from sodium ribbon under nitrogen. Diethylamine was dried over finely ground potassium hydroxide and used without further purification. The compounds $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (9) and $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ (10) were prepared by literature methods. Bis(diethylamino)acetylene was prepared by a procedure modified from three published reports (11–13), as detailed below.

Physical measurements

NMR spectra were measured on Varian VXR-400, Varian Gemini-200, and JEOL FX-90Q NMR spectrometers. Internal tetramethylsilane was employed as a shift standard in ^1H and $^{13}C\{^1H\}$ NMR measurements and $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% phosphoric acid. Data for GC–MS experiments were collected on a HP-5890 instrument with mass-sensitive detector.

X-ray crystallography[2]

General methods

Single crystals of $1\cdot 2CH_2Cl_2$ and 2 were selected for data collection and mounted on glass fibers in random orientations. X-ray diffraction data were collected with an Enraf–Nonius CAD4 diffractometer in the ω–2θ mode. Data were collected for $1\cdot 2CH_2Cl_2$ to a maximum of 2θ of 44° and for 2 to a maximum of 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 structures were refined in full-matrix least squares where the function minimized was

$$\Sigma\omega(|F_o| - |F_c|)^2$$

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[2] Copies of tables of all bond distances and angles and thermal parameters may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Tables of bond distances and angles have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

and the weight ω was defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from the standard literature (14). Anomalous dispersion effects were included in F_c. The unweighted and weighted agreement factors are defined as

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|, \ R_w = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega(|F_o|^2))^{1/2}$$

All calculations were performed on a VAX 3100 computer using MolEN (15).

Synthesis of bis(diethylamino)acetylene

(i) Preparation of lithium diethylamide

A three-necked, 300-mL, round-bottomed flask was equipped with a magnetic stirrer bar, dropping funnel, gas inlet, and mineral oil bubbler. The flask was charged with diethylamine (10.5 mL, 0.20 mol) and freshly distilled diethyl ether (50 mL). The contents of the flask were cooled to 0°C and a solution of *n*-butyllithium in hexanes (50 mL, 0.20 mol) was added dropwise under an atmosphere of argon. The resulting lithium diethylamide was used directly in the next step.

*(ii) Preparation of 1,2-dichloro-1-(*N,N*-diethylamino)ethene*

A three-necked, 1000-mL, round-bottomed flask was equipped with a mechanical stirrer, reflux condenser, gas inlet, and mineral oil bubbler. An atmosphere of argon was maintained throughout the procedure. To the flask was added freshly distilled diethyl ether (120 mL), and trichloroethylene (18 mL, 0.20 mol). The solution was cooled to −90°C with a Dry Ice – diethyl ether cooling bath. To the stirring solution, the lithium diethylamide solution (see above) was added via cannula over a period over 10 min while maintaining a temperature below −70°C. Additional diethylamine (21 mL, 0.4 mol) was then added and the flask allowed to warm slowly to 30°C using a water bath. The mixture was allowed to stir for 45 min at 30°C and then the water bath was removed and the reaction flask allowed to come to room temperature over a period of 1 h. The resulting brown, heterogeneous mixture was filtered through a coarse frit covered with dry, finely ground, potassium carbonate. The flask and frit were washed with three 20-mL portions of dry diethyl ether and the washings combined with the filtrate. The filtrate was concentrated to a volume of 100 mL with a rotary evaporator while maintaining a bath temperature below 40°C. The resulting brownish-red solution was analyzed by GC–MS and used without further purification for conversion to the chloroketeneaminal.

(iii) Preparation of 2-chloro-1,1-bis(diethylamino)ethene

The product from (*ii*) was placed in a three-necked, 250-mL, round-bottomed flask with diethylamine (15 mL, 0.30 mol). The flask was equipped with a magnetic stirrer bar and a reflux condenser while an atmosphere of argon was maintained. The contents of the flask were brought to reflux by use of a water bath maintained at 70°C. After 1 h of reflux, some separation of solid material was noted. Additional diethylamine (15 mL, 0.30 mol) was then added in three equal portions over a period of 1 h. The mixture was allowed to reflux for 12 h at which time additional diethylamine (5 mL, 0.10 mol) was added and reflux continued for 8 h longer. The water bath was removed and the flask allowed to cool to room temperature over a period of 1 h. The mixture was then filtered through a coarse frit and the reaction flask and frit were washed with three 20-mL portions of dry diethyl ether and the washings combined with the filtrate. The filtrate was then reduced to a volume of 50 mL with a rotary evaporator while maintaining a bath temperature below 40°C. The resulting brown-red solution was analyzed by GC–MS and used without further purification for the final step.

(iv) Preparation of bis(diethylamino)acetylene

To a three-necked, 250-mL, round-bottomed flask equipped with a magnetic stirrer bar, dropping funnel, gas inlet, and mineral oil bubbler, the chloroketeneaminal (50 mL, 80% by GC–MS) was added with freshly distilled diethyl ether (75 mL). The flask was cooled to 0°C with an ice bath and freshly prepared lithium diethylamide (10.5 mL, 0.20 mol, see (*i*), above) was added via cannula. The solution was allowed to warm to room temperature and stirred overnight under flowing argon. Analysis by GC–MS showed complete conversion. The brown suspension was filtered through a coarse frit covered with Celite using a water aspirator equipped with a potassium hydroxide tube for protection. The Celite was washed with three 10-mL portions of diethyl ether and the washings combined with the filtrate. The solvent was removed by distillation through a 40-cm Vigreux column while maintaining the bath temperature below 70°C. The resulting red-brown liquid (40 mL, 84% by GC–MS) was transferred via cannula to a 100-mL, three-necked, round-bottomed flask equipped for vacuum distillation. The acetylene distilled as a clear oil at 30°C and 0.25 Torr (1 Torr = 133.3 Pa). Yield: 28 mL, 25 g, 74%. ^{1}H NMR ($CDCl_3$): δ 1.1 (CH_3, t), 2.8 (CH_2, q); J(H, H) 7.15 Hz; $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 12.9 (CH_3), 49.6 (CH_2), 74.3 (-C≡C-); MS: M* = 168 (100%).

Reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution

$[Pd_2Cl_2(\mu\text{-dppm})_2]$ (0.135 g, 1.3×10^{-4} mol) was placed in a 25-mL, argon-filled Schlenck tube containing a magnetic stirrer bar and freshly distilled methylene chloride (25 mL) was added. The solution was cooled to −78°C in a Dry Ice – acetone bath. In a separate flask, freshly distilled methylene chloride (10 mL) was added to bis(diethylamino)acetylene (0.24 mL, 0.22 g, 1.3×10^{-3} mol, 10× excess). The acetylene solution was added via cannula to the cooled solution of $[Pd_2Cl_2(\mu\text{-dppm})_2]$. The reaction mixture was allowed to warm to room temperature by slow evaporation of carbon dioxide from the cooling bath over a period of 6 h. The color of the reaction mixture changed from orange to red. The reaction mixture was then filtered via cannula into a Schlenk flask and concentrated to a volume of 7 mL on a vacuum line. Freshly dried diethyl ether (25 mL) was layered onto the methylene chloride solution and the flask cooled in a freezer for 24 h. A solid precipitate formed that was filtered from the orange supernatant liquid (see below). The yellow-gold solid was washed with two 10-mL portions of diethyl ether and dried under vacuum for 3 h. The product was identified as $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ as follows: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 14.9; ^{1}H NMR (CD_2Cl_2): δ 1.65 (quintet) (μ-CH_2), $J_{(P,H)}$ = 7.7 Hz, δ 7.90 (m), 7.64 (m), 7.42 (m), 7.28 (m) 7.13 (t) (Ph_2P-), δ 3.5 (m) (P-CH_2-P), $J_{(P,H)}$ = 4.7 Hz, $J_{(H,H)}$ = 14 Hz, δ 2.8 (m) (P-CH_2-P) $J_{(P,H)}$ = 3.4 Hz, $J_{(H,H)}$ = 14 Hz. Anal. calcd. (found) for $C_{51}H_{46}Cl_2P_4Pd_2$: C 57.4 (56.9), H 4.3

Table 1. X-ray data for $\mathbf{1}\cdot 2CH_2Cl_2$ and $\mathbf{2}$.

	$\mathbf{1}\cdot 2CH_2Cl_2$	**2**
Formula	$C_{53}H_{50}Cl_6Pd_2P_4$	$C_{18}H_{60}N_6$
fw	1236.40	360.72
F(000)	2488	630
Crystal dimensions, mm	0.24 × 0.18 × 0.12	0.30 × 0.20 × 0.15
Radiation (λ, Å)	Mo K_α (0.71073)	Mo K_α (0.71073)
Temperature, K	190 ± 1	294 ± 1
Space group	$P4_3$	$R\bar{3}$
Cell dimensions		
a, Å	21.129(5)	18.147(3)
c, Å	14.267(4)	8.151(1)
V, $Å^3$	6369(5)	2325(1)
Z	4	3
D_{calc}, g/cm^3	1.29	0.78
μ, cm^{-1}	9.4	0.45
No. of parameters	509	95
R	0.062	0.038
R_w	0.096	0.044
S	2.83	1.41
Maximum residual density, e/$Å^3$	1.83	0.15

(4.3). Yield = 39.2 mg (36% based on Pd). Crystals of $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]\cdot 2CH_2Cl_2$ suitable for X-ray diffraction experiments were obtained by slow evaporation of methylene chloride.

The orange supernatant liquid (see above) was reduced in volume to 2 mL under vacuum. The resulting oily liquid was cooled in a freezer at 0°C for 7 days during which time clear, colorless crystals formed that were found to be suitable for X-ray diffraction and were identified as hexakis(diethylamino)benzene (<5% yield).

X-ray crystallography

(i) $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]\cdot 2CH_2Cl_2$ ($\mathbf{1}\cdot 2CH_2Cl_2$)

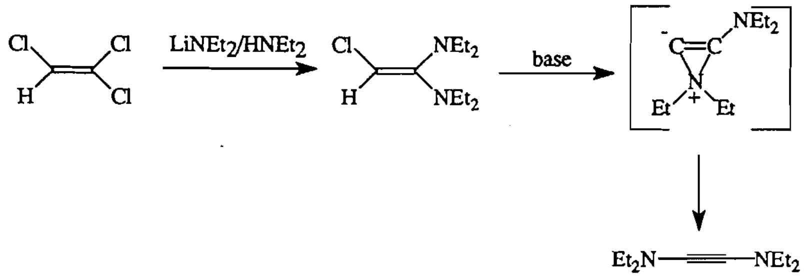
Slow evaporation of the solvent, CH_2Cl_2, yielded yellow single crystals. The crystals diffracted X-rays poorly. They lost solvent and turned into a yellow powder within about 10 min at room temperature. Rapid handling and cooling (190 K) circumvented this problem. The tetragonal unit cell constants and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $10 < \Theta < 13°$. As a check on crystal stability the intensities of three representative reflections were measured every 60 min, indicating a total loss in intensity of 1.9%. An anisotropic decay correction was applied with correction factors on *I* in the range from 0.963 to 1.103. A total of 4340 reflections were collected, of which 4077 were unique. Intensities of equivalent reflections were averaged, the agreement factors were 3.0% based on *I* and 2.1% based on F_0. A total of 3321 reflections with $F_0^2 > 3.0\sigma(F_0^2)$ were used in the calculations.

