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Inorganica Chimica Acta 259 (1997) 173–178

Inorganica Chimica Acta

Hydride-bridged dipalladium complexes containing diphosphine ligands

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Received 20 August 1996; revised 20 September 1996; accepted 23 October 1996

Abstract

A series of hydride-bridged dipalladium complexes supported by bis(diphenylphosphino)methane (dppm) ligands has been prepared. The complexes $[Pd_2R_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ (R = Me, Et, Bu, CH_2SiMe_3, Ph) were generated by reduction, using $NaBH_3CN$, of the corresponding halide-bridged species. The products are thermally stable, yellow solids, and they have been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The ethyl complex $[Pd_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ has been characterized further by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.6160$ (1), $b = 12.8637$ (1), $c = 25.3739$ (3) Å, $\beta = 97.479$ (1)° and $Z = 2$. The cation adopts an A-frame structure, with a Pd–Pd distance of 2.9933 (7) Å.

Keywords: Crystal structures; Palladium complexes; Hydride-bridged complexes; Dinuclear complexes

1. Introduction

Many di- and trinuclear platinum hydride complexes bridged by diphosphine ligands are known [1–5]. Among the dinuclear species are the platinum(I) species $[Pt_2HL(\mu\text{-dppm})_2]^+$ (L = CO, PPh_3, $PMePh_2$, PMe_2Ph, η^1-dppm) and $[Pt_2H(SR)(\mu\text{-dppm})_2]$ (dppm = bis(diphenylphosphino)-methane) [6–9]. Platinum(II) complexes may contain only terminal hydride ligands, as in the case of $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ [10], but more commonly they contain bridging hydrides. The trihydride complex $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, prepared by $NaBH_4$ reduction of $[PtCl_2(dppm)]$, has been studied extensively, and serves as a catalyst for the water gas shift reaction [8,11,12]. The related complexes $[Pt_2HMe(\mu\text{-H})(\mu\text{-dppm})_2]^+$ and $[Pt_2R_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (R = Me, Et) have also been prepared [13–15]. We have shown that unsymmetrical hydride-bridged complexes may be prepared by reaction of cations of the type $[PtR(dppm\text{-}PP)(dppm\text{-}P)]^+$ with $[PtClR'(cod)]$, followed by reduction to give $[RPt(\mu\text{-H})(\mu\text{-dppm})_2PtR']^+$, and this may also be extended to mixed platinum–palladium species [16,17]. All of these complexes exhibit considerable thermal stability.

In contrast, there are few examples of hydridopalladium compounds with dppm ligands, and these have been reported to be of limited thermal stability. Treatment of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with 1 or 2 equiv. of Me_3Al at −78°C, followed by $NaBPh_4$ and ethanol, has been shown to generate $[Pd_2HMe(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ or $[Pd_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ respectively [18]. We have shown previously that hydride-bridged dipalladium species may be prepared by $NaBH_4$ reduction of $[Pd_2R_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ (R = Me, Ph), and that these compounds are stable in solution at ambient temperature for extended periods of time [16]. Here we report alternative approaches to these compounds, and extension of this series to provide a general route to hydride-bridged dipalladium complexes.

2. Results and discussion

The previously reported complex $[Pd_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]BPh_4$ was prepared by apparent protonation of the palladium(I) complex $[Pd_2Me_2(\mu\text{-dppm})_2]$ using ethanol at low temperature [18]. Our approach to this and related hydride-bridged dipalladium complexes has been by reduction of the corresponding chloride-bridged A-frame complexes $[Pd_2R_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$. We have shown that the methyl and phenyl species may be prepared by addition of 2 equiv. of dppm to the chloride-bridged dimers $[Pd_2R_2(\mu\text{-Cl})_2(AsPh_3)_2]$, where triphenylarsine serves as a suitable leaving group [16]. The methyl derivative may also be produced by addition of dppm to $[PdClMe(cod)]$ (cod = 1,5-cyclooctadiene), prepared from $[PdCl_2(cod)]$ and $SnMe_4$ [19,20], but the corresponding phenyl precursor is unavailable. Alternatively, we have found that $[Pd_2Me_2(\mu\text{-}$

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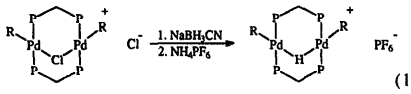
PII S0020-1693(97)05446-7

Cl)(μ-dppm)$_2$]Cl may be prepared cleanly by treatment of [PdCl$_2$(dppm)] with SnMe$_4$ (the corresponding reaction with SnPh$_4$ proved unsuccessful) or MeMgBr.

