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Preparation of Dinuclear Phosphine-Bridged Palladium(II) Species and Their Silica-Bound Analogues as Catalysts for the Cyclization of Aminoalkynes

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Two new dinuclear palladium complexes, [$Pd_2Me_2Cl_2(dmpm)_2$] (**4**) and [PdMe(Cl)-$(dmpm)_2PdCl_2$] (**5**), have been prepared and their structures determined by single-crystal X-ray analysis. **5** is an interesting example of a complex with both a *cis*-$PdCl_2$ center and a *trans*-MePdCl center, within the same molecule. The reactivity of **4**, as well as the previously reported complexes [$Pd_2Me_2Cl_2(dppm)_2$] (**1**), [$Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$] (**2**), and [$Pd_2Me_4(dmpm)_2$] (**3**), toward silica have been investigated. The complexes react readily with either dichloromethane or benzene suspensions of silica to give chemisorbed species, presumably by reaction of the Pd−Me group with the O−H bond of the surface silanol groups, in the case of **1**, **3**, and **4**, and protonation of the methylene bridge, in the case of **2**. The complexes containing the more basic phosphine, dmpm, gave much higher palladium loadings (wt % Pd 1.37−2.47) on silica, compared to the dppm complexes (wt % Pd 0.55−0.80). The molecular and grafted materials were initially tested as catalysts for the cyclization of 6-aminohex-1-yne to give 2-methyl-1,2-dehydropiperidine. The silica/dmpm complexes were found to be the most active catalysts for this reaction and were also tested for the cyclization of 5-phenyl-4-pentyn-1-amine.

Introduction

We previously reported that mononuclear methylpalladium(II) complexes are immobilized on silica by stirring as a suspension in common organic solvents.[1] These species proved to be active catalysts for the cyclization of aminoalkynes. We were further interested in preparing silica-bound dinuclear palladium complexes, since the proximity of two metal centers may be important in some catalytic cycles,[2−5] and we hoped that they would prove to be even more active catalysts than their mononuclear analogues.

We chose to study complexes of the general formula [$Pd_2Me_2X_2(R_2PCH_2PR_2)_2$], because methyl transition-metal complexes can form chemisorbed species on the surface of silica by the elimination of methane,[6] and bis(phosphino)methane complexes preferentially form dimers with diphosphine bridges.[4,7−10] The dppm complex [$Pd_2Me_2Cl_2(dppm)_2$] (**1**) was previously reported by Stille and co-workers.[4] **1** is prepared from the palladium(I) chloride dimer [$Pd_2Cl_2(dppm)_2$] by the addition of a methylating agent and forms as a 1:1 mixture with the A-frame methylene-bridged dimer [$Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$] (**2**). Anderson and co-workers reported the preparation of a similar complex, [$Pd_2Me_2(\mu\text{-}Cl)(dppm)_2$]Cl, either by the addition of 2 equiv of dppm to the chloride-bridged dimer [$Pd_2Me_2(\mu\text{-}Cl)(AsPh_3)_2$]Cl or by treatment of [$PdCl_2(dppm)$] with $SnMe_4$.[11] They also reported the preparation of the analogous CH_2SiMe_3 and 2-$C_6H_2Me_3$ complexes by addition of 1 equiv of HCl to the mononuclear complexes [$PdR_2(dppm)$] (R = CH_2SiMe_3, 2-$C_6H_2Me_3$), which initially forms [PdR(Cl)(dppm)] but upon standing undergoes conversion to the dinuclear species [$Pd_2R_2(\mu\text{-}Cl)(dppm)_2$]Cl.

In this paper we report the synthesis of two new dmpm complexes, [$PdMe(Cl)(dmpm)_2PdCl_2$] (**5**) and [$Pd_2Me_2Cl_2(dmpm)_2$] (**4**), which have each been characterized by single-crystal X-ray analysis. We have investigated the reactivity of methylpalladium(II) dppm- and dmpm-bridged complexes with silica and the activity of the silica-bound palladium species for the cyclization of aminoalkynes.

Experimental Section

Starting Materials and Analytical Methods. All manipulations of air-sensitive materials were carried out using

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standard Schlenk techniques. Solvents were appropriately dried and distilled before use. 6-Aminohex-1-yne (**12**)[11] and 5-phenyl-4-pentyn-1-amine (**14**)[12] were prepared by literature methods, distilled from calcium hydride under reduced pressure, degassed by freeze−pump−thaw cycles, and then stored under a nitrogen atmosphere in a Schlenk flask. [$PdMe_2$(tmeda)],[13] [$Pd_2Me_2Cl_2(dppm)_2$],[4] [$Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$],[4] [$Pd_2Me_4(dmpm)_2$],[14] and [$H(OEt_2)_2$]$BAr'_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$)[15] were prepared either by or by analogy to literature procedures. A nonporous fumed silica (Degussa Aerosil-200, 200 m^2/g) was used as the oxide support in all experiments. The silica was partially dehydroxylated under dynamic vacuum at 500 °C. This treatment does not change the surface area of the silica, but it standardizes the number of surface hydroxyl groups to 1.2 OH/nm^2 or 0.40 mmol OH/g.[16]

