J. Am. Chem. Soc. **2001,** *123,* 10521−10525

Preparation of New Catalysts by the Immobilization of Palladium(II) Species onto Silica: An Investigation of Their Catalytic Activity for the Cyclization of Aminoalkynes

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Received June 1, 2001

Abstract: Silica-immobilized palladium catalysts are readily prepared by treating partially dehydroxylated silica with solutions of the palladium(II) complexes, *cis*-[PdMeXL$_2$] (X = Me, L$_2$ = dmpe; X = Cl, L$_2$ = dmpe, dppe, phen, bipy, 2PMe$_3$), *trans*-[PdMeXL$_2$] (X = Cl, NO$_3$, OTf, L = PMe$_3$; X = Cl, L = PPh$_3$), or [PdPh(OH)L]$_2$ (L = PPh$_3$, PCy$_3$), at room temperature. A chemisorption reaction is presumed to occur on the surface Si−OH groups, with elimination of 1 equiv of methane, benzene, or water and the initial formation of a covalent Pd−O bond to the silica surface. The amount of chemisorbed material is strongly dependent on the nature of the complex employed, and the Pd content of the materials, determined by ICP analysis, was found to vary widely (from 1.47 to 0.021 wt %). It appears that the complexes stabilized by more basic ligands undergo a more facile reaction with the surface. The catalytic activity of the materials was first tested in the cyclization of 6-aminohex-1-yne. Higher conversions were found for those catalysts containing more basic ligands, due to the higher loadings, and for those complexes containing more weakly coordinating anions. Silica/*trans*-[PdMe(NO$_3$)(PMe$_3$)$_2$] was identified as the best catalyst and was used to test the generality of the catalytic cyclization method with two other alkynes, namely, 5-phenyl-4-pentyn-1-amine and 6-phenyl-5-hexyn-1-amine. The catalysts prepared here show rates comparable to, or greater than, those found for homogeneous late transition metal complexes, including their molecular precursors. Furthermore, the supported catalysts are only slightly air-sensitive and can be recycled, after filtration in air, with only moderate loss of activity.

Introduction

Cationic palladium(II) complexes are homogeneous catalysts for both intramolecular[1−4] and intermolecular[5−7] hydroamination reactions.[8] Although the catalytic activity of palladium, and other late transition metal,[1−3,9] complexes for the cyclization of aminoalkynes is significantly lower than that reported for early transition metal complexes,[10−16] such complexes have the advantage of being far less sensitive to trace amounts of moisture and oxygen. As we were interested in preparing heterogeneous catalysts which could be recycled without the need for extreme precautions in their handling, and as palladium(II) complexes have been the most thoroughly studied of the late transition metals as homogeneous catalysts for hydroamination reactions, we decided to investigate the preparation of silica-bound palladium species.

One of us previously reported that, when *trans*-[RhMe(CO)(PMe$_3$)$_2$] is sublimed at 50 °C onto partially dehydroxylated silica, methane is formed as an irreversible grafting reaction occurs.[17] The progress of the reaction was monitored by in situ infrared spectroscopy of a self-supporting silica disk, and the results were consistent with the formation of a surface organometallic fragment, eq 1.

$$\equiv\text{SiOH} + \text{CH}_3\text{Rh(CO)(PMe}_3)_2 \rightarrow \equiv\text{SiORh(CO)(PMe}_3)_2 + \text{CH}_4 \quad (1)$$

Another method for the direct chemisorption of a late transition metal complex onto silica was reported by Kaplan and Bergman.[18] When the hydroxoruthenium(II) complex, [RuH(OH)(dmpe)$_2$], is treated with silica as a suspension in THF, water is eliminated and the surface complex ≡SiORuH(dmpe)$_2$ is formed, eq 2.

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10.1021/ja0113450 CCC: $20.00

$$\equiv\text{SiOH} + \text{HORu(H)(dmpe)}_2 \rightarrow \equiv\text{SiORu(H)(dmpe)}_2 + \text{H}_2\text{O} \quad (2)$$

However, no catalytic activity was investigated, and consequently the stability of the surface species under catalytic conditions is unknown. Stable methyl and hydroxo complexes of palladium are both reported in the literature. We hoped they would show similar reactivity toward silica, to give stable chemisorbed palladium species which would display catalytic activity for the cyclization of aminoalkynes.