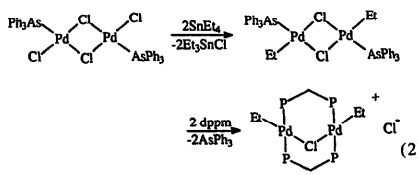
In our earlier report [16], we described the reduction of [Pd$_2$R$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ (R = Me, Ph) using sodium borohydride as the reducing agent. We have now found that sodium cyanoborohydride is a superior reagent for this purpose, since it is a milder reducing agent which is more soluble in organic solvents. Thus, treatment of [Pd$_2$R$_2$(μ-Cl)(μ-dppm)$_2$]Cl (R = Me, Ph), generated in situ, with 2 equiv. of NaBH$_3$CN in CH$_2$Cl$_2$/MeOH solution, followed by addition of NH$_4$PF$_6$ and purification by passing the solution through a short Hyflo Super Cel column, gave the hydride-bridged complexes in good yield (Eq. (1)).



(1)

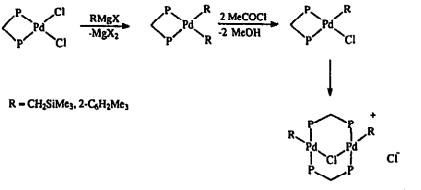
P⌒P = dppm; R = Me, Ph

We have reported that [PdCl(CH$_2$Ph)(cod)] may be prepared from [PdCl$_2$(cod)] and Sn(CH$_2$Ph)$_4$, and the analogous ethyl complex may be generated similarly, but with some difficulty [21]. Treatment of [PdCl(CH$_2$Ph)(cod)] with 1 equiv. of dppm gave [Pd$_2$(CH$_2$Ph)$_2$(μ-Cl)(μ-dppm)$_2$]Cl (δP 11.9), which could be prepared alternatively from [Pd$_2$(CH$_2$Ph)$_2$(μ-Cl)$_2$(AsPh$_3$)$_2$] and dppm. Although [PdClEt(cod)] can be prepared, it undergoes β-elimination of ethene and rearrangement to a cyclooctenylpalladium species, so we decided to approach the ethylpalladium A-frame complexes by the arsine route. Thus, when [Pd$_2$Cl$_2$(μ-Cl)$_2$(AsPh$_3$)$_2$] was treated with SnEt$_4$, followed by 2 equiv. of dppm, [Pd$_2$Et$_2$(μ-Cl)$_2$(μ-dppm)$_2$]Cl (δP 17.3) was formed. In contrast to the cyclooctadiene complex, the ethylpalladium A-frame does not undergo β-elimination readily in solution at ambient temperature.



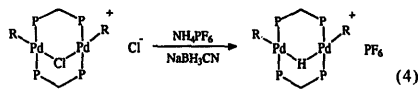
(2)