Solution NMR spectra were recorded at 20.5 °C, unless otherwise indicated, on a Varian Gemini-200 (^1H at 199.97 MHz) or a Bruker 300 NMR spectrometer (^1H at 300.13 MHz and $^{31}P\{^1H\}$ at 121.49 MHz). The ^{31}P CP/MAS (cross polarization/magic angle spinning) NMR spectra, frequency 81.00 MHz, were recorded on a Bruker ASX-200 spectrometer. Solid samples were prepared by transfer of the relevant material to a 5 mm o.d. Pyrex NMR tube and connected to a high-vacuum stopcock in a M.Braun GmbH glovebox. The sample was then removed from the drybox, placed under high vacuum and, without breaking vacuum, sealed off at 30 mm lengths. The tubes were then placed in zirconia rotors and balanced, if necessary, with Teflon tape.

Elemental analyses (C, H) were performed by M-H-W Laboratories, Phoenix, AZ. The amount of chemisorbed palladium was determined by quantitative extraction at the end of the experiment. A 20−60 mg portion of the modified silica sample was treated with 4 mL of aqua regia and heated for 30 min at 90 °C. The solution was diluted to 10 mL with distilled water and analyzed by ICP.

[$Pd_2Me_2Cl_2(dmpm)_2$] (4). A CH_2Cl_2 (15 mL) and MeOH (5 mL) solution of **3** (0.150 g, 0.275 mmol) cooled to 0 °C was treated dropwise with acetyl chloride (40 μL, 0.561 mmol). The reaction mixture was stirred at 0 °C for 30 min, allowed to warm to room temperature, then stirred for an additional 30 min. The solvent was removed in vacuo to give an almost quantitative yield of a light yellow powder. The analytically pure white product was obtained by crystallizing from CH_2Cl_2 (2 mL)/Et_2O (10 mL), washing with Et_2O (2 × 10 mL), and drying under high vacuum to ensure no solvent of crystallization remained (0.082 g, 51%). ^1H NMR ($CDCl_3$): δ 2.36 (m, J = 4.80 Hz, 4H, CH_2), 1.53 (br s, 24H, PMe), 0.65 (m, J = 3.45 Hz, 6H, PdMe); ^1H NMR (C_6D_6): δ 1.77 (m, J = 4.46 Hz, 4H, CH_2), 1.37 (br s, 12H, PMe^A), 0.94 (m, J = 3.42 Hz, 6H, PdMe), 0.91 (br s, 12H, PMe^B). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.03 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −6.89 (s). ^{31}P CP/MAS NMR: δ −8.3. Anal. Calcd for $C_{12}H_{34}Cl_2P_4Pd_2$: C, 24.60; H, 5.85. Found: C, 24.81; H, 5.69.

[$PdMe(Cl)(\mu\text{-}dmpm)_2PdCl_2$] (5). **3** (0.075 g, 0.138 mmol) was treated with acetyl chloride (30 μL, 0.421 mmol), under conditions similar to the preparation of **4**. An aliquot was removed after 1 h, at which time the $^{31}P\{^1H\}$ NMR spectrum showed **5** formed along with **4**, in approximately a 1:4 ratio. If the reaction mixture is left overnight, or a larger amount of acetyl chloride is added, the relative yield of **5** is not increased, but other unidentified products are formed. Attempted preferential crystallization of **5** increased its purity, but it was not possible to obtain **5** in analytically pure form due to persistent contamination by small amounts of **4**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 12.66 (dd, J = 23.9, 26.7 Hz, P^A), −4.49 (dd, J = 24.5, 26.6 Hz, P^B).

Table 1. Crystallographic Data for 4·CH_2Cl_2 and 5 at 203(2) K (Mo Kα = 0.710 73 Å)

	4·CH_2Cl_2	**5**
formula	$C_{13}H_{36}Cl_4P_4Pd_2$	$C_{11}H_{31}Cl_3P_4Pd_2$
fw	670.90	606.39
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	$Pbca$
a, Å	12.2960(11)	14.954(4)
b, Å	13.0952(12)	16.329(5)
c, Å	15.7416(14)	17.548(5)
α, deg	90	90
β, deg	90.112(2)	90
γ, deg	90	90
V, Å	2534.7(4)	4285(2)
Z	4	8
R1[a] ($I > 2\sigma(I)$)	0.0333	0.0755
wR2[b] ($I > 2\sigma(I)$)	0.1077	0.1332

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2]^{1/2}$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$ and $P = (F_o^2 + 2F_c^2)/3$.

Structural Determination of 3, 4·CH_2Cl_2, and 5. Crystal data and refinement details are reported in Table 1. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[17]

Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. Two-half-molecules in the asymmetric unit of **3** were located at inversion centers. A molecule of dichloromethane was located in the asymmetric unit of **4**·CH_2Cl_2. Attempts to model possible chloride/methyl disorder in **5** were computationally unstable and were abandoned. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHEXTL 5.10 program library.[18]

Preparation of Silica-Bound Complexes. Silica/[$Pd_2Me_2Cl_2(dppm)_2$] (6). A flask was charged with a mixture of silica (0.100 g, 0.04 mmol of SiOH groups) and [$Pd_2Me_2Cl_2(dppm)_2$] (0.020 g, 0.018 mmol). CH_2Cl_2 (20 mL) was added and the reaction mixture stirred under an inert atmosphere at room temperature for 3 days. The solid was filtered, washed three times with CH_2Cl_2 (20 mL), and dried in vacuo. ^{31}P CP/MAS NMR: δ 15 (br s). ICP %: Pd 0.80.