The activity of homogeneous cationic palladium hydroamination catalysts is reported to be strongly dependent on the nature of the anion. For example, [Pd(triphos)](OTf)$_2$ shows a rate which is close to 10 times that of its chloro analogue, [Pd(triphos)]Cl$_2$, for the cyclization of 6-aminohex-1-yne.[3] However, the size of the anion may also be important, as the catalytic activity of [Pd(triphos)]OTf$_2$ is nearly 3 times that of the analogous salt containing the less coordinating but also less bulky BF_4^- anion.[3]

We report here our initial studies of the preparation of silica-bound palladium(II) species from organometallic precursors, the effect of the nature of anionic and stabilizing ligands on the reaction with the silica surface, and the subsequent catalytic activity of the new materials in the cyclization of aminoalkynes.

Experimental Section

Starting Materials and Analytical Methods. All manipulations of air-sensitive materials were carried out using standard Schlenk techniques. Solvents were appropriately dried and distilled before use. 6-Aminohex-1-yne,[2] 5-phenyl-4-pentyn-1-amine,[11] and 6-phenyl-5-hexyn-1-amine[11] were prepared by literature methods and distilled from calcium hydride under reduced pressure, degassed by freeze−pump−thaw cycles, and stored under a nitrogen atmosphere in a Schlenk flask. [PdMe$_2$(tmeda)],[19] [PdMe$_2$(dmpe)],[19] [PdMeCl(dmpe)],[20] [PdMeCl(dppe)],[20] *cis*-/*trans*-[PdMeCl(PMe$_3$)$_2$],[20] *trans*-[PdMe(NO$_3$)(PMe$_3$)$_2$],[20] *trans*-[PdMe(OTf)(PMe$_3$)$_2$],[20] *trans*-[PdMeCl(PPh$_3$)$_2$],[21] [PdMeCl(bipy)],[21] [PdMeCl(phen)],[22] [PdPh(OH)(PPh$_3$)]$_2$,[23] [PdPh(OH)(PCy$_3$)]$_2$,[23] NaBAr′$_4$,[24] and [H(OEt$_2$)$_2$]BAr′$_4$[24] (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) were prepared either by, or analogously 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 of OH/g.[25]

Solution NMR spectra were recorded at 20.5 °C, unless otherwise indicated, on a Varian Gemini-200 (^{1}H at 199.97 MHz and ^{13}C{^{1}H} at 50.28 MHz) or a Bruker 300 NMR spectrometer (^{1}H at 300.13 MHz, ^{13}C{^{1}H} at 75.48 MHz, and ^{31}P{^{1}H} at 121.49 MHz). The ^{13}C and ^{31}P CP/MAS (cross polarization/magic angle spinning) NMR spectra, frequency 50.32 and 81.00 MHz, respectively, 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 an 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.

The amount of chemisorbed palladium was determined by quantitative extraction at the end of the experiment. Modified silica (20−60 mg) 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.

Preparation of Catalysts. In a typical procedure, a mixture of silica (0.350 g, 0.14 mmol of SiOH groups), *trans*-[PdMe(NO$_3$)(PMe$_3$)$_2$] (0.012 g, 0.035 mmol), and CH$_2$Cl$_2$ (20 mL) was stirred under an inert atmosphere at room temperature for 24 h. The white solid was filtered, washed three times with CH$_2$Cl$_2$ (20 mL), and dried in vacuo. In the preparation of silica/*trans*-[PdMe(Cl)(PPh$_3$)$_2$], the same procedure was used, but CH$_2$Cl$_2$ was replaced by THF due to the low solubility of *trans*-[PdMe(Cl)(PPh$_3$)$_2$] in CH$_2$Cl$_2$. A second method was used for the preparation of silica/*trans*-[PdMe(Cl)(PPh$_3$)$_2$], where C$_6$H$_6$ was used as the solvent. In addition, the relative amount of the palladium complex was doubled, and the reaction time was increased to 5 days.

