

Preparation of the palladium(II) dimethylamide $\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\text{)(NMe}_2\text{)}$ at low temperatures and its ligand exchange with the dicyclohexylamide

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Abstract

The title complex $\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\text{)(NMe}_2\text{)}$ (**2**) has been prepared from deprotonation of $[\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\text{)(NHMe}_2\text{)}]\text{OTf}$ (**1**) by a stoichiometric amount of dicyclohexylamide anion at low temperatures. VT NMR experiments showed that **2** was stable below -10°C , and slowly underwent decomposition to give a couple of unidentified species at elevated temperatures. However, the reaction of **1** with an excess of lithium dicyclohexylamide (> ten equivalents) generated the monomeric palladium(II) hydride $2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\text{PdH}$ (**3**). The reaction of $(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\text{Pd}(\text{OTf})$ with an excess of lithium dicyclohexylamide also produced the hydride. A d_8 -THF solution of **3** was stable for 16 h at ambient temperature. However, an attempt to isolate **3** resulted in the formation of a small amount of the hydride-bridged dipalladium $[\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)_2(\mu\text{-H})]^+$ (**4**) and mostly decomposed species. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Dimethylamido palladium complex; Catalytic amination; Palladium hydride; Beta-hydrogen transfer

1. Introduction

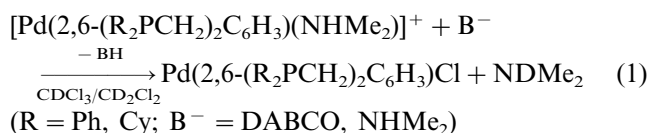
Alkylamido complexes of late transition metals are known as reactive intermediates in metal-catalyzed amination [1,2]. Such complexes, however, are rare because a facile β -hydrogen transfer proceeds to generate metal hydrides or reduced species [3]. It is also noteworthy that alkylamido complexes with a flexible ligand framework such as monodentate tertiary phosphines undergo β -hydrogen elimination more easily than the complexes with a rigid ligand framework [3–6]. Although β -hydrogen elimination of such complexes is common, a direct decomposition pathway has been rarely observed. Recently it has been reported that β -hydrogen transfer of the benzylamido complex $\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{N}(\text{CH}_2\text{Ph})\text{Ph})$ proceeds via a dissociative pathway involving three coordinated 14 e intermediate [7]. Even though many efforts to isolate dimethylamido complexes of late transition metals were not successful

[8], recent study revealed that substantial dialkylamido species were involved in the catalytic amination of arylhalides via C–N reductive elimination at ambient temperature [2]. On the premise of previous examples and mechanistic information for β -hydrogen elimination of alkylamido complexes, stability examination for such complexes bearing a rigid tridentate ligand is of interest in the context with the possible roles as intermediates in many catalytic reactions.

We have previously reported that cationic dimethylamine complexes of palladium(II) containing rigid tridentate ligands, $[\text{Pd}(2,6\text{-(R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\text{)(NHMe}_2\text{)}]^+$ underwent chlorine abstraction to produce chloropalladium(II) complexes in the presence of a base [9] (Eq. (1)). In the reaction, we suggested a palladium(II) dimethylamide as transient species, which immediately reacted with chlorinated solvents forming the chloro complexes. In this paper, we describe the synthesis and thermal stability of the dimethylamido palladium(II) complex having a tridentate ligand with PCP donor sets with a hope that rigidity of the ligand framework could inhibit decomposition.

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2. Results and discussion

When the dimethylamine complex $[\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)](\text{OTf})$ (**1**) reacted with an excess of lithium dicyclohexylamide in tetrahydrofuran at -78°C , slight color-change of the solution from colorless to pale-orange was observed. Removal of the solvent under high vacuum at low temperatures ($< 0^\circ\text{C}$) gave a pale-orange residue, which was extracted with dry d_6 -acetone. The $^{31}\text{P}\{\text{H}\}$ -NMR spectrum of the extract displayed several resonances; one was sharp at δ 43.0 and the others were rather broad at δ 35 ($\Delta\nu_{1/2} \cong 42$ Hz). The ^1H -NMR spectrum of this solution exhibited an upfield hydride resonance at δ -8.60 as a quintet ($^2J(\text{PH}) = 14.2$ Hz). This hydride was verified as the cationic hydride-bridged dipalladium species $[(\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3))_2(\mu\text{-H})]^+$ (**4**) by evidences of the ^1H - and $^{31}\text{P}\{\text{H}\}$ -NMR spectra. The NMR spectral data of this complex in d_6 -acetone are fully consistent with those of the precedent that was previously prepared by the reaction of $[\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{acetone})]^+$ and NaO_2CH [10].