Silica/[$Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$] (7). This compound was prepared by the same method used for **6**, but with silica (0.200 g, 0.08 mmol of SiOH groups), [$Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$] (0.040 g, 0.037 mmol), and CH_2Cl_2 (20 mL). ^{31}P CP/MAS NMR: δ 16 (br s). ICP %: Pd 0.55.

Silica/[$Pd_2Me_4(dmpm)_2$] (8). To prevent the formation of **4**, **8** was also prepared in benzene. A flask was charged with silica (0.400 g, 0.12 mmol of SiOH groups), to which **3** (0.041 g, 0.076 mmol) and C_6H_6 (30 mL) were added. The suspension was stirred under an inert atmosphere at room temperature for 3 days. The solid was filtered, washed three times with C_6H_6 (15 mL), and dried in vacuo. ^{31}P CP/MAS NMR: δ −10.3 (sh s). ICP %: Pd 2.47.

Silica/[$Pd_2Me_2Cl_2(dmpm)_2$] (9). This compound was prepared by the same method used for **6**, but with silica (0.300 g, 0.12 mmol of SiOH groups), **4** (0.033 g, 0.056 mmol), and

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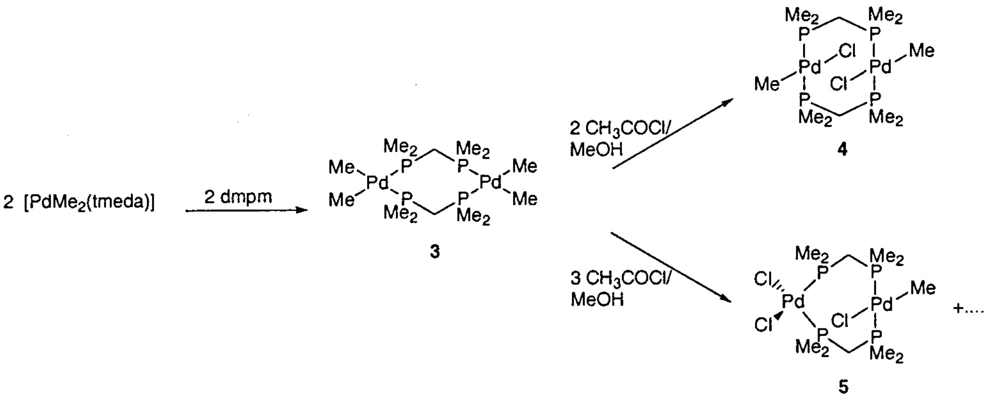
Scheme 1



CH_2Cl_2 (20 mL). ^{31}P CP/MAS NMR: δ 10 (br s, weak), −9.8 (sh s, strong). ICP %: Pd 2.16.

Silica/[$Pd_2Me_2(OTf)_2(dmpm)_2$] (10). [$Pd_2Me_2(OTf)_2(dmpm)_2$] was generated in situ because, although it seems to be reasonably stable in solution, it is far less stable as a solid and it was not possible to isolate it. A CH_2Cl_2 (20 mL) solution of **4** (0.045 g, 0.077 mmol) was treated with solid AgOTf (0.050 g, 0.195 mmol) and stirred in the dark for 2 h. The silver salts were allowed to settle, and the supernatant ($^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ −5.94 (s)) transferred by a cannula, fitted with a filter stick, onto a stirred CH_2Cl_2 (5 mL) suspension of silica (0.300 g, 0.12 mmol of SiOH groups). The reaction mixture was stirred for 3 days. The solid was then filtered, washed three times with CH_2Cl_2 (10 mL), and dried in vacuo. ^{31}P CP/MAS NMR: δ 26.3 (sh s, strong), 3.9 (br s, weak), −7.9 (sh s, medium). ICP %: Pd 2.14.

Catalyst Generated from 8 and HBAr′$_4$ (11). A CH_3CN (5 mL) suspension of **8** (0.100 g, 0.0232 mmol) was cooled to −30 °C and then treated with a CH_3CN (5 mL) solution of [$H(OEt_2)_2$]BAr′$_4$ (0.020 g, 0.0198 mmol). The reaction mixture was stirred at −30 °C for 1 h, warmed to room temperature, and then stirred for an additional 1 h period. This reaction mixture was then tested for the cyclization of 6-aminohex-1-yne. The same catalyst for the cyclization of 5-phenyl-4-pentyn-1-amine was prepared similarly from **8** (0.030 g, 5.94 μmol of Pd), [$H(OEt_2)_2$]BAr′$_4$ (0.007 g, 6.9 μmol) and CH_3CN (5 mL + 2 mL).