Due to the thermal instability of *trans*-[PdMe(OTf)(PMe$_3$)$_2$], it was prepared and immediately added to silica at low temperature. A Schlenk tube was charged with *trans*-[PdMe(Cl)(PMe$_3$)$_2$] (0.050 g, 0.162 mmol) and AgOTf (0.044 g, 0.171 mmol) and cooled to −78 °C. CH$_2$Cl$_2$ (10 mL) was added, and the solution was stirred at −78 °C for 30 min, allowed to warm to room temperature, and then immediately filtered through a pad of Celite. Half of this solution was then added dropwise to a stirred CH$_2$Cl$_2$ (10 mL) suspension of silica (0.350 g, 0.14 mmol of OH groups), cooled to −78 °C. The reaction mixture was allowed to warm slowly to room temperature and then stirred overnight. The product isolated, after filtering, washing 3 times with CH$_2$Cl$_2$ (10 mL), and drying in vacuo, was black in color, presumably due to decomposition to metallic palladium.

For the dinuclear complexes, [PdPh(OH)(PPh$_3$)]$_2$ and [PdPh(OH)(PCy$_3$)]$_2$, 14.8 mg (0.015 mmol) and 14.9 mg (0.015 mmol) were used, respectively, for 150 mg (0.06 mmol of SiOH groups) of silica. This corresponds to the same molar ratio as for the preparations for the mononuclear complexes described above, but the ratio of Pd:SiOH is obviously doubled.

Catalytic Reactions. In a typical procedure, a tube with a Young valve was charged with 0.100 g of catalyst and 5 mL of CH$_3$CN. The aminoalkyne was then added dropwise: either 100 μL (0.88 mmol) of 6-aminohex-1-yne, 150 μL (0.96 mmol) of 5-phenyl-4-pentyn-1-amine, or 150 μL (1.15 mmol) of 6-phenyl-5-hexyn-1-amine. The Young valve was then closed, and the reaction mixture was heated to 90 °C for 20 h (for the cyclizations of 6-aminohex-1-yne and 5-phenyl-4-pentyn-1-amine) or to 90 °C for 90 h (for the cyclization of 6-phenyl-5-hexyn-1-amine). In experiments where silica/[PdMeCl(dmpe)] (100 mg, 6.11 μmol of Pd) was used as the catalyst with the additives AgO$_2$CCF$_3$ (2 mg, 14.7 μmol), NaBAr′$_4$ (7 mg, 6.76 μmol), or [H(OEt$_2$)$_2$]BAr′$_4$ (4 mg, 3.95 μmol), the reaction mixture was stirred as a CH$_3$CN suspension for 1 h before the addition of 6-aminohex-1-yne. The same procedure was used for silica/*cis*-[PdMe(Cl)(PMe$_3$)$_2$] (100 mg, 10.5 μmol Pd) and NaBAr′$_4$ (10 mg, 9.66 μmol) or AgOTf (5 mg, 19.45 μmol). To determine whether the additive itself had any activity, silica (100 mg)/NaBAr′$_4$ (20 mg, 19.3 μmol) was tested as a catalyst for the cyclization of 6-aminohex-1-yne (100 μL, 0.88 mmol). No conversion was observed even after heating at 90 °C for 20 h. However, silica (100 mg)/AgOTf (5 mg, 19.5 μmol) showed a conversion of 33% under similar conditions.

At the completion of a reaction, the mixture was allowed to cool and filtered, and the solids were washed several times with CH$_2$Cl$_2$. In the cyclization of 6-aminohex-1-yne, the product was isolated 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. For the cyclization of 5-phenyl-4-pentyn-1-amine and 6-phenyl-5-hexyn-1-amine, the solvent was simply removed in vacuo. The product distributions were determined by ^{1}H NMR spectroscopy by comparison with the NMR spectroscopic data of authentic samples reported previously.[2,11] The catalyst was allowed to dry in air before being recycled.