In order to investigate the stability and decomposition features of the dimethylamido species, VT NMR experiments have been performed. Addition of d_8 -THF at -78°C to an approximately equimolar mixture of $[\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)](\text{OTf})$ and lithium dicyclohexylamide in a screw-capped NMR tube allowed the spectroscopic detection of dimethylamido species. The $^{31}\text{P}\{\text{H}\}$ -NMR spectrum of the d_8 -THF solution at -50°C cleanly displayed a single resonance at δ 30.9. The $^{31}\text{P}\{\text{H}\}$ -NMR resonance corresponding to the starting compound $[\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)]^+$, which appears at δ 37.7 in d_8 -THF, was not observed at all, indicating that the coordinated dimethylamine immediately deprotonated by the highly hindered dicyclohexylamide anion. The ^1H -NMR spectrum of the solution, at -50°C , exhibited methyl resonances at δ 2.76 as a 1:2:1 triplet splitting with the very small coupling constant ($^4J(\text{PH}) = 2.1$ Hz) assignable to the dimethylamido moiety, and methylene resonances at δ 3.99 as a pseudo triplet due to the virtual *trans*-couplings ($|^2J(\text{PH}) + ^4J(\text{PH})| = 8.6$ Hz) [11]. The relative intensity ratio observed for the methyl and methylene resonances is 3:2. We assigned this species as the dimethylamido complex, $\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NMe}_2)$ (**2**). The complex **2** was stable at low temperatures up to -10°C ; The ^1H - and $^{31}\text{P}\{\text{H}\}$ -NMR resonances observed for **2** remained intact for at least more than 3 h without any signal broadening. Warming of

this solution to 0°C , the complex started to decompose, resulting in the signals broadening and the decreases of peak intensities in the ^1H - and $^{31}\text{P}\{\text{H}\}$ -NMR spectra. Finally this compound in d_8 -THF completely decomposed within 30 min at 10°C , giving a couple of unidentified phosphorus-containing compounds as evidenced by the signals observed at δ 32.0 and δ 33.6 in the $^{31}\text{P}\{\text{H}\}$ -NMR spectrum but no hydride species. This observation is in contrast with the above result, where we observed the dinuclear species from the reaction of $[\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)](\text{OTf})$ with an excess of lithium dicyclohexylamide. The difference between the two independent reactions is the amount of lithium dicyclohexylamide used, i.e. the former with excess and the latter with a nearly equimolar amount.

Further VT NMR experiments by using more than a tenfold excess of lithium dicyclohexylamide showed that the species generated from the reaction at low temperatures exhibited another signal, broad at δ 34.7 (in d_8 -THF) in the $^{31}\text{P}\{\text{H}\}$ -NMR. Judging from the NMR resonances, we suggest this species dicyclohexylamide derivative presumably formed via exchange with dicyclohexylamide anion used in excess. This species, however, was unstable and slowly converted into the monomeric hydrido complex $(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{-PdH}$ (**3**). The complex can be verified by the upfield triplet hydride resonance at δ -2.18 ($^2J(\text{PH}) = 12.6$ Hz) in the ^1H -NMR and single sharp resonance at δ 45.3 in the $^{31}\text{P}\{\text{H}\}$ -NMR spectroscopy. This complex **3** with the phenyl substituted terdentate ligand has not been reported. However, the analogous monomeric hydrido complex with sterically bulky *t*-butyl substituents, $(2,6\text{-('Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{-PdH}$, was previously prepared [12]. The ^1H -NMR spectral data observed for **3** is closely related with those of $(2,6\text{-('Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{-PdH}$; for comparison, the hydride signal of $(2,6\text{-('Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{-PdH}$ resonates at δ -3.86 ($^2J(\text{PH}) = 13.5$ Hz) in CDCl_3 . A d_8 -THF solution of **3** was stable at ambient temperature for at least 16 h. However, an attempt to isolate this complex from the solution was unsuccessful, resulting in the formation of a small amount of the hydride-bridged dipalladium complex, $[(\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3))_2(\mu\text{-H})]^+$ (^1H -NMR (in d_8 -THF): -8.58 quintet ($^2J(\text{PH}) = 14.2$ Hz), $^{31}\text{P}\{\text{H}\}$ -NMR: δ 46.6), and mostly decomposed species.