We have also investigated the reactions of [PdCl$_2$(dppm)] with RMgBr (R = Me, n-Bu, CH$_2$CMe$_3$, 2-C$_6$H$_2$Me$_3$ (mesityl)) or Me$_3$SiCH$_2$MgCl. When R = Me, n-Bu or CH$_2$CMe$_3$, the reaction proceeded to give the chloride-bridged A-frame complex cleanly (in the neo-pentyl case, the bromide-bridged complex or a mixture of chloride- and bromide-bridged species was obtained (δP 12.5 and 16.3), depending on the reaction conditions), but the reaction of [PdCl$_2$(dppm)] with Me$_3$SiCH$_2$MgCl or 2-C$_6$H$_2$Me$_3$MgBr did not. In the latter two cases, low Grignard to Pd ratios led to mixtures of [PdR$_2$(dppm)], [PdCl$_2$(dppm)] and the appropriate halide-bridged A-frame complex. Addition of a large excess of the appropriate Grignard reagent, however, generated the diorganopalladium species [PdR$_2$(dppm)] cleanly, and this could be converted to the chloride-bridged A-frame complex, via the monomeric species [PdClR(dppm)], by reaction with 1 equiv. of HCl (generated in situ from acetyl chloride and methanol) (Eq. (3)). Thus, treatment of [PdCl$_2$(dppm)] with 8 equiv. of Me$_3$SiCH$_2$MgCl produced [Pd(CH$_2$SiMe$_3$)$_2$(dppm)] in quantitative yield (δP −26.2), and addition of 1 equiv. of MeCOCl and a small amount of methanol produced [PdCl(CH$_2$SiMe$_3$)(dppm)] (δP −7.0 d, δP −39.5 d, ^2J(PP) = 72 Hz) which, on standing, underwent complete conversion to [Pd$_2$(CH$_2$SiMe$_3$)$_2$(μ-Cl)(μ-dppm)$_2$]Cl (δP 13.9). Similarly, the dimesitylpalladium complex reacted with HCl to give first [PdCl(C$_6$H$_2$Me$_3$)(dppm)] (δP −23.3 d, δP −44.7 d, ^2J(PP) = 63 Hz), which converted to the chloride-bridged A-frame complex (δP 8.3).



(3)

As mentioned above, the methyl and phenyl chloride-bridged A-frame complexes may be converted to [Pd$_2$R$_2$(μ-H)(μ-dppm)$_2$]$^+$ using NaBH$_4$ or NaBH$_3$CN as the reducing agent. The ethyl, n-butyl and trimethylsilylmethyl derivatives have also been prepared, using NaBH$_3$CN as the reducing agent (Eq. (4)). In each case, [Pd$_2$R$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ was generated in situ in CH$_2$Cl$_2$ solution, and NaBH$_3$CN was added as a THF solution at 0°C. The product was isolated as its hexaflourophosphate salt by addition of excess NH$_4$PF$_6$, because the hydride-bridged complexes are less stable as their chloride salts. Although the methyl, ethyl and phenyl derivatives could be prepared as chlorides and then converted to their PF$_6^-$ salts by metathesis, the butyl and trimethylsilylmethyl compounds were so unstable as their chlorides that NH$_4$PF$_6$ was introduced prior to reduction of the chloride-bridged A-frame. The benzyl complex [Pd$_2$(CH$_2$Ph)$_2$(μ-H)(μ-dppm)$_2$]$^+$ was formed in good yield in solution at low temperature (δH −9.04 q, ^2J(PH) = 18 Hz; δP 17.7), but it decomposed on attempted isolation. [Pd$_2$(CH$_2$CMe$_3$)$_2$(μ-Cl)$_2$(μ-dppm)$_2$]$^+$ reacted with NaBH$_3$CN below ambient temperature, but a number of products were observed by ^{31}P NMR spectroscopy and no hydride resonance could be detected in the ^{1}H NMR spectrum. On the other hand, the mesityl complex [Pd$_2$(C$_6$H$_2$Me$_3$)$_2$(μ-Cl)(μ-dppm)$_2$]Cl was recovered unchanged even after prolonged stirring with either NaBH$_3$CN or NaBHEt$_3$ at ambient temperature.