Results and Discussion

Preparation and Characterization of Silica-Bound Species. The reactivity of silica with several hydroxo (Scheme 1) and

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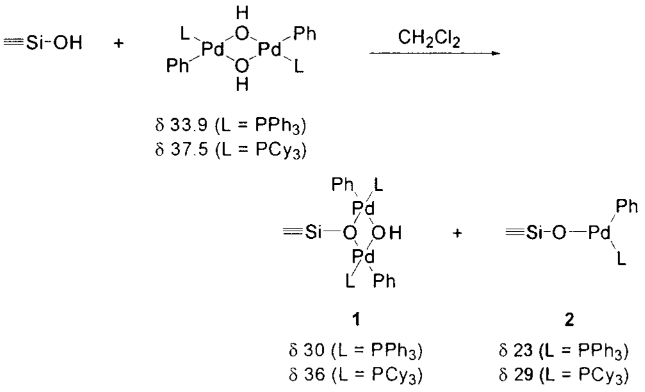
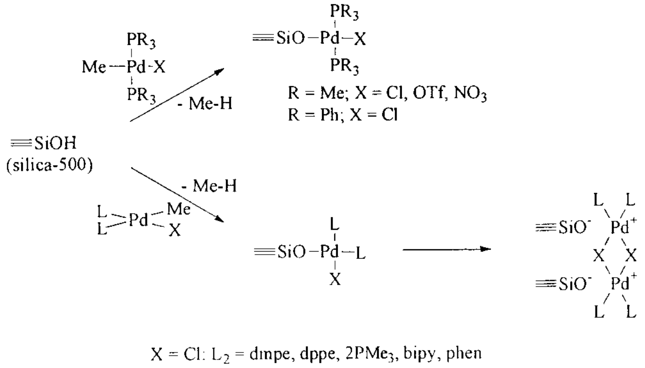
Scheme 1



Scheme 2



methyl (Scheme 2) palladium complexes has been investigated. Silica dehydroxylated at 500 °C, which has a relatively low density of surface silanols, was chosen as the support, and the molar ratio of the palladium precursor to the relative number of surface silanols was kept low (~1:4) in order to achieve active site isolation, so that aggregation and consequent loss of activity might be prevented. Reactions were performed by stirring a suspension of silica and the appropriate palladium complex. The solids were filtered and washed several times to ensure that no unreacted, physisorbed material remained. Although the amount of added palladium relative to surface Si$-$OH groups was kept constant for all chemisorption/grafting reactions, the Pd loading of the resulting materials varied widely (Table 1). For the mononuclear Pd precursors, values ranged from 1.12 wt % Pd for silica/*cis*-[PdMe(Cl)(PMe$_3$)$_2$] to 0.021 wt % Pd for silica/*trans*-[PdMe(Cl)(PPh$_3$)$_2$]. In an attempt to increase the palladium loading of silica/*trans*-[PdMe(Cl)(PPh$_3$)$_2$], the reaction was performed in C_6H_6, and the reaction time was increased from 24 h to 5 days. The Pd loading increased slightly, to 0.037%. We also tried treating silica-200 with a benzene solution of [PdMe$_2$(PPh$_3$)$_2$]; however, the reaction turned black almost immediately, presumably due to decomposition to metallic palladium. It appears that the mononuclear Pd complexes which contain more basic ligands (e.g., PMe$_3$ or dmpe) undergo a more facile reaction with the surface. However, the dimeric complexes, [PdPh(OH)L]$_2$ (L = PPh$_3$, PCy$_3$), show Pd loadings of 1.47 wt % when L = PPh$_3$ but only 0.90 wt % when L = PCy$_3$, a more basic phosphine.