Structure solution and refinement: The positions of the two palladium atoms were found by direct methods. The remaining atoms were located by repeated least-squares refinements followed by difference Fourier syntheses. A total of two equivalents of highly disordered CH_2Cl_2 were found per metal complex. The disorder was modeled and refined in the following ways. C(60), Cl(5), Cl(5a), Cl(6), and Cl(6a) comprised 3/4 equivalent of CH_2Cl_2 disordered over two positions with occupancies for C(60) of 3/4, for Cl(5) and Cl(6) of 1/2, and for Cl(5a) and Cl(6a) of 1/4. Similarly, another 3/4 equivalent of CH_2Cl_2 included C(61) (multiplicity = 3/4), Cl(7) and Cl(8) (occupancy = 1/2), as well as Cl(7a) and Cl(8a) (occupancy = 1/4). C(62), C(l9) and Cl(10) represented another 1/2 equivalent of CH_2Cl_2. The atomic positions of the solvent were fixed and only isotropic thermal parameters were refined. The relatively high maximum residual electron density (1.83 e/$Å^3$) might be due to further small quantities of disordered solvent that we were unable to include in our model. The carbon atoms, C(2), C(7), C(11), C(41), C(47), C(50), and C(51), of the metal complex were refined with isotropic thermal parameters. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms of the metal complex were calculated and included in the least-squares refinement as riding atoms, $U_{iso} = 1.3U_{eq}$ (bonding atom). The hydrogen positions for the disordered CH_2Cl_2 were not calculated. The final cycle of refinement included 509 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.062$ and $R_w = 0.096$. Further details are given in Table 1.

(ii) $C_6(NEt_2)_6$ (2)

Cooling a solution of **2** in CH_2Cl_2 yielded colorless single crystals. The rhombohedral 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 $4 < \Theta < 15°$. As a check on crystal stability the intensities of three representative reflections were measured every 60 min, indicating a total gain in intensity of 0.2%. An

Fig. 5. Synthesis of $Et_2NC\equiv CNEt_2$.



anisotropic decay correction was applied with correction factors on I in the range from 0.983 to 1.035. A total of 1111 reflections were collected, of which 1011 were unique. Intensities of equivalent reflections were averaged, the agreement factors were 1.6% based on I and 1.6% based on F_o. A total of 624 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ were used in the calculations.

Structure solution and refinement: The positions of six atoms were found by direct methods. The remaining atoms were located in succeeding difference Fourier syntheses. The molecule lies on a $\bar{3}$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic thermal parameters. The final cycle of refinement included 95 parameters and converged with unweighted and weighted agreement factors of $R = 0.038$ and $R_w = 0.044$. Further details are given in Table 1.

Reaction of $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ with $Et_2NC\equiv CNEt_2$ in methylene chloride solution

$[Pd_2Cl_2(\mu\text{-dmpm})_2]$ (0.110 g, 2.0×10^{-4} mol) was placed in a 100-mL, nitrogen-filled Schlenck tube containing a magnetic stirrer bar, and freshly distilled methylene chloride (25 mL) was added. Bis(diethylamino)acetylene (50 μL, 2.65×10^{-4} mol) was added slowly via syringe over a period of 5 min. The reaction mixture was allowed to stir for 6 h at room temperature. The color of the reaction mixture changed from yellow to dark red. The reaction mixture was then filtered via cannula into a Schlenck flask and concentrated to a volume of less than 10 mL on a vacuum line. Freshly dried diethyl ether (15 mL) was layered onto the methylene chloride solution and the flask allowed to stand at room temperature overnight followed by cooling in a freezer for 24 h. A solid precipitate formed that was filtered from the orange supernatant liquid. The yellow-black solid was washed with two 10-mL portions of diethyl ether and dried under vacuum for 2 h. The solid was then dissolved in the minimum amount of methylene chloride and allowed to stand overnight during which time a black precipitate formed. The yellow supernatant was filtered from the black solid via cannula, and diethyl ether (15 mL) was layered onto the methylene chloride solution. After 24 h at room temperature a yellow solid had formed that was isolated by cannula filtration, washed with two 25-mL portions of diethyl ether, and dried under vacuum for 8 h. The product was identified as $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dmpm})_2]$ as follows: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −4.1; ^1H NMR (CD_2Cl_2): δ 1.3 (quintet) (μ-CH_2), $J_{(P,H)} = 7.7$ Hz, δ 1.7 (s) 1.6 (s) (Me_2P-), δ 2.26 (m), 1.52 (m) (P-CH_2-P), $J_{(P,H)} = 4.7$ Hz, $J_{(H,H)} = 14$ H. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.9 (s) (μ-CH_2), δ 23.0 (t) (P-CH_2-P), δ 15.6 (qn), 14.6 (qn) (Me_2P-). Anal. calcd. (found) for $C_{11}H_{30}Cl_2P_4Pd_2$: C 23.2.(23.3), H 5.3 (5.2). Yield = 28.6 mg (25.3% based on Pd).