(4)

R = Et, Bu, CH_2SiMe_3

The isolated compounds $[Pd_2R_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ (R = Me, Et, n-Bu, CH_2SiMe_3, Ph) are air-stable yellow powders. The methyl, ethyl and phenyl derivatives are soluble in polar organic solvents, such as acetone or dichloromethane, but not in non-polar solvents. The butyl complex is slightly soluble in benzene, whereas the trimethylsilylmethyl compound displays significant solubility in benzene or toluene. Their NMR spectra have been recorded in acetone-d_6 or $CDCl_3$ solution. In each case, the ^{31}P resonance appears 5–6 ppm to high frequency of that in the corresponding chloride-bridged complex, indicating that the P atoms are less shielded in the hydride-bridged species. The ^1H NMR spectrum of each complex exhibits a hydride resonance in the range −7.5 to −9.1 ppm, the greatest shielding being observed in the phenyl derivative. A similar range of chemical shifts was found for the corresponding platinum complexes [16]. In each case, the resonance appears as a quintet ($^2J(PH) \approx 15$–16 Hz) due to coupling to the four equivalent P atoms. The dppm CH_2 groups give rise to a single, slightly broad resonance in each case, indicating that the molecules are fluxional at ambient temperature, as has been found for other hydride-bridged A-frame complexes [16,22]. In the ethyl and n-butyl species the ^1H signal due to the CH_2 group attached to Pd appears around 1 ppm, but the other CH_2 and CH_3 resonances are shifted to lower frequency. In $[Pd_2(CH_2SiMe_3)_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ the CH_2 signal appears at 0.57 ppm, whereas in the methyl derivative the CH_3 resonance is close to 0 ppm.

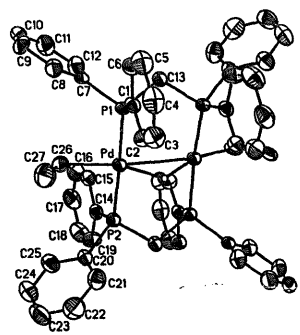


Fig. 1. Projection view of the molecular structure of the $[Pd_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ cation showing the atom-labeling scheme, with non-hydrogen atoms represented by 50% probability ellipsoids. The disordered ethyl groups and bridging hydride are omitted for clarity.

Crystals of the ethyl complex suitable for X-ray diffraction were obtained from toluene solution. The crystal structure belongs to the space group $P2_1/c$. The lattice contains two molecules of toluene and one molecule of benzene (present from an earlier purification step) per $[Pd_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ unit. The molecular structure of the cation is shown in Fig. 1, and selected bond distances and angles are presented in Table 1. This represents the first reported structure of a hydride-bridged dipalladium A-frame complex. The cation lies on a center of inversion, and the eight-membered $Pd_2P_4C_2$ ring adopts an elongated 'chair' conformation. The ethyl groups and the bridging hydride are disordered over two positions, with the ethyl CH_2 groups bent about 20° out of the Pd_2P_4 plane. Although the present crystallographic data are ambiguous on this point, consistency with previously reported structures requires that the bridging hydride be located on the face opposite that occupied by the ethyl groups, giving the A-frame type structure. The Pd–P distances lie at the short end of the range observed for other dppm-bridged dipalladium A-frame complexes (2.29–2.37 Å) [18,23–28]. The Pd–C bonds are longer than those found in halide-bridged A-frames [18,24], or the face-to-face complex $[Pd_2Cl_2Me_2(\mu\text{-dppm})_2]$ [18], suggesting a higher *trans*-influence for the bridging hydride. (It should be pointed out that the structural disorder may result in small systematic errors in the atomic coordinates, and some caution should be exercised when interpreting these bond distances.) The Pd–Pd distance of 2.9933(7) Å is greater than the sum of the van der Waal's radii, and is not indicative of a metal–metal bond. It is shorter, however, than those found in other palladium A-frames, with the exception of the carbonyl-bridged complex $[Pd_2(OCOCF_3)_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ (2.896 Å) [27].