In an effort to determine the nature of the palladium species bound to the surface, CP/MAS ^{31}P NMR spectroscopy was employed. For previously reported silica-bound late transition metal species containing phosphine ligands, the chemical shifts of the immobilized fragments are very similar to those of their molecular precursors. For example, the CP/MAS ^{31}P NMR spectrum of ≡SiORh(CO)(PMe$_3$)$_2$ shows a singlet at -10.1 ppm,[17] whereas the solution NMR spectrum of *trans*-[RhMe(CO)(PMe$_3$)$_2$] shows a peak at -9.7 ppm. Similarly, ≡SiORuH(dmpe)$_2$ shows a signal at 44.0 ppm, compared to 46.8 ppm for *trans*-[Ru(OH)H(dmpe)$_2$].[18]

Table 1. Catalytic Cyclization of 6-Aminohex-1-yne[a]

catalyst	wt % Pd	additive	conv (%)	TON (h^{-1})[b]
silica/*trans*-[PdMe(NO$_3$)(PMe$_3$)$_2$]	0.50		74	6.9
silica/*trans*-[PdMe(OTf)(PMe$_3$)$_2$]	*c*		64	*c*
silica/*cis*-[PdMe(Cl)(PMe$_3$)$_2$]	1.12		51	2.1
silica/*cis*-[PdMe(Cl)(PMe$_3$)$_2$]	1.12	AgOTf	85	3.6
silica/*cis*-[PdMe(Cl)(PMe$_3$)$_2$]	1.12	NaBAr′$_4$	62	2.6
silica/*trans*-[PdMe(Cl)(PMe$_3$)$_2$]	0.42		15	1.7
silica/*trans*-[PdMe(Cl)(PPh$_3$)$_2$][d]	0.021		11	24.5
silica/*trans*-[PdMe(Cl)(PPh$_3$)$_2$][e]	0.037		23	29.1
silica/[PdMe(Cl)(dmpe)]	0.65		21	1.5
silica/[PdMe(Cl)(dmpe)]	0.65	NaBAr′$_4$	31	2.2
silica/[PdMe(Cl)(dmpe)]	0.65	NaO$_2$CCF$_3$	24	1.7
silica/[PdMe(Cl)(dmpe)]	0.65	HBAr′$_4$	13	0.9
silica/[PdMe(Cl)(dppe)]	0.24		6	1.2
silica/[PdMe(Cl)(phen)]	0.065		20	14.4
silica/[PdMe(Cl)(bipy)]	0.023		8	16.3
silica/[PdMe$_2$(dmpe)]	0.93		0	0
silica/[PdPh(OH)(PCy$_3$)]$_2$	0.90		37	1.9
silica/[PdPh(OH)(PPh$_3$)]$_2$	1.47		33	1.1
trans-[PdMe(NO$_3$)(PMe$_3$)$_2$]	*c*		51[f,g]	1.3
trans-[PdMe(Cl)(PMe$_3$)$_2$]	*c*		7[f,g]	0.2
Pd on carbon	10		85[h,i]	0.4

[a] Reactions were conducted using 100 mg of catalyst for 20 h in acetonitrile, unless otherwise stated. [b] The TONs were determined after 20 h, not at a standard % conversion, and this should be noted when comparing the results. [c] Not measured. Sample black/obvious decomposition. [d] Catalyst prepared in THF over 24 h. [e] Catalyst prepared in benzene over 5 days. [f] Substrate-to-catalyst ratio of 50:1. [g] Reaction turned black in color. [h] Palladium, 10% on carbon, was obtained from Lancaster. [i] Substrate-to-catalyst ratio of 10:1.