Results and discussion

Simple acetylenes, such as $CF_3C\equiv CCF_3$, react with dinuclear palladium(I) complexes of the type $[Pd_2X_2(\mu\text{-PP})_2]$ to yield acetylene-bridged products (1–3), as illustrated in Fig. 1, while the sulfur-substituted acetylene $MeSC\equiv CSMe$ reacts according to the pathways illustrated in Figure 2, with formation of a vinylidene-bridged complex under Lewis-acid-promoted conditions (4, 5). Other heteroatom-substituted acetylenes, such as $IC\equiv CI$ (6), $ClC\equiv CCl$ (16), $PhC\equiv CCl$ (17), $MeSC\equiv CMe$ (4, 5), and $MeOC\equiv CMe$[3] have also been shown to yield vinylidene-bridged products in reactions with $[Pd_2X_2(\mu\text{-PP})_2]$ complexes via 1,2-heteroatom shifts under certain conditions. Since the nitrogen-substituted acetylene, $MeC\equiv CNMe_2$, is known (7) to undergo a 1,2-heteroatom shift in the reaction with $[Mn_2(CO)_9(NCMe)]$, we sought to investigate the reactions of nitrogen-substituted acetylenes with dinuclear palladium(I) complexes. Our work with sulfur-substituted acetylenes has revealed significant differences in reactivity between symmetrically substituted acetylenes and unsymmetrically substituted acetylenes (e.g., $MeSC\equiv CSMe$ vs. $MeSC\equiv CMe$ (4,5)) and so we first began to investigate the reactivity of the symmetrically substituted, nitrogen-containing acetylene, $Et_2NC\equiv CNEt_2$, with $[Pd_2X_2(\mu\text{-PP})_2]$ (X = anionic ligand, PP = dppm, dmpm) complexes.

The synthesis of $Et_2NC\equiv CNEt_2$, detailed in the experimental section, was derived from literature reports (11–13) and followed the pathway outlined in Fig. 5. Our modifications to the reported methods led to isolation of $Et_2NC\equiv CNEt_2$ in a 74% overall yield.

The reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with a tenfold excess of $Et_2NC\equiv CNEt_2$ in methylene chloride solution was investigated. The reaction was monitored by removal of aliquots and measurement of the $^{31}P\{^1H\}$ NMR spectra, which revealed a complex mixture of species in solution. Precipitation with diethyl ether allowed isolation of a single complex (δP = 14.9 ppm) whose ^1H NMR spectrum revealed, in addition to resonances attributed to the bridging dppm ligands, a quintet at

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[3] J.A. Davies, C. Kluwe, and J. Müller. Unreported results.

Fig. 6. ORTEP diagram of $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ (**1**).

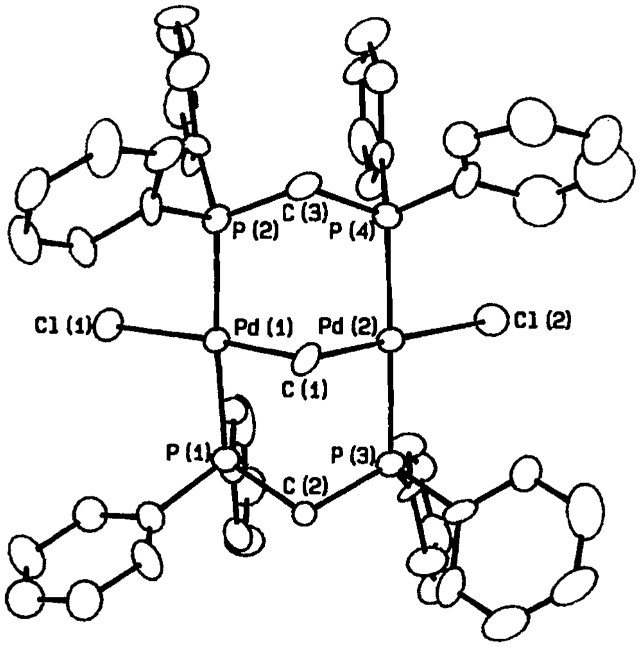


Table 2. Selected bond angles and distances for $\mathbf{1}\cdot 2CH_2Cl_2$.

(*a*) Bond angles (°).

Atom 1	Atom 2	Atom 3	Angle
Cl(1)	Pd(1)	P(1)	90.4(2)
Cl(1)	Pd(1)	P(2)	95.3(2)
Cl(1)	Pd(1)	C(1)	174.8(7)
P(1)	Pd(1)	P(2)	174.3(2)
P(1)	Pd(1)	C(1)	88.1(6)
P(2)	Pd(1)	C(1)	86.2(6)
Cl(2)	Pd(2)	P(3)	92.6(2)
Cl(2)	Pd(2)	P(4)	92.0(2)
Cl(2)	Pd(2)	C(1)	176.6(6)
P(3)	Pd(2)	P(4)	174.2(2)
P(3)	Pd(2)	C(1)	87.3(6)
P(4)	Pd(2)	C(1)	87.9(6)
Pd(1)	C(1)	Pd(2)	103(1)

(*b*) Bond lengths (Å).

Atom 1	Atom 2	Distance
Pd(1)	Cl(1)	2.429(5)
Pd(1)	P(1)	2.311(6)
Pd(1)	P(2)	2.321(6)
Pd(1)	C(1)	2.04(2)
Pd(2)	Cl(2)	2.419(6)
Pd(2)	P(3)	2.300(6)
Pd(2)	P(4)	2.319(6)
Pd(2)	C(1)	2.03(2)
Pd(1)	Pd(2)	3.171(2)[a]

[a] Refers to the Pd(1)·······Pd(2) separation.