The structure of the $[Pd_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ cation is similar to that of the previously reported complex $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ [14]. Both structures adopt the elongated 'chair' conformation for the $M_2P_4C_2$ unit, in contrast to the 'boat' conformation found for most Pd or Pt A-frames. Among other Pd and Pt A-frame structures, only the carbonyl-bridged complexes $[Pd_2(OCOCF_3)_2(\mu\text{-CO})$-

Table 1
Selected bond distances (Å) and angles (°) for the $[Pd_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ cation

Bond distances			
Pd···Pd' [a]	2.9933(7)	Pd–P(1)	2.2871(13)
Pd–P(2)	2.2855(13)	Pd–C(26)	2.148(12)
Pd–C(26')	2.129(13)	P(1)–C(1)	1.821(5)
P(1)–C(7)	1.819(5)	P(1)–C(13)	1.834(5)
P(2)–C(14)	1.811(5)	P(2)–C(20)	1.822(5)
P(2)–C(13')	1.823(5)		
Bond angles			
P(1)–Pd–P(2)	175.51(5)	P(1)–Pd–C(26)	92.2(3)
P(2)–Pd–C(26)	84.7(3)	Pd'–Pd–C(26)	159.4(3)
Pd–C(26)–C(27)	108.2(11)	Pd–P(1)–C(13)	112.6(2)
Pd–P(2)–C(13')	112.8(2)	P(1)–C(13)–P(2')	114.0(3)

[a] Pd' is generated by the symmetry transformation $-x+1, -y, -z$.

(μ-dppm)$_2$] [27] and [Pd_2Cl_2(μ-CO)(μ-dmpm)$_2$] [29] have been reported to adopt 'chair' conformations.

In summary, we have prepared a series of dppm-bridged palladium A-frame complexes containing bridging hydrides, and have characterized them using NMR spectroscopy and, in one case, X-ray crystallography. Although they are not as easily handled as their platinum analogues, they do exhibit considerable thermal stability, and studies of their reaction chemistry are underway.

3. Experimental

All reactions were carried out under an atmosphere of argon. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ARX-500 or a Varian Unity plus 300 spectrometer. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. [Pd_2Me_2(μ-Cl)$_2$($AsPh_3$)$_2$] was prepared as described previously [20]. [Pd_2Ph_2(μ-Cl)$_2$($AsPh_3$)$_2$] was prepared similarly and obtained as a white solid in 69% yield. *Anal.* Found: C, 54.84; H, 3.90. Calc. for $C_{48}H_{40}As_2Cl_2Pd_2$: C, 54.89; H, 3.84%.

3.1. Preparation of [Pd_2Me_2(μ-H)(μ-dppm)$_2$]PF_6

3.1.1. Method A

[Pd_2(μ-Cl)$_2Me_2$($AsPh_3$)$_2$] (0.185 g, 0.200 mmol) and dppm (0.154 g, 0.400 mmol) were dissolved in CH_2Cl_2 (15 ml) and allowed to react for 1 h at ambient temperature. The solution was cooled to 0°C, and $NaBH_4$ (0.0303 g, 0.802 mmol) was added. Methanol (2 ml) was added dropwise, and the solution changed from pale yellow to dark brown. After 1 h, NH_4PF_6 (0.130 g, 0.800 mmol) was introduced, and the mixture was stirred for a further 15 min. The solvents were removed, and the solid was washed with pentane and redissolved in CH_2Cl_2. The CH_2Cl_2 solution was passed down a Hyflo Super Cel column, then evaporated. After washing with benzene, pentane and ethanol, the product was obtained as a pale yellow solid (0.201 g, 86%). *Anal.* Found: C, 53.43; H, 4.41. Calc. for $C_{52}H_{51}F_6P_5Pd_2$: C, 53.96; H, 4.44%. ^{1}H NMR (acetone-d_6): −7.54 (q, ^2J(PH) = 15 Hz, Pd*H*Pd), 0.07 (s, CH_3), 4.58 (m, PCH_2P), 7.3–7.7 (m, C_6H_5). ^{31}P{^{1}H} NMR: 23.4 (s).