The silica-bound materials formed from the dimeric complexes, [PdPh(OH)L]$_2$ (L = PPh$_3$, PCy$_3$), both give similar ^{31}P CP/MAS NMR spectra. Silica/[PdPh(OH)(PPh$_3$)]$_2$ shows a broad peak at 30 ppm and a sharper peak at 23 ppm, whereas silica/[PdPh(OH)(PCy$_3$)]$_2$ shows a broad peak at 36 ppm and a sharper singlet at 29 ppm. The broad peak at 36 ppm cannot be assigned to tricyclohexylphosphine oxide (O=PCy$_3$ δ (CDCl$_3$) 54.2 ppm). Thus, it appears that in each case more than one palladium species is formed on the surface. As mentioned above, when silica is treated with *trans*-[Ru(OH)H(dmpe)$_2$], the hydroxo group rather than the hydrido ligand reacts with the surface silanols. Therefore, on the basis of the ^{31}P CP/MAS NMR spectra, we propose the formation of dinuclear (**1**) and mononuclear (**2**) species (Scheme 1). The ^{31}P{^{1}H} NMR spectra of the molecular complexes, [PdPh(OH)(PPh$_3$)]$_2$ and [PdPh(OH)(PCy$_3$)]$_2$, as CDCl$_3$ solutions give singlets at 33.9 and 37.5 ppm, respectively. These values correspond reasonably well with those assigned to the grafted dinuclear species (**1**) of δ 30 (L = PPh$_3$) and 36 (L = PCy$_3$). The previously reported monuclear hydroxo complexes, [PdPh(OH)L$_2$] (L = PPh$_3$, PCy$_3$), show peaks at δ(CH$_2$Cl$_2$) 23.1 and δ(C$_6$D$_6$) 22.2 (L = PCy$_3$) which are shifted upfield, compared with those of the analogous dinuclear complexes.[23] The peaks at δ 23 (L = PPh$_3$) and δ 29 (L = PCy$_3$) are also shifted upfield from those assigned to the silica-supported dinuclear complexes and are tentatively assigned to the mononuclear species (**2**). Free rotation about the SiO$-$Pd bond would be expected in **2**, and the sharper signals assigned to **2** are consistent with this observation.

Table 2. ^{31}P NMR Spectroscopic Data for Trans Complexes

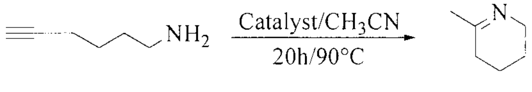
palladium complex	molecular complex δ (CD_2Cl_2)	silica-bound complex δ (CP/MAS)
trans-[PdMe(Cl)(PMe_3)$_2$]	−13.7 (s)	−7 (br), −17 (sh s)
trans-[PdMe(NO_3)(PMe_3)$_2$]	−11.1 (s)	3 (br m)
trans-[PdMe(Cl)(PPh_3)$_2$]	30.5 (s)	27 (br)

Table 3. ^{31}P NMR Spectroscopic Data for Cis Complexes

palladium complex	molecular complex δ (CD_2Cl_2)	silica-bound complex δ (CP/MAS)
[$PdMe_2$(dmpe)]	21.7 (s)	53 (br)
[PdMe(Cl)(dmpe)]	40.8 (d), 27.6 (d) (J_{PP} = 23 Hz)	60 (br)
[PdMe(Cl)(dppe)]	61.6 (d), 34.0 (d) (J_{PP} = 27 Hz)	62 (br)
cis-[PdMe(Cl)(PMe_3)$_2$]	42.5 (d), 29.3 (d) (J_{PP} = 22 Hz)	51 (br)

The silica-supported methyl palladium complexes prepared from trans precursors show a comparatively small shift relative to their molecular precursors (Table 2). For example, *trans*-[PdMe(Cl)(PPh_3)$_2$] shows a singlet at 30.5 ppm compared to 27 ppm for silica/*trans*-[PdMe(Cl)(PPh_3)$_2$]. However, for the silica-supported cis complexes there is a large downfield shift compared to their molecular precursors (Table 3). If the silica-supported cis Pd complexes were formed by a simple grafting reaction, then the ^{31}P CP/MAS NMR spectrum should show two signals due to the inequivalent phosphines; however, only one broad signal was observed. This is not consistent with a simple cis-to-trans rearrangement, because the trans complexes give materials which are spectroscopically different, which also display different reactivity (vide infra). This may be due to the two phosphines experiencing similar magnetic environments because of the formation of dinuclear cations on the surface (Scheme 2).[26] The preparation of the dinuclear cationic molecular species, [Pd_2(μ-Cl)$_2$(dppe)$_2$](ClO_4)$_2$, has been reported previously without ^{31}P{^{1}H} NMR spectroscopic details.[27] We found that it gives a broad signal in the ^{31}P{^{1}H} NMR spectrum at δ 71.7 in methanol, shifted downfield from the neutral [PdMe(Cl)(dppe)]. Although we can only postulate as to the cause of the large CP/MAS ^{31}P NMR downfield shifts of the silica-bound palladium species formed from cis precursors, the chemical shifts are not consistent with simple oxidation of the phosphines.[28]

Catalytic Activity of Silica-Bound Species. The silica-supported palladium compounds were initially investigated as catalysts for the cyclization of 6-aminohex-1-yne, eq 3.