1.65 ppm. A comparison to literature data (18–20) suggested that this signal could be attributed to a methylene group bridging the palladium centers and that the complex, isolated in 36% yield, was $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$. Single crystals of $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]\cdot 2CH_2Cl_2$ ($\mathbf{1}\cdot 2CH_2Cl_2$) suitable for X-ray diffraction were obtained from a methylene chloride solution by slow solvent evaporation. The structure of $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ is shown in Fig. 6, selected bond angles and distances are presented in Table 2, and positional parameters and B_{eq} are shown in Table 3.

The two palladium centers are spanned by two bridging dppm ligands and the bridging methylene group. The structure adopts the typical "A-frame" coordination mode common to related systems. Each palladium center is approximately square-planar with terminal chloride ligands *trans* to the bridging methylene group. The most significant deviations from square-planar geometry occurred in the angles P1-Pd1-P2 (174.3(2)°), P3-Pd2-P4 (174.2(2)°), Cl1-Pd1-P2 (95.3(2)°), P1-Pd1-C1 (88.1(6)°), and P2-Pd1-C1 (86.2(6)°). These deviations most likely arise from the incompatibility of the optimum Pd·····Pd separation and the ideal tetrahedral geometry of the bridging methylene group. The structure corresponds closely to that reported previously for the platinum analog (21).

The origin of the methylene bridge in $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ was shown to be the methylene chloride solvent by repeating the reaction of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ with $Et_2NC{\equiv}CNEt_2$ in d_2-methylene chloride solution. The resulting product exhibited an identical $^{31}P\{^1H\}$ NMR spectrum to that described above ($\delta P = 14.9$ ppm), but the ^1H NMR spectrum lacked the quintet at 1.65 ppm, confirming incorporation of a $\mu\text{-}CD_2$ group in place of $\mu\text{-}CH_2$. In the absence of $Et_2NC{\equiv}CNEt_2$, $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ was shown to be unreactive towards methylene chloride under conditions comparable to those employed in the reaction. Thus, stirring a methylene chloride solution of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ at room temperature for 3 weeks or refluxing a methylene chloride solution of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ overnight gave no evidence for formation of $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ by $^{31}P\{^1H\}$ NMR spectroscopy. These data suggest that $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ reacts with $Et_2NC{\equiv}CNEt_2$ to generate one or more species capable of further reaction with methylene chloride to form $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$.

The second product isolated in low yield from the reaction of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ with a tenfold excess of $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution was identified crystallographically as hexakis(diethylamino)benzene, the cyclotrimerization product derived from $Et_2NC{\equiv}CNEt_2$. The structure of $C_6(NEt_2)_6$ is shown in Fig. 7, selected bond angles and distances are presented in Table 4, and positional parameters and B_{eq} are shown in Table 5.

The molecule possesses approximate C_{6h} symmetry. The bond lengths and angles have normal values and correspond well to those reported for $C_6(NMe_2)_6$ (22). The diethylamino substituents adopt a conformation such that the nitrogen lone pair does not participate in the aromatic π-system and the C_{Ar}—N bond distances reflect the single bond character.

Palladium-promoted cyclotrimerization reactions of acetylene are well known (23) but much of the reported work concerns reactions of simple acetylenes promoted by complexes of palladium(0) or palladium(II). Reactions of functionalized

Table 3. Positional parameters and B_{eq} for $\mathbf{1}\cdot 2CH_2Cl_2$.