Catalytic Cyclization of Aminoalkynes. Formation of 2-Methyl-1,2-dehydropiperidine (13). In a typical procedure, a tube with a Young valve was charged with 0.100 g of catalyst and 5 mL of CH_3CN. 6-Aminohex-1-yne (100 μL, 0.88 mmol) was then added dropwise. The Young valve was then closed and the reaction mixture was heated to 90 °C for 20 h. At the completion of the reaction the solids were allowed to settle, and the supernatant was removed by cannula. The solids were washed several times with CH_2Cl_2 and then dried in vacuo, before being recycled. The product was isolated together with the remaining starting material as a mixture of their hydrochlorides by the addition of an ether solution of HCl followed by drying in vacuo. Product distributions were determined by ^1H NMR spectroscopy, by comparison to the spectrum of an authentic sample of **13** reported previously.[11]

Formation of 2-Benzyl-1-pyrroline (15). A procedure similar to that for the catalytic formation of **13** was used, with 0.030 g of catalyst and 100 μL (0.64 mmol) of 5-phenyl-4-pentyn-1-amine. The product was isolated simply by removing the solvent from the filtrate in vacuo. Product distributions were determined by ^1H NMR spectroscopy, by comparison to the spectrum of an authentic sample of **15** reported previously.[12]

Results and Discussion

Preparation and Characterization of Dinuclear Palladium Complexes. We found previously that methylpalladium(II) complexes containing more basic phosphine ligands undergo a more facile reaction with silica and consequently give higher palladium loadings.[1] Therefore, to prepare silica-bound dinuclear palladium species, we first set about preparing complexes of the basic diphosphine bis(dimethylphosphino)methane. Dinuclear palladium complexes stabilized by bis(diphenylphosphino)methane have been studied widely,[4,7−10] especially as palladium(I) dimers.[19−21] As mentioned above, [$Pd_2Me_2Cl_2(dppm)_2$] was prepared by the addition of 1 equiv of $AlMe_3$ to [$Pd_2Cl_2(dppm)_2$], initially giving the palladium(I) species [$Pd_2MeCl(dppm)_2$], which disproportionates to give the palladium(II) complex [$Pd_2Me_2Cl_2(dppm)_2$], and the palladium(0) complex [$Pd_2(dppm)_2$].[4] We reasoned that a more efficient route to [$Pd_2Me_2Cl_2(dmpm)_2$] (**4**) would be by the addition of HCl to the dimethylpalladium dimer [$Pd_2Me_4(dmpm)_2$] (**3**), which was reported previously by Fink and co-workers.[14] Indeed, **3** can be converted into the dinuclear methylpalladium chloro complex [$Pd_2Me_2Cl_2(dmpm)_2$] (**4**), by treatment with 2 equiv of HCl, generated in situ from acetyl chloride and methanol (Scheme 1). **4** gives a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ −6.03 and −6.89 ppm in $CDCl_3$ and C_6D_6, respectively. In its solid-state ^{31}P CP/MAS NMR spectrum, **4** gives a peak at −8.3 ppm. The ^1H NMR spectrum of **4** in $CDCl_3$ is a multiplet at δ 2.36 due to the CH_2 groups, a broad peak at δ 1.53 due to the PMeMe′ groups, and a multiplet at δ 0.65 due to the $PdMe_2$ groups. The ^1H NMR spectrum in C_6D_6 is similar; however, the inequivalent PMeMe′ groups appear as two signals of equal intensity, at δ 1.37 and 0.91 ppm. The solid-state structure of **4**, which cocrystallized with one molecule of dichloromethane, was confirmed by X-ray analysis. The structure of **4** consists of two *trans*-PdMeCl fragments bridged by two $Me_2PCH_2PMe_2$ ligands to form a face-to face dimer with the methyl groups in an anti geometry. Both metal centers have typical square-planar geometries. The structure is similar to that which has been reported for the analogous dppm complex [$Pd_2Me_2Cl_2(dppm)_2$] by Stille and co-workers.[4] An ORTEP diagram is shown in Figure 1.

In the attempted preparation of **4**, it was found that an excess of acetyl chloride generated a small amount of a second compound, characterized by two sets of

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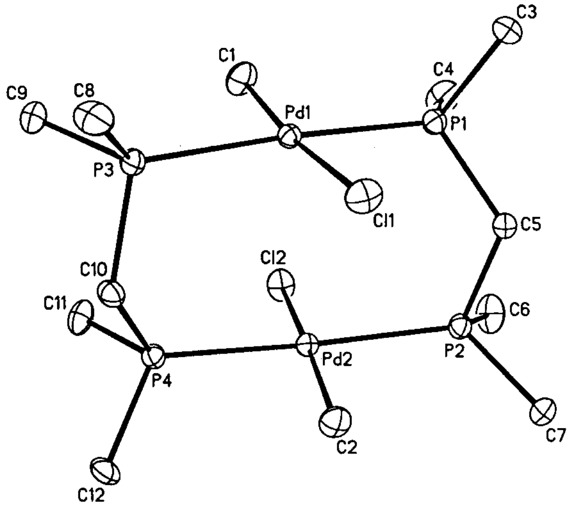

Figure 1. ORTEP diagram of $[Pd_2Me_2Cl_2(dmpm)_2]\cdot CH_2Cl_2$ (**4**·CH_2Cl_2) (hydrogen and solvent atoms omitted for clarity). Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å): Pd1−P1 = 2.2873(9), Pd1−C1 = 2.047(4), Pd1−Cl1 = 2.4446(9), Pd1···Pd2 = 3.304(1). Selected bond angles (deg): C1−Pd1−P1 = 88.37(12), C1−Pd1−P3 = 91.31(12), P1−Pd1−Cl1 = 89.71(3), P3−Pd1−Cl1 = 91.07(3).