(3)

Table 4. Catalytic Cyclization of 5-Phenyl-4-pentyn-1-amine

catalyst	solvent	run no. (cat. wt.)	conv (%)	TON (h^{-1})
silica/*trans*-[PdMe(NO_3)(PMe_3)$_2$]	CH_3CN	1 (100 mg)^a	100	>5.50^f
		2 (94 mg)	100	*b*
		3 (70 mg)^c	65	16.6
silica/*trans*-[PdMe(NO_3)(PMe_3)$_2$]	toluene	1 (100 mg)^a	100	>5.50^f
		2 (90 mg)	90	*b*
		3 (80 mg)	50	*b*
trans-[PdMe(NO_3)(PMe_3)$_2$]	toluene	1 (5 mg)^{d,e}	90	3.14

[a] Aminoalkyne-to-catalyst ratio of 110:1. [b] Pd loading was not measured. [c] Pd loading was measured by ICP to be 0.14% at the completion of the reaction. [d] Aminoalkyne-to-catalyst ratio of 60:1. [e] Reaction turned black in color. [f] The TON is at least the number specified, as the reaction was already complete at 20 h.

This reaction has been studied widely using a range of catalysts, facilitating comparison with the catalysts prepared here. The same mass of catalyst (100 mg) was used for all reactions. Acetonitrile slurries were heated at 90 °C for 20 h, at which time the conversion was determined. In general, higher conversions were found for materials containing more basic phosphines. This observation appears to be simply a consequence of their higher Pd loadings. For example, silica/*trans*-[PdMe(Cl)(PPh_3)$_2$], with a Pd loading of 0.037 wt %, gave a moderate conversion of 23%, after 20 h, whereas silica/*trans*-[PdMe(Cl)(PMe_3)$_2$], with over 10 times the Pd loading, resulted in only 15% conversion in the same time period. Furthermore, activity is greater when more weakly coordinating anionic ligands are present: for example, silica/*trans*-[PdMe(NO_3)(PMe_3)$_2$] (0.50 wt %Pd) gave 74% conversion in the cyclization of 6-aminohex-1-yne. Therefore, it appears that if it were possible to prepare a material with significant palladium loading, less basic donor ligands (e.g., PPh_3 or phen), and weakly coordinating anionic ligands (e.g., triflate), then a highly active catalyst would result. The silica-bound dinuclear complexes, silica/[PdPh(OH)(PPh_3)]$_2$ and silica/[PdPh(OH)(PCy_3)]$_2$, give much higher loadings even with weakly basic ligands, PPh_3, but conversion is only moderate, presumably due to the lack of a leaving group, although some is coordinatively unsaturated (i.e., **2**).

In an effort to increase the catalytic activity of silica/*cis*-[PdMe(Cl)(PMe_3)$_2$] and silica/[PdMeCl(dmpe)] for the cyclization of 6-aminohex-1-yne, NaBAr′$_4$, NaO_2CCF_3, or AgOTf was added in an attempt to displace chloride with a less coordinating anion. The additives had a positive effect on the activities of the catalysts in acetonitrile. For example, the conversion for silica/*trans*-[PdMe(Cl)(PMe_3)$_2$] increased from 51 to 62 and 85% when NaBAr′$_4$ and AgOTf were added, respectively. For silica/[PdMeCl(dmpe)], the conversion increased from 21 to 24 and 31% when NaO_2CCF_3 and NaBAr′$_4$ were added, respectively. However, the conversion was reduced to 13% when HBAr′$_4$ was added. For the catalytic system silica/[PdMeCl(dmpe)]/NaBAr′$_4$, cyclization in CH_3CN, toluene, and CH_2Cl_2 gave conversions of 31, 29, and 17%, respectively. Although acetonitrile is more coordinating and probably competes with the alkyne for the free coordination site, as a polar solvent it presumably assists in the ionization of the Pd−Cl bond. The catalyst forms a much finer suspension in toluene; however, it settles much faster in CH_3CN, which facilitates extraction of the organic product at the end of the reaction.