3.1.2. Method B

[PdClMe(cod)] (0.200 g, 0.755 mmol) was dissolved in CH_2Cl_2 (50 ml) and the solution was cooled to 0°C. dppm (0.289 g, 0.755 mmol) was added and the solution was stirred for 30 min, then $NaBH_3CN$ (0.095 g, 1.50 mmol) was introduced, followed by 2.0 ml of methanol. After a further 1.5 h at 0°C, NH_4PF_6 (0.300 g, 1.84 mmol) was added, and the mixture was stirred for another 30 min. The solvent was removed in vacuo overnight and the residue was washed with diethyl ether, hexane and benzene. The remaining solid was dissolved in CH_2Cl_2 (10 ml), and the solution was passed through a Hyflo Super Cel column, eluting with another 50 ml of CH_2Cl_2. The combined solution was evaporated to dryness, leaving the product as a yellow powder (0.357 g, 82%).

3.1.3. Method C

[$PdCl_2$(dppm)] (0.100 g, 0.178 mmol) was dissolved in CH_2Cl_2 (100 ml) and MeMgBr (0.1 ml of a 3.0 M diethyl ether solution, diluted with 20 ml of diethyl ether) was added over 10 min. Water (0.1 ml) was then added and the solvents were removed in vacuo overnight. The residue was dissolved in CH_2Cl_2 (50 ml) and the solution was cooled to 0°C. A THF solution of $NaBH_3CN$ (0.35 ml of a 1.0 M solution) was added. After 1.5 h, NH_4PF_6 (0.202 g, 1.24 mmol) was introduced and, after stirring for a further 30 min, the solvents were removed. The residue was washed with diethyl ether, hexane and benzene, then dissolved in CH_2Cl_2 (10 ml) and passed down a Hyflo Super Cel/neutral alumina column. The column was washed with an additional 150 ml of CH_2Cl_2. The solvent was evaporated to leave the product as a yellow powder (0.083 g, 81%).

3.2. Preparation of [Pd_2Ph_2(μ-H)(μ-dppm)$_2$]PF_6

This complex was prepared according to Method A (Section 3.1.1), starting from [Pd_2Ph_2(μ-Cl)$_2$($AsPh_3$)$_2$] (0.210 g, 0.200 mmol). The product was obtained as a white powder (0.180 g, 70%). *Anal.* Found: C, 58.17; H, 4.37. Calc. for $C_{62}H_{55}F_6P_5Pd_2$: C, 58.10; H, 4.33%. ^{1}H NMR (acetone-d_6): −9.11 (q, ^2J(PH) = 15 Hz, Pd*H*Pd), 4.61 (m, PCH_2P), 6.35, 6.55 (m, PdC_6H_5), 7.3–7.7 (m, PC_6H_5). ^{31}P{^{1}H} NMR: 23.4 (s).

3.3. Preparation of [Pd_2Et_2(μ-H)(μ-dppm)$_2$]PF_6

[Pd_2Cl_2(μ-Cl)$_2$($AsPh_3$)$_2$] (0.200 g, 0.206 mmol) was suspended in CH_2Cl_2 (50 ml) and cooled to 0°C. Tetraethyltin (0.053 ml, 0.267 mmol) was added by syringe. The reaction was allowed to stir for 3 h at 0°C, during which time the palladium complex gradually dissolved. dppm (0.158 g, 0.412 mmol) was then introduced and stirring was continued for a further 1 h. The solvent was then removed in vacuo and the residue was washed with diethyl ether and hexane. The resulting solid was dissolved in CH_2Cl_2 (50 ml) and cooled to 0°C, and $NaBH_3CN$ (0.052 g, 0.824 mmol) was added, followed by methanol (2.5 ml). After 1.5 h, NH_4PF_6 (0.202 g, 1.24 mmol) was added and stirring was continued for 30 min. The solvent was removed and the residue was washed with diethyl ether, hexane and benzene, then dissolved in CH_2Cl_2 (10 ml). The CH_2Cl_2 solution was passed down a Hyflo Super Cel/neutral alumina column, and the column was washed with CH_2Cl_2 (150 ml). The combined CH_2Cl_2 solution was evaporated to leave the product as a yellow powder (0.203 g, 83%). ^{1}H NMR (acetone-d_6): −7.79 (q, ^2J(PH) = 16 Hz, Pd*H*Pd), −0.07 (m, CH_2CH_3), 1.05 (m, CH_2CH_3), 4.50 (m, PCH_2P), 7.2–7.9 (m, C_6H_5). ^{31}P{^{1}H} NMR: 23.9 (s).