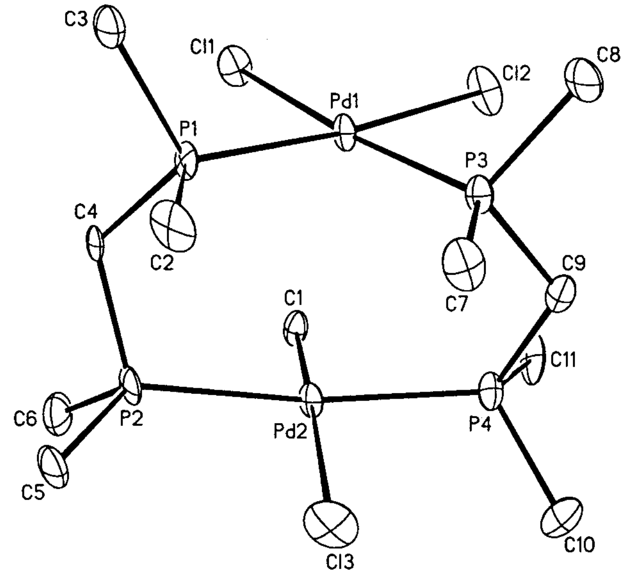

Figure 2. ORTEP diagram of $[PdMe(Cl)(\mu\text{-dmpm})_2PdCl_2]$ (**5**) (hydrogen atoms omitted for clarity). Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å): Pd1−Cl1 = 2.382(3), Pd1−Cl2 = 2.365(2), Pd1−P1 = 2.263(2), Pd1−P3 = 2.250(3), Pd2−C1 = 2.065(9), Pd2−Cl3 = 2.409(3), Pd2−P2 = 2.289(3), Pd2−P4 = 2.301(3), Pd1···Pd2 = 3.420(2). Selected bond angles (deg): Cl2−Pd1−Cl1 = 89.25(10), P1−Pd1−Cl1 = 85.17(10), P3−Pd1−Cl2 = 84.25(10), P3−Pd1−P1 = 101.25(10), C1−Pd2−P2 = 87.9(3), C1−Pd2−P4 = 89.6(3), P2−Pd2−Cl3 = 92.87(11), P4−Pd2−Cl3 = 90.63(11).

doublets of doublets, at δ 12.66 (J = 23.9, 26.7 Hz) and −4.49 (J = 24.5, 26.6 Hz), in the $^{31}P\{^1H\}$ NMR spectrum. On this basis, the new compound was assumed to be a dinuclear species containing inequivalent phosphines. Attempts to isolate the new compound by adding 3 equiv of acetyl chloride to **3** and extending the reaction time were unsuccessful due to the formation of other unidentified products, but it was possible to increase its relative amount. Although it was not possible to obtain the new compound in analytically pure form, due to the presence of small amounts of **4**, it did crystallize preferentially, in low yield, when a dichloromethane solution was layered with pentane. The crystals were suitable for single-crystal X-ray analysis, and the structure revealed a *cis*-$PdCl_2$ fragment and a *trans*-PdMeCl fragment bridged by two $Me_2PCH_2PMe_2$ ligands, $[PdMe(Cl)(\mu\text{-dmpm})_2PdCl_2]$ (**5**). An ORTEP diagram is shown in Figure 2.

Both metal centers have the expected square-planar geometries. The P1−Pd1−P3 angle of the P_2PdCl_2 fragment is 101.25(10)°, similar to the P−Pd−P angles found in **3**, 102.75(3)°.[14] In fact, the remaining angles of the dimetallacycle **5** are similar to the corresponding angles in **3**, except for the P2−Pd2−P4 angle of the P_2PdMeCl fragment, which is much greater at 172.18(12)° due to the trans geometry about this metal center. The Pd−P bond lengths of the cis fragment are 2.263(2) and 2.250(3) Å and are typical for P trans to Cl. For example, Davies et al. reported Pd−P bond lengths of 2.264(1) and 2.265(1) Å for the related structure of $[Pd_2Cl_4(dmpm)_2]$.[23] The Pd−P bond lengths of the trans fragment are 2.289(3) and 2.301(3) Å, similar to those found for the structure of **4**, 2.2873(9) and 2.2986(9) Å. The Pd−P bond lengths are in accord with the weaker trans influence expected for Cl compared to P.