Atom	*x*	*y*	*z*	B^a (Å^2)
Pd(1)	0.51034(7)	0.21788(7)	0.477	1.58(3)
Pd(2)	0.43228(8)	0.11260(7)	0.5856(2)	1.72(3)
Cl(1)	0.6076(2)	0.2790(3)	0.4710(5)	2.6(1)
Cl(2)	0.4314(3)	0.0440(3)	0.7213(4)	2.9(1)
Cl(5)	0.293	0.238	0.256	6.9(4)*
Cl(5a)	0.310	0.225	0.288	4.5(6)*
Cl(6)	0.404	0.276	0.158	3.0(2)*
Cl(6a)	0.419	0.249	0.207	8(1)*
Cl(7)	0.204	0.174	0.023	5.5(3)*
Cl(7a)	0.185	0.164	−0.003	9(1)*
Cl(8a)	0.239	0.313	0.001	6.6(8)*
Cl(8)	0.243	0.296	−0.017	4.9(3)*
Cl(9)	0.251	0.124	0.471	8.8(5)*
Cl(10)	0.224	0.083	0.280	10.6(7)*
P(1)	0.5596(3)	0.1346(3)	0.4017(4)	1.9(1)
P(2)	0.4516(3)	0.2958(3)	0.5520(4)	1.8(1)
P(3)	0.4747(3)	0.0352(2)	0.4913(4)	1.9(1)
P(4)	0.3834(3)	0.1938(3)	0.6677(4)	1.9(1)
C(1)	0.4279(9)	0.1680(9)	0.470(2)	2.0(4)
C(2)	0.5116(9)	0.0636(9)	0.380(1)	1.4(4)*
C(3)	0.3773(9)	0.2709(9)	0.603(2)	2.0(5)
C(4)	0.583(1)	0.154(1)	0.283(2)	2.7(5)
C(5)	0.548(1)	0.146(1)	0.205(1)	2.4(5)
C(6)	0.568(1)	0.166(1)	0.119(2)	3.5(6)
C(7)	0.626(1)	0.192(1)	0.109(2)	3.5(5)*
C(8)	0.667(1)	0.201(1)	0.185(2)	4.2(6)
C(9)	0.644(1)	0.182(1)	0.275(2)	3.1(6)
C(10)	0.629(1)	0.103(1)	0.461(2)	2.5(5)
C(11)	0.6479(9)	0.126(1)	0.546(2)	2.0(4)*
C(12)	0.700(1)	0.098(1)	0.590(2)	4.4(6)
C(13)	0.732(1)	0.046(1)	0.549(2)	3.2(6)
C(14)	0.712(1)	0.026(1)	0.465(2)	3.8(6)
C(15)	0.664(1)	0.052(1)	0.422(2)	3.1(5)
C(16)	0.4252(9)	0.3541(9)	0.470(2)	2.0(4)
C(17)	0.367(1)	0.3844(9)	0.480(2)	2.7(5)
C(18)	0.350(1)	0.430(1)	0.408(2)	3.9(6)
C(19)	0.393(1)	0.447(1)	0.339(2)	3.0(5)
C(20)	0.451(1)	0.416(1)	0.334(2)	3.4(5)
C(21)	0.464(1)	0.371(1)	0.395(2)	2.5(5)
C(22)	0.487(1)	0.340(1)	0.650(2)	2.0(5)
C(23)	0.456(1)	0.392(1)	0.688(2)	3.3(6)
C(24)	0.481(1)	0.423(1)	0.766(2)	4.0(6)
C(25)	0.535(1)	0.403(1)	0.802(2)	3.2(6)
C(26)	0.569(1)	0.354(1)	0.765(2)	3.7(6)
C(27)	0.5441(9)	0.3211(9)	0.686(1)	1.7(4)
C(28)	0.533(1)	−0.0174(9)	0.540(2)	2.0(5)
C(29)	0.564(1)	−0.005(1)	0.620(2)	2.2(5)
C(30)	0.611(1)	−0.043(1)	0.653(2)	3.4(6)
C(31)	0.628(1)	−0.100(1)	0.607(2)	3.7(6)
C(32)	0.597(1)	−0.114(1)	0.520(2)	4.5(7)
C(33)	0.548(1)	−0.0728(9)	0.491(2)	2.7(5)
C(34)	0.413(1)	−0.017(1)	0.451(2)	2.5(5)
C(35)	0.416(1)	−0.046(1)	0.362(2)	3.4(6)
C(36)	0.366(1)	−0.084(1)	0.331(2)	4.2(6)
C(37)	0.317(1)	−0.097(1)	0.391(2)	3.8(6)
C(38)	0.312(1)	−0.070(1)	0.479(2)	5.0(7)
C(39)	0.362(1)	−0.029(1)	0.509(2)	3.7(6)
C(40)	0.423(1)	0.216(1)	0.776(1)	1.9(5)
C(41)	0.396(1)	0.265(1)	0.833(2)	2.7(4)*
C(42)	0.434(1)	0.286(1)	0.913(2)	4.3(7)
C(43)	0.489(1)	0.258(1)	0.931(2)	3.1(6)
C(44)	0.515(1)	0.210(1)	0.878(2)	3.5(6)
C(45)	0.4813(9)	0.191(1)	0.798(2)	2.1(5)
C(46)	0.301(1)	0.180(1)	0.701(2)	3.6(6)
C(47)	0.251(1)	0.220(1)	0.680(2)	2.9(5)*
C(48)	0.192(1)	0.199(1)	0.702(2)	5.0(7)
C(49)	0.176(1)	0.146(1)	0.740(2)	4.2(7)
C(50)	0.221(2)	0.112(2)	0.766(3)	8(1)*
C(51)	0.289(2)	0.120(2)	0.746(3)	6.4(8)*
C(60)	0.363	0.277	0.258	8(1)*
C(61)	0.268	0.077	0.380	6(2)*
C(62)	0.252	0.224	−0.044	5(1)*

[a] Starred atoms 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 4. Selected bond angles and distances for **2**.

(*a*) Bond angles (°).

Atom 1	Atom 2	Atom 3	Angle
C(1)	N(1)	C(2)	115.3(1)
C(1)	N(1)	C(4)	115.6(1)
C(2)	N(1)	C(4)	110.9(1)
N(1)	C(2)	C(3)	115.2(1)
N(1)	C(1)	C(1′)	117.0(1)
N(1)	C(1)	C(1″)	123.0(1)
C(1″)	C(1)	C(1)′	120.0(1)

(*b*) Bond lengths (Å).

Atom 1	Atom 2	Distance
N(1)	C(1)	1.447(2)
N(1)	C(2)	1.469(2)
N(1)	C(4)	1.468(2)
C(2)	C(3)	1.507(3)
C(1)	C(1′)	1.409(1)

[a] Symmetry transformation (′): $1 + y, 1 - x + y, 2 - z$; (″): $x - y, -1 + z, 2 - z$.

acetylenes and reactions promoted by palladium(I) are much less common. The cyclotrimerization of the dimethyl ester of acetylene dicarboxylic acid to yield hexamethyl mellitate, promoted by $[Pd_2Cl_2(\mu\text{-dppm})_2]$, has been described and a mechanism proposed (24). In the case of the cyclotrimerization of $Et_2NC{\equiv}CNEt_2$, a comparable mechanism suggests pathways by which $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ might be formed. Fig-

Table 5. positional parameters and B_{eq} for **2**.