3.4. Preparation of $[Pd_2(CH_2SiMe_3)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$

$[PdCl_2(dppm)]$ (0.200 g, 0.356 mmol) was dissolved in CH_2Cl_2 (100 ml), and Me_3SiCH_2MgCl (2.85 ml of a 1 M diethyl ether solution) was added by syringe. The mixture was stirred for 25 min, then water (0.1 ml) was added to quench the remaining Grignard reagent. Acetyl chloride (3.31 ml of a 0.14 M CCl_4 solution) was added, followed by methanol (0.5 ml). NH_4PF_6 (0.202 g, 1.24 mmol) was added and the mixture was stirred for 30 min, then the solvents were removed in vacuo. The residue was washed with pentane and dried, then dissolved in CH_2Cl_2 (50 ml) and passed through a Hyflo Super Cel column. The column was washed with additional CH_2Cl_2 (30 ml), and the combined CH_2Cl_2 solution was cooled to 0°C. $NaBH_3CN$ (0.713 ml of a 1.0 M THF solution) was added and the solution was stirred for 3 h. The solvent was evaporated, and the residue was dried in vacuo. The resulting solid was extracted with benzene and filtered, then the bezene solution was evaporated. The resulting powder was washed with pentane and diethyl ether, then it was dissolved in CH_2Cl_2 (10 ml). The resulting solution was passed through a Hyflo Super Cel/neutral alumina column, the column being washed with CH_2Cl_2 (150 ml). The solvent was removed to leave the product as a dark yellow powder (0.096 g, 41%). ^1H NMR ($CDCl_3$): −8.15 (q, $^2J(PH) = 16$ Hz, Pd*H*Pd), −0.78 (s, $Si(CH_3)_3$), 0.57 (s, CH_2SiMe_3), 4.11 (m, PCH_2P), 7.28–7.47 (m, C_6H_5). $^{31}P\{^1H\}$ NMR: 17.2 (s). $^{29}Si\{^1H\}$ NMR: 0.15 (s).

3.5. Preparation of $[Pd_2Bu_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$

$[PdCl_2(dppm)]$ (0.200 g, 0.357 mmol) was dissolved in CH_2Cl_2 (100 ml) and BuMgBr (2.0 ml of a 0.5 M solution, diluted with 15 ml of diethyl ether) was added dropwise. After stirring for 5 min at ambient temperature, water (0.1 ml) was added to quench the remaining Grignard reagent. NH_4PF_6 (0.202 g, 1.24 mmol) and methanol (0.5 ml) were added. The reaction was continued for 15 min, then the solvents were evaporated. The residue was washed with diethyl ether and pentane, then dissolved in CH_2Cl_2 (50 ml). The resulting solution was passed through a Hyflo Super Cel column, and the column was washed with an additional 30 ml of CH_2Cl_2. The combined solution was cooled to 0°C and $NaBH_3CN$ (0.726 ml of a 1 M THF solution) was added by syringe. The solution was stirred for 35 min, then the solvents were removed and the residue was washed with benzene, diethyl ether and pentane. The residue was dissolved in CH_2Cl_2 (10 ml) and the solution was passed through a Hyflo Super Cel/alumina column, the column being washed with CH_2Cl_2 (150 ml). The resulting solution was evaporated to dryness, leaving the product as a yellow–brown solid (0.126 g, 58%). ^1H NMR ($CDCl_3$): −7.68 (q, $^2J(PH) = 16$ Hz, Pd*H*Pd), −0.26 (t, $^3J(HH) = 7$ Hz, CH_3), 0.07 (m, CH_2CH_2), 0.95 (m, $PdCH_2$), 4.05 (m, PCH_2P), 7.21–7.42 (m, C_6H_5). $^{31}P\{^1H\}$ NMR: 22.5.