Reactivity of Dinuclear Palladium Complexes with Silica. Silica-bound dinuclear palladium species were prepared by stirring suspensions of silica and the relevant palladium complex (**1**−**4**) for 3 days. The solids were filtered and washed several times to ensure no unreacted physisorbed material remained. Presumably the immobilization of palladium on the silica surface occurs by reaction with the silanol groups, accompanied by the elimination of 1 equiv of methane and the consequent formation of a covalent Pd−O bond. Silica partially dehydroxylated at 500 °C was chosen as the support, since it has a relatively low surface density of silanols and it was hoped that active site isolation would prevent aggregation and consequent loss of catalytic activity.

Initially, the reactivity of the dppm complexes $[Pd_2Me_2Cl_2(dppm)_2]$ (**1**) and $[Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2]$ (**2**) toward silica was investigated. Although the grafting reactions were allowed to proceed for 3 days, the palladium loadings measured by ICP were quite low: 0.80 and 0.55 wt % Pd for silica/**1** (**6**) and silica/**2** (**7**), respectively. The ^{31}P CP/MAS NMR spectra of the two materials are quite similar, with a broad peak at δ 15 ppm for **6** and a broad peak at δ 16 ppm for **7**. The species on the surface may well be similar. As shown in Scheme 2, **1** may react with a surface Si−OH group with elimination of methane and the formation of a Pd−O bond, while **2** may react by addition of an O−H

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(22) The statistical differences in some of the bond distances and angles for the two crystallographically unique molecules of **3** (**3a** and **3b**) are not seen in the solution NMR spectroscopic data and are presumably due to crystal-packing forces in the solid state.

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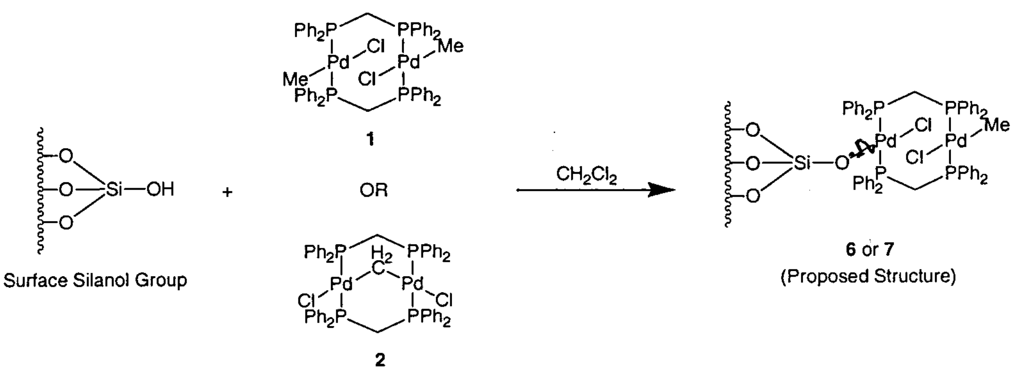
Scheme 2



bond of a silanol across a Pd−CH_2 bond to form Pd−Me and a Pd−O bond. However, although it might be expected that the geometry of silica/**1** and silica/**2** are transoid and cisoid, respectively, the exact structure of the silica-bound species cannot be assigned from the ^{31}P CP/MAS NMR spectra. It should be noted that CD_2Cl_2 solutions of **1** and **2** show peaks at δ 19.8 and δ 17.3 ppm, respectively, in their $^{31}P\{^1H\}$ NMR spectra.

In our study of the related reactions of mononuclear methylpalladium complexes with silica,[1] we found that compounds containing stronger donor ligands, such as PMe_3 and dmpe, undergo a more facile reaction with the surface of silica than do analogous complexes stabilized by weaker donor ligands, such as PPh_3 and dppe. This was found to be true also for the dinuclear complexes we studied here. The dmpm complexes $[Pd_2Me_4(dmpm)_2]$ (**3**) and $[Pd_2Me_2Cl_2(dmpm)_2]$ (**4**) gave much higher palladium loadings than the dppm complexes.

The ^{31}P CP/MAS NMR spectrum of the solids resulting from the reaction of silica with **4** (**9**) displays a very weak broad signal at δ 10 and a sharp strong signal at δ −9.8 ppm. The ^{31}P CP/MAS NMR spectrum of **4** is a sharp singlet at −8.3 ppm. When the reaction of **3** with silica was performed in dichloromethane, **3** decomposed to **4**. This conclusion is based on the $^{31}P\{^1H\}$ NMR spectrum of the material extracted by dichloromethane washings, which showed a signal consistent with the formation of **4**. Indeed, when a CD_2Cl_2 solution of **3** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy over a period of days, **4** was slowly formed. Consequently, the reaction of **3** with silica was carried out in benzene rather than dichloromethane, as no decomposition to **4** is possible. The pale yellow color of the supernatant disappeared within 1 h as the silica acquired this color. The ^{31}P CP/MAS NMR spectrum of this material, **8**, shows only a sharp singlet at δ −10.3 ppm.