Atom	x	y	z	B^a (Å^2)
N(1)	0.87327(7)	0.04885(7)	1.0173(2)	2.52(3)
C(1)	0.93566(8)	0.02184(9)	1.0018(2)	2.15(3)
C(2)	0.8230(1)	0.0225(1)	1.1692(2)	3.39(4)
C(3)	0.8726(1)	0.0311(1)	1.3232(2)	3.95(5)
C(4)	0.81828(9)	0.0327(1)	0.8739(2)	3.32(4)
C(5)	0.7790(1)	0.0894(1)	0.8690(3)	4.94(5)
H(21)	0.799(1)	0.062(1)	1.179(2)	4.4(4)*
H(22)	0.7741(9)	−0.0373(9)	1.160(2)	3.7(4)*
H(31)	0.917(1)	0.091(1)	1.342(2)	5.8(5)*
H(32)	0.835(1)	0.014(1)	1.421(2)	5.3(4)*
H(33)	0.898(1)	−0.005(1)	1.321(2)	5.4(4)*
H(41)	0.770(1)	−0.031(1)	0.871(2)	4.2(4)*
H(42)	0.8546(9)	0.0444(9)	0.772(2)	3.4(4)*
H(51)	0.738(1)	0.076(1)	0.960(3)	7.0(6)*
H(52)	0.820(1)	0.149(1)	0.884(2)	6.9(5)*
H(53)	0.752(1)	0.086(1)	0.761(3)	7.7(6)*

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

Fig. 7. ORTEP diagram of $C_6(NEt_2)_6$ (**2**).

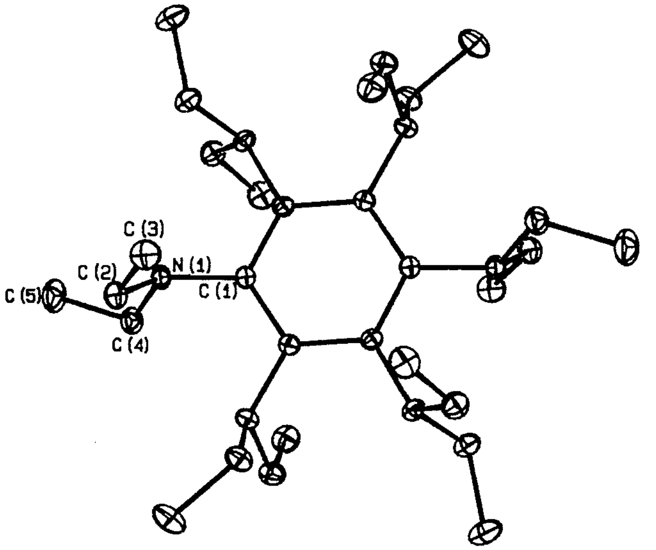
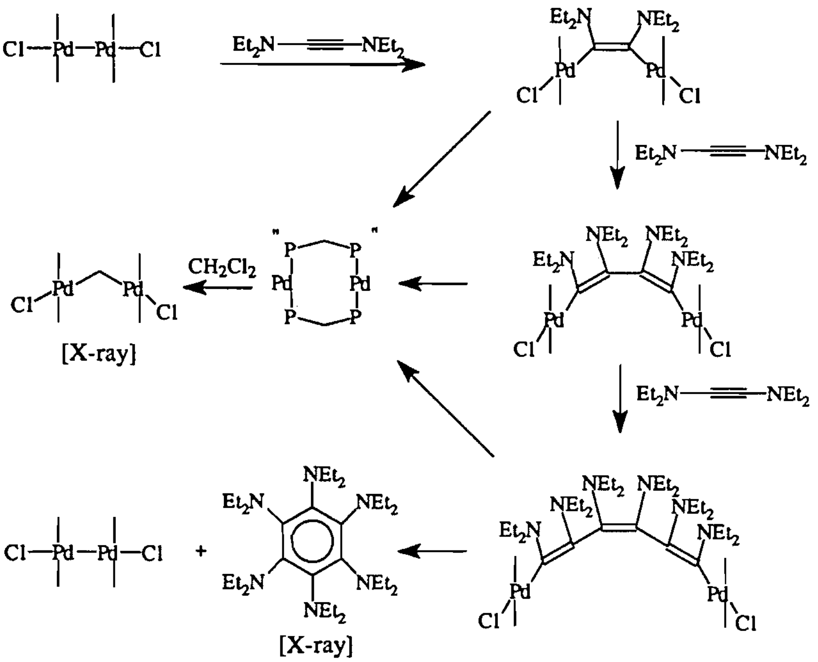


Fig. 8. Possible mechanism for cyclotrimerization of $Et_2NC{\equiv}CNEt_2$.



ure 8 outlines a possible mechanism for cyclotrimerization of $Et_2NC{\equiv}CNEt_2$ that is based upon that proposed for hexamethyl mellitate formation (24).

Included in the pathway are intermediates capable of reductive elimination of chlorinated organic fragments. Such processes would lead to the generation of palladium(0) species that might subsequently react with methylene chloride to form $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$. It is noteworthy that $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ was synthesized earlier by the reaction between the binuclear palladium(0) complex, $[Pd_2(\mu\text{-dppm})_3]$, and methylene chloride (21). Binuclear palladium(0) complexes of the type $[Pd_2(\mu\text{-PP})_2]$, although not known with dppm as the bridging ligand, have been isolated and characterized crystallographically with the sterically demanding

$Cy_2P(CH_2)_2PCy_2$ ligand to provide kinetic stabilization (25). Thus, the mechanism illustrated in Fig. 8 appears to be a reasonable pathway, which accounts for the formation of both $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ and $C_6(NEt_2)_6$ from the reaction between $[Pd_2Cl_2(\mu\text{-dppm})_2]$ and $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution. However, all attempts, by GC–MS, to detect chlorinated organic products resulting from the various reductive elimination pathways in Fig. 8 failed (26) and so the possibility exists that reactive palladium(0) species, capable of oxidative addition of methylene chloride, arise from other pathways distinct from those illustrated in Fig. 8. Similarly, we cannot exclude the possibility that cyclotrimerization is promoted by a palladium-containing decomposition product.