3.6. Structure of $[Pd_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6 \cdot 2C_6H_5CH_3, C_6H_6$

Colorless rectangular plates were obtained by slow diffusion of toluene into a CH_2Cl_2 solution of the complex at 213 K. A crystal of dimensions 0.20 × 0.06 × 0.06 mm was mounted on a glass fiber in random orientation. Preliminary examination and data collection were performed at 193 K using a Siemens SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Preliminary unit cell constants were determined with a set of 45 narrow frame (0.3° in ϖ) scans. A total of 3325 frames of intensity data was collected with a frame width of 0.3° in ϖ and counting time of 10 s/frame at a crystal to detector distance of 4.930 cm. The double pass method of scanning was used to exclude any noise. Data were collected at 193 K for a total time of 6.0 h. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. The SMART software package [30] was used for data collection as well as frame integration. Analysis of the integrated data did not indicate any crystal decay. Final cell constants were determined by a global refinement of *xyz* centroids of 8192 reflections ($\theta < 19.0°$). An empirical absorption correction was applied to all data using the SADABS [31] program. The correction was based upon an empirical transmission surface as sampled by the multiple symmetry-equivalent and azimuth rotation-equivalent intensiy measurements within the 28 497 strongest reflections ($T_{max}/T_{min} = 0.93/0.52$, $R_{int} = 11.9$ and 9.8% before and after absorption correction, respectively. Due to the empirical nature of the correction, T_{max}/T_{min} values necessarily reflect correction for any minor systematic errors in addition to absorption). The integration process yielded 63 468 reflections, of which 8273 ($2\theta < 56°$) were independent reflections. Crystal data and intensity data collection parameters are collected in Table 2.

Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package [32]. The structure was solved by the Patterson method and refined successfully in the space group $P2_1/c$. Full-matrix least squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using appropriate riding models. The bridging hydride was located from the difference Fourier map and was held fixed. The ethyl group is disordered and the disorder was modeled using two positions for each carbon. The occupancy factor refined to 48%, hence partial occupancy of 50% was used for each part. The compound crystallized with one molecule of toluene and half a molecule of benzene per Pd. The benzene molecule, which was centered around the inversion center, was disordered and was refined with bond angle and bond distance restraints. The final residual values were $R(F) = 6.97\%$ for 5251 observed reflections ($I > 2\sigma(I)$) and $wR(F^2) = 18.16\%$; $s(F^2) = 1.01$ for all data. The final dif-

Table 2
Crystallographic data for $[Pd_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6 \cdot 2C_6H_5CH_3, C_6H_6$

Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.6160(1)
b (Å)	12.8637(1)
c (Å)	25.3739(3)
b (°)	97.479(1)
Cell volume (Å^3)	3435.61(6)
Z	2
D(calc.) (Mg m^{-3})	1.400
Temperature (K)	193(2)
Absorption coefficient (mm^{-1})	0.697
θ Range (°)	1.93–28.00
Reflections collected	63468
Independent reflections	8273
Observed reflections	5251 ($F>4.0\sigma(F)$)
Absorption correction	empirical
No. parameters refined	425
$R(F)$, $R_w(F^2)$ ($F^2>2.0\ \sigma(F^2)$)	0.0697, 0.1562
$R(F)$, $R_w(F^2)$ (all data)	0.1207, 0.1816
Goodness-of-fit	1.019

ference Fourier map had maximum electron densities of + 1.3 and − 2.3 e Å^{-3}, located 0.91 and 0.99 Å from the Pd atom, respectively. Structure refinement parameters are listed in Table 2.

4. Supplementary material

Atomic coordinates and anisotropic displacement coefficients for the non-hydrogen atoms, positional and isotropic displacement coefficients for the hydrogen atoms, complete lists of bond distances and angles, and calculated and observed structure factors are available from the author.

Acknowledgements

Thanks are expressed to the National Science Foundation (grant No. CHE-9508228) for support of this work, to Johnson Matthey Aesar/Alfa for a generous loan of palladium salts, to the National Science Foundation (grant Nos. CHE-9318696 and 9309690), the U.S. Department of Energy (grant No. DE-FG02-92CH10499) and the University of Missouri Research Board for instrumentation grants.

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