We also sought to prepare a Pd_2 complex with weakly coordinating anionic ligands, because such a species might prove to be a highly active catalyst when immobilized onto silica. When a dichloromethane solution of **4** was treated with silver triflate, a new species was formed, with a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ −5.94 ppm. Repeated attempts to isolate this compound were unsuccessful. Therefore, we decided to react it in situ with silica, since transition-metal species when immobilized onto silica may become more thermally stable.[1,24−26] The ^{31}P CP/MAS NMR spectrum of the grafted material is not consistent with the formation of just one surface species: a strong sharp peak at δ 26.3, a weak broad peak at δ 3.88, and a sharp peak of medium intensity at δ −7.9 ppm were evident. By comparison to the $^{31}P\{^1H\}$ NMR spectrum of the soluble complex generated in situ and the ^{31}P CP/MAS NMR spectra of **8** and **9**, the desired species, silica/$[PdMe_2(OTf)_2(dmpm)_2]$ (**10**), can be assigned the peak at δ −7.9 ppm. The other peaks are presumably due to species formed from thermal decomposition of $[PdMe_2(OTf)_2(dmpm)_2]$ on silica. We propose that the structure of the supported dmpm complexes are similar to that proposed for the dppm complex (Scheme 2).

Table 2. Catalytic Cyclization of 6-aminohex-1-yne (12)[a]

cat.	run no.	conversn (%)	TON (h^{-1})[c]
silica/$[Pd_2Me_2Cl_2(dppm)_2]$ (**6**)	1	39[b]	6.5
silica/$[Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2]$ (**7**)	1	43[b]	10.4
silica/$[Pd_2Me_4(dmpm)_2]$ (**8**)	1	22	0.8
silica/$[Pd_2Me_2Cl_2(dmpm)_2]$ (**9**)	1	100	>4.3[h]
	2	46	*g*
	3	32	4.4[e]
silica/$[Pd_2Me_2(OTf)_2(dmpm)_2]$ (**10**)	1	100[f]	>4.4[h]
	2	40	*g*
	3	21	1.8[e]
silica/$[Pd_2Me_4(dmpm)_2]$/$HBAr'_4$ (**11**)	1	100	>3.8[h]
	2	50	*g*
	3	26	2.3[e]
$[Pd_2Me_2Cl_2(dppm)_2]$ (**1**)	1	60[c,d]	5.7
$[Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2]$ (**2**)	1	47[c,d]	4.4
$[Pd_2Me_4(dmpm)_2]$ (**3**)	1	5[c,d]	0.2
$[Pd_2Me_2Cl_2(dmpm)_2]$ (**4**)	1	18[c,d]	0.9

[a] Reactions were conducted using 100 mg of catalyst and 100 μL of 6-aminohex-1-yne (0.88 mmol) for 20 h in acetonitrile, unless otherwise stated. [b] 70 mg of catalyst was used. [c] The TONs were determined after 20 h, not at a standard percent conversion, and this should be noted when comparing the results. [c] 5 mg of catalyst was used. [d] Decomposition to palladium metal. [e] After three cycles the % Pd was measured to be 0.68 for **9**, 1.09 for **10**, and 1.05 for **11**. [f] 75% conversion after 2 h or a TON of 66. [g] Palladium loading was not measured. [h] The TON is at least the number specified, as the reaction was already complete at 20 h.

Catalytic Activity of Silica-Bound Complexes for the Cyclization of Aminoalkynes. The silica-bound complexes were initially tested for the cyclization of 6-aminohex-1-yne (Table 2). Care should be taken when comparing the TON's reported in Table 2, as they are at a constant time, not conversion. The molecular compounds stabilized by dppm, $[Pd_2Me_2Cl_2(dppm)_2]$ (**1**)

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(24) Amor Nait Ajjou, J.; Rice, G. L.; Scott, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 13436.

(25) Amor Nait Ajjou, J.; Rice, G. L.; Scott, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 415.

(26) Scott, S. L.; Dufour, P.; Santini, C. C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2011.

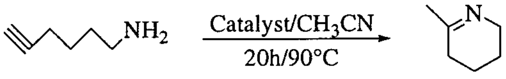
Table 3. Catalytic Cyclization of 5-phenyl-4-pentyn-1-amine (14)[a]

cat.	run no.	conversn (%)	TON (h^{-1})[b]
silica/[$Pd_2Me_2Cl_2(dmpm)_2$] (**9**)	1	100	>10.5[f]
	2	49	*e*
	3	23	8.4[d]
silica/[$Pd_2Me_2(OTf)_2(dmpm)_2$] (**10**)	1	100[c]	>10.6[f]
	2	38	*e*
	3	19	8.0[d]
silica/[$Pd_2Me_4(dmpm)_2$]/HBAr′$_4$ (**11**)	1	88	8.1
	2	38	*e*
	3	21	*e*

[a] Reactions were conducted using 30 mg of catalyst and 100 μL of 5-phenyl-4-pentyn-1-amine (0.64 mmol) for 20 h in acetonitrile, unless otherwise stated. [b] The TONs were determined after 20 h, not at a standard percent conversion, and this should be noted when comparing the results. [c] 15% of an impurity was observed, proposed to be the nitroso compound $PhC_2(CH_2)_3N{=}O$, on the basis of ^1H NMR and GCMS evidence. [d] After three cycles the % Pd was measured by ICP to be 0.62 for **9** and 0.54 for **10**. [e] Palladium loading was not measured. [f] The TON is at least the number specified, as the reaction was already complete at 20 h.