The molecular complexes *trans*-[PdMe(Cl)(PMe_3)$_2$] and *trans*-[PdMe(NO_3)(PMe_3)$_2$] were tested as homogeneous catalysts for the cyclization of 6-aminohex-1-yne under the same conditions as the silica-bound materials and found to give moderate conversions (Table 1). However, they are significantly less active than the analogous silica-bound species, presumably due to their lower stability under the experimental conditions. Indeed, the reaction mixtures turned black in color during the course of the reaction, presumably due to decomposition to metallic palladium.

Of the silica-immobilized catalysts with reasonable (>0.2 wt %) palladium loadings, silica/*trans*-[PdMe(NO_3)(PMe_3)$_2$] showed

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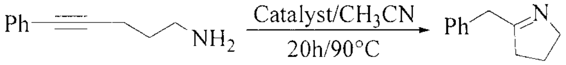
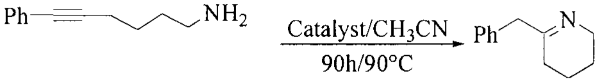
the highest activity for the cyclization of 6-aminohex-1-yne. Therefore, this catalyst was chosen to test the generality of the method for the cyclization of other aminoalkynes, namely, 5-phenyl-4-pentyn-1-amine and 6-phenyl-5-hexyn-1-amine. At room temperature, the reactions were extremely slow. The cyclization of 5-phenyl-4-pentyn-1-amine, eq 4, was consequently investigated at 90 °C and the percent conversion determined after 20 h, i.e., under the same conditions used for the cyclization of 6-amino-hex-1-yne. In either CH_3CN or toluene, 70% conversion was achieved after 5 h and full conversion after 20 h (Table 4). The catalyst was recycled and showed reasonable conversion up to the third recycling. The molecular compound *trans*-$[PdMe(NO_3)(PMe_3)_2]$, not immobilized onto silica, was tested as a catalyst for this reaction and found to be reasonably active; 90% conversion was achieved under similar conditions. However, the reaction mixture turned black, presumably due to formation of metallic palladium.



(4)

As expected, the cyclization of 6-phenyl-5-hexyn-1-amine, eq 5, to form a six-membered ring was significantly slower. At 90 °C, using acetonitrile as the solvent and a substrate-to-catalyst ratio of 245:1, only 55% conversion was observed after 90 h (TON 1.5). In toluene, under similar conditions, only 40% conversion was observed (TON 1.1).



(5)

Conclusions

Palladium species immobilized on silica can be prepared by the simple addition of alkyl- or hydroxopalladium(II) complexes to partially dehydroxylated silica. The silica-bound species are more stable than their molecular precursors and are efficient catalysts for the cyclization of aminoalkynes. Although the rates of reaction are significantly lower than those found for the analogous reactions using lanthanide complexes, e.g., $[Cp'_2SmCH(SiMe_3)_2]$,[10−13] the rates are comparable to or faster than those found using late transition metal catalysts, e.g., $[Ru_3(CO)_{12}]$,[2] $[Rh(COD)(DiPAMP)]BF_4$,[1,2] or $[Pd(triphos)](OTf)_2$.[3] The major advantage of the catalysts discussed here is that they are only slightly air-sensitive and can be recycled, after filtration in air, with only moderate loss of activity.

Acknowledgment. We are grateful to Glenn Facey for recording the CP/MAS NMR spectra, Victor Boyko of the National Research Council, Canada, for ICP measurements, and the NSERC for support of this research through a strategic grant award.

JA0113450