In the reactions, it is believed that the hydride was from the dicyclohexylamide but not the dimethylamide. This was confirmed by the independent reaction of $\text{Pd}(2,6\text{-(Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{OTf})$ with an excess of lithium dicyclohexylamide in d_8 -THF resulting in the formation of the monomeric palladium(II) hydride, clearly indicating that the dicyclohexylamide is responsible for the hydride source. Thus, a plausible pathway for the observed reactions involves the facile ligand exchange

with the dicyclohexylamide to form a highly reactive species toward β -hydrogen transfer. The greater propensity for β -hydrogen elimination of the dicyclohexylamide against the dimethylamide is likely due to the steric congestion of the bulkier substituents which facilitates β -hydrogen abstraction resulting in the generation of the hydride. An alternative pathway involving free radicals from the Pd–N homolysis of the highly hindered amide cannot be ruled out (see Scheme 1 for an outline of the reaction mechanisms).

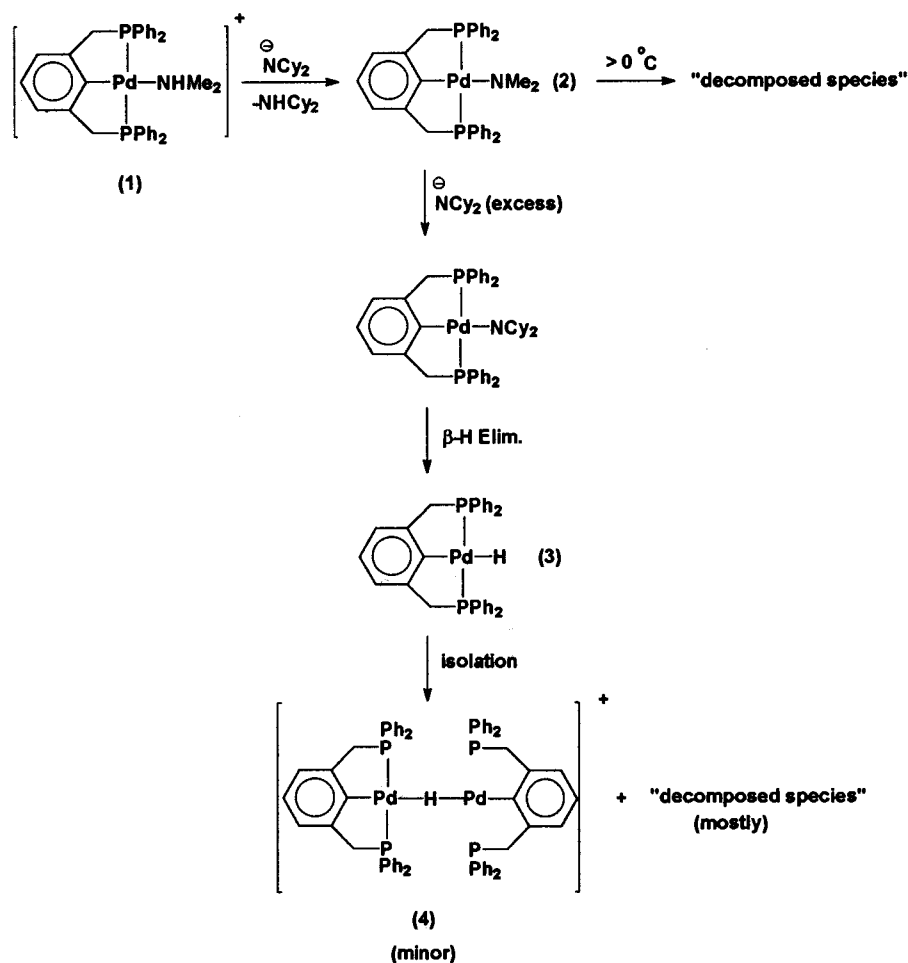
3. Experimental

All preparations of air sensitive compounds were carried out on a standard Schlenk line or in a glove box under an argon atmosphere. Anhydrous dimethylamine, lithium dicyclohexylamide, and deuterated NMR solvents were purchased from the Aldrich Chemical Co. d_8 -THF was dried and deaerated by means of solvent diffusion under high vacuum from sodium/benzophenone ketyl, and stored over activated molecular

sieves. All other reagents were from various commercial companies. The complex $[\text{Pd}(2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{-}(\text{NMe}_2)](\text{OTf})$ was prepared according to the previous method [9]. ^1H - (199.975 MHz) and $^{31}\text{P}\{^1\text{H}\}$ - (80.950 MHz) NMR spectra were measured on a Varian Gemini 200 spectrometer using the deuterium signal of the solvent as an internal lock frequency. ^1H and $^{31}\text{P}\{^1\text{H}\}$ chemical shifts were reported relative to TMS and 85% H_3PO_4 , respectively.