and [$Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$] (**2**), proved to be significantly more active catalysts than the dmpm complexes [$Pd_2Me_4(dmpm)_2$] (**3**) and [$Pd_2Me_2Cl_2(dmpm)_2$] (**4**). However, when immobilized onto silica, the dmpm species show much higher conversions. Even when the higher palladium loadings of the silica-bound dmpm complexes **8**−**11** are taken into account, they are still far more active than the supported dppm complexes **6** and **7**. For example, [$Pd_2Me_2(OTf)_2(dmpm)_2$] (**10**) showed a conversion of 75% after just 2 h, which corresponds to a TON of 66. Therefore, **10** is more active than a recently reported Zn-ion exchanged zeolite (BEA), which showed a TON of approximately 30 at 75% conversion, when the cyclization of **12** was conducted in toluene at 111 °C.[27] The higher activity of the silica-bound dinuclear palladium complexes, compared to their molecular precursors, may be attributed to the greater thermal stability of the palladium complexes when immobilized. For the molecular complexes **1**−**4**, almost complete decomposition to metallic palladium was observed in the course of the catalytic reactions. Also, the formation of a Pd−O−Si≡ bond upon immobilization presumably renders the metal center more electrophilic and thus better able to activate the alkyne.

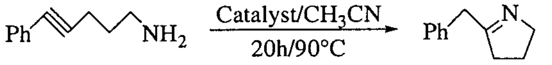
A noncoordinating anionic group was shown to promote high activity. For example, when silica/[$Pd_2Me_4(dmpm)_2$] (**8**) was tested as a catalyst for the cyclization of **12**, only 22% conversion was detected (eq 1). However, when **8** was treated with HBAr′$_4$ before the catalytic reaction, the conversion increased to 100%. Presumably, the acid protonates one of the Pd−Me groups and generates an open coordination site by elimination of methane.



(1)

12 **13**

The silica-supported dmpm complexes **9**−**11** also proved to be active catalysts for the cyclization of 5-phenyl-4-pentyn-1-amine (**14**) (Table 3 and eq 2). Best results were obtained with silica/[$Pd_2Me_2Cl_2(dmpm)_2$] (**9**), which gave higher conversions than silica/[$Pd_2Me_4(dmpm)_2$]/HBAr′$_4$ (**11**). When silica/[$Pd_2Me_2(OTf)_2(dmpm)_2$] (**10**) was used as the catalyst, approximately 15% of an unidentified impurity was formed.



(2)

14 **15**

The silica-supported dinuclear Pd complexes are significantly more active catalysts than any of the silica-bound complexes generated from mononuclear Pd compounds we reported previously.[1] For example, 100 mg of silica/[PdMe(Cl)(dmpe)] (wt % Pd 0.65) and **9** (wt % Pd 2.16) give a conversion of 21 and 100%, respectively, for the cyclization of 6-aminohex-1-yne under the same conditions. Therefore, the activity, per Pd, of **9** is at least 1.43 times that of silica/[PdMe(Cl)(dmpe)]. Unfortunately, the activity of the catalysts for the cyclization of **12** and **14** declined by about 50% after each recycling. ICP analysis showed significant amounts of leaching. Furthermore, the catalysts became quite dark in color, especially for **10**, after the first and second runs, presumably due to decomposition of the active sites. The use of a solvent less polar than acetonitrile (e.g. hexane or ether) may improve the recyclability of the catalysts.

Conclusions

Two new dinuclear palladium(II) complexes with bridging dmpm ligands have been prepared and fully characterized, including single-crystal X-ray analysis: [$Pd_2Me_2Cl_2(dmpm)_2$] and [$PdMe(Cl)(dmpm)_2PdCl_2$]. [$Pd_2Me_2Cl_2(dmpm)_2$], as well as the known complexes [$Pd_2Me_4(dmpm)_2$], [$Pd_2Me_2Cl_2(dppm)_2$], and [$Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$], were successfully immobilized on silica by simply stirring the compounds, in either CH_2Cl_2 or benzene, with a suspension of silica. ICP analysis showed that the complexes containing the more basic dmpm ligands gave much higher palladium loadings, in accordance with our previous observations for grafting of mononuclear methylpalladium(II) compounds. The silica-bound *dinuclear* species proved to be significantly more active catalysts for the cyclization of 6-aminohex-1-yne and 5-phenyl-4-pentyn-1-amine than similar silica-bound *mononuclear* palladium(II) species, as well as the dinuclear molecular precursors. Our results demonstrate the distinction between silica-bound mononuclear and dinuclear species and, importantly, the beneficial effects of the silica-bound dinuclear species on the cyclization reactions of aminoalkynes.

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Supporting Information Available: Tables of crystal data and structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters of **4**·CH_2Cl_2 and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020026U

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(27) Penzion, J.; Muller, T. E.; Lercher, J. A. *Chem. Commun.* **2000**, 1753.