The complex $[Pd_2Cl_2(\mu\text{-dppm})_2]$ was found to be unreactive towards $Et_2NC{\equiv}CNEt_2$ in chloroform and monitoring a $CHCl_3$ solution of these compounds by $^{31}P\{^1H\}$ NMR spectroscopy over a period of several hours gave no evidence for any reaction. $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ was found to react with $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution and $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dmpm})_2]$ could be isolated in pure form from the reaction mixture in 25.3% yield.

Conclusions

The palladium(I) complex, $[Pd_2Cl_2(\mu\text{-dppm})_2]$, has been shown to react with $Et_2NC{\equiv}CNEt_2$ in methylene chloride solution to yield the product of acetylene cyclotrimerization, $C_6(NEt_2)_6$, and the methylene-bridged complex, $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$, as isolable products. Formation of $C_6(NEt_2)_6$ suggests initial generation of an acetylene complex capable of further reaction, via two insertion steps and a reductive elimination step, to generate the hexasubstituted benzene. Isolation of $[Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ is suggestive of a deactivation pathway that involves generation of a palladium(0) intermediate capable of oxidative addition of the methylene chloride solvent. The results, together with those extant in the literature (24) show that binuclear palladium(I) complexes serve as promoters for the synthesis of hexasubstituted benzenes by acetylene cyclotrimerization and that this reaction is possible even with heteroatom-substituted acetylenes that lead to highly functionalized aromatics. In the case described here, however, the possibility of catalysis by unidentified palladium-containing decomposition products cannot be excluded.

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References

1. A.L. Balch, C.-L. Lee, C.H. Lindsay, and M.M. Olmstead. J. Organomet. Chem. **177**, C22 (1979).
2. B.L. Shaw and S.J. Higgins. J. Chem. Soc. Chem. Commun. 1629 (1986).
3. B.L. Shaw and S.J. Higgins. J. Chem. Soc. Dalton Trans. 457 (1988).
4. J.A. Davies, K. Kirschbaum, and C. Kluwe. Organometallics, **13**, 3664 (1994).
5. C. Kluwe and J.A. Davies. Organometallics, **14**, 4257 (1995).
6. J.A. Davies, A.A. Pinkerton, R. Syed, and M.J. Vilmer, J. Chem. Soc., Chem. Commun. 47 (1988).
7. R.D. Adams, G. Chen, L. Chen, M.P. Pompeo, and J. Yin. Organometallics, **10**, 2541 (1991).
8. R.B. King and C.A. Harmon. Inorg. Chem. **15**, 879 (1976).
9. A.L. Balch and L.S. Benner. Inorg. Synth. **21**, 47 (1982).
10. J.A. Davies, S. Dutremez, and M. Vilmer, J. Prakt. Chem. **334**, 34 (1992).
11. L. Brandsma and R. van der Heiden. Synthesis, 76 (1987).
12. L. Brandsma and H.D. Verkruijsse. Synth. Commun. **21**, 811 (1991).
13. H.G. Viehe and S.Y. Delavarenne. Chem. Ber. **103**, 1209 (1970).
14. D.T. Cromer and J.T. Waber. International tables for X-ray crystallography. Vol. IV. Kynoch Press, Birmingham, England. 1974.
15. C.K. Fair. MolEN: An interactive intelligent system for crystal structure analysis; User Manual. Enraf–Nonius, Delft, The Netherlands. 1990.
16. M. Vilmer. Ph.D. Thesis, University of Toledo, 1991.
17. S. Zheng. M.S. Thesis, University of Toledo, 1993.
18. H.G. Viehe and M. Reinstein. Angew. Chem. Intl. Ed. Engl. **3**, 506 (1964).
19. M.P. Brown, J.R. Fisher, R.J. Puddephatt, and K.R. Seddon. Inorg. Chem. **18**, 2808 (1979).
20. A.L. Balch, C.T. Hunt, C.L. Lee, M.M. Olmstead, and J.P. Farr. J. Am. Chem. Soc. **103**, 3764 (1981).
21. R.J. Puddephatt, K.A. Azam, A.A. Frew, B.R. Lloyd, L. Monojlovic-Muir, and K.W. Muir. Organometallics, **4**, 1400 (1985).
22. K. Mislow, J.P. Toscano, A.B. Buda, B. Kahr, and J.M. Chance. J. Org. Chem. **53**, 3226 (1988).
23. J.A. Davies. *In* Comprehensive organometallic chemistry II. Vol. 9. *Edited by* E.W. Abel, F.G.A. Stone, and G. Wilkinson (Volume edited by R.J. Elsevier, Oxford. 1995. Puddephatt) p. 291.
24. A.L. Balch, C.T. Hunt, and C.-L. Lee. Inorg. Chem. 20, 2498 (1981).
25. Y. Pan, J.T. Mague, and M.J. Fink. J. Am. Chem. Soc. **115**, 3842 (1993).
26. S. Klopfenstein. M.S. Thesis, University of Toledo, 1995.