3.1. NMR spectroscopic data for complexes 2–4

For $\text{Pd}(2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NMe}_2)$ (**2**): ^1H -NMR (d_8 -THF): δ 2.76 t (6H, Pd–NMe₂, $^4J(\text{PH}) = 2.1$ Hz), δ 3.99 t (4H, CH₂, $|^2J(\text{PH}) + ^4J(\text{PH})| = 8.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (d_8 -THF): δ 30.9 s. For $(2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{PdH}$ (**3**): ^1H -NMR (d_8 -THF): δ -2.18 t (1H, Pd–H, $^2J(\text{PH}) = 12.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (d_8 -THF): δ 45.3 s. For $[(\text{Pd}(2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3))_2(\mu\text{-H})]\text{OTf}$ (**4**): ^1H -NMR (d_6 -acetone): δ -8.60 quintet (1H, Pd–H–Pd, $^2J(\text{PH}) = 14.2$ Hz), δ 4.02 t (4H, CH₂, $|^2J(\text{PH}) + ^4J(\text{PH})| = 9.2$ Hz). δ 6.9–7.8 m (23H,



Scheme 1.

Table 1
NMR data (ppm) in d_8 -THF for the palladium complexes bearing P,C,P pincer ligands

Complex	^1H	$^{31}\text{P}\{^1\text{H}\}$	Ref.
$[(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Pd}(\text{NHMe}_2)]^+$ (1)	2.20 d (Pd–HNMe ₂ ; $^3J(\text{HH}) = 5.8$ Hz) ^a	41.1 ^a , 37.7	[9]
$(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Pd}(\text{NMe}_2)$ (2)	2.76 t (Pd–NMe ₂ ; $^4J(\text{PH}) = 2.1$ Hz) ^b	30.9 ^b	This work
$(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Pd}(\text{NCy}_2)$		34.7	This work
$(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Pd}-\text{H}$ (3)	–2.18 t (Pd–H; $^2J(\text{PH}) = 12.6$ Hz)	45.3	This work
$(2,6-(^t\text{Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Pd}-\text{H}$	–3.86 t (Pd–H; $^2J(\text{PH}) = 13.5$ Hz) ^a		[12]
$[(\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3))_2(\mu-\text{H})]^+$ (4)	–8.60 quintet (Pd–H–Pd; $^2J(\text{PH}) = 14.2$ Hz) ^c	43.0 ^c , 46.6	[10]

^a In CDCl₃.

^b At –50°C.

^c In d_6 -acetone.

phenyl). $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ 43.0 s (in d_6 -acetone), δ 46.6 s (in d_8 -THF) (see Table 1).

3.2. Reaction of $[\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)](\text{OTf})$ (**1**) with lithium dicyclohexylamide

To the mixture of $[\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)]\text{OTf}$ (**1**) (50 mg, 0.065 mmol) and LiNCy₂ (122 mg, 0.65 mmol) was added a cooled THF (10 ml) at –78°C. The reaction mixture was stirred for 2 h. Removal of the solvent under high vacuum at low temperature (<0°C) resulted in a pale-orange solid, which was extracted with d_6 -acetone. The NMR spectroscopic data showed that a small amount of $[(\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3))_2(\mu-\text{H})](\text{OTf})$ (**4**) was present in the solution as well as several unidentified species. Complex **4** can be isolated from acetone–*n*-hexane in ca. 15% yield.

3.3. VT NMR experiments

A 0.5 ml sample of d_8 -THF was injected, by means of a gas tight syringe at –78°C, into a mixture of $[\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)](\text{OTf})$ and lithium dicyclohexylamide in a screw-capped NMR tube (Wilmad, 528-TR), which was prepared in a glove box under argon. This sample was inserted into the pre-cooled NMR probe at –50°C, and the ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopic data at various temperatures were obtained by switching the radio frequencies for both nuclei. A series of experiments were similarly performed by employing a different mole ratio of lithium dicyclohexylamide to the palladium complex. The formations of **2–4** were verified by ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy.

Acknowledgements

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