

Preliminary communication

Carbonylation of diamino-ligated methylpalladium(II) methoxide complexes

Gerardus M. Kapteijn, Michel J. Verhoef, M.A. Frederik H. van den Broek, David M. Grove,
Gerard van Koten *

Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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Abstract

The methylpalladium(II) methoxide complexes $[\text{Pd}(\text{Me})(\text{OMe})(\text{N}\sim\text{N})]$ ($\text{N}\sim\text{N} = \text{tmeda}$ or bpy) have been synthesized by alkoxide-methanol exchange of $[\text{Pd}(\text{Me})(\text{OCH}(\text{CF}_3)_2)(\text{N}\sim\text{N})]$ in MeOH . The bpy complex undergoes insertion of CO to give either a methyl(methoxycarbonyl) complex $[\text{Pd}(\text{Me})(\text{CO}_2\text{Me})(\text{bpy})]$ (at -60°C) or an acyl(methoxycarbonyl) complex $[\text{Pd}(\text{COMe})(\text{CO}_2\text{Me})(\text{bpy})]$ (at -25°C). Both carbonylated species were isolated and characterized at low temperature.

Keywords: Palladium; Methoxycarbonyl complexes; Acyl; Carbonylation; Methoxide; Perfluoroalkoxide

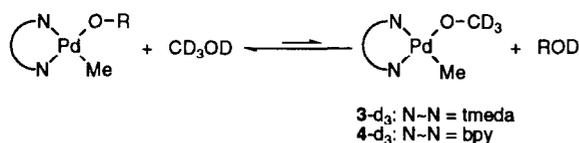
The insertion of CO into a $\text{Pd}\text{--}\text{OMe}$ bond is one of the fundamental steps in various palladium-catalyzed organic reactions such as (i) the copolymerization of CO and alkenes [1] and (ii) the methoxycarbonylation of propyne to give methyl methacrylate [2]. Surprisingly, however, only a limited number of palladium methoxide complexes have been detected in solution, and the only isolated complexes, *trans*- $[\text{Pd}(\text{R})(\text{OMe})(\text{PPh}_3)_2]$, also contain electronegative R groups such as C_6F_5 and $\text{CCl}=\text{CCl}_2$ [3]. However, Tóth reported that from a solution of $[\text{Pd}(\text{Me})(\text{O}^i\text{Bu})\{(S, S)\text{-bdpp}\}]$ ($(S, S)\text{-bdpp} = (2S, 4S)\text{-2,4-bis(diphenylphosphino)pentane}$) in dry MeOH it was possible to isolate $[\text{Pd}(\text{Me})(\text{OMe})\{(S, S)\text{-bdpp}\}]$ in 95% purity [4]. When the latter complex was treated with CO the methoxycarbonyl complex $[\text{Pd}(\text{Me})(\text{CO}_2\text{Me})\{(S, S)\text{-bdpp}\}]$ was generated, and, furthermore, in situ-generated $[\text{Pd}(\text{OMe})_2(\text{bpy})]$ was found to undergo stepwise insertion of CO to give the thermally stable $[\text{Pd}(\text{CO}_2\text{Me})_2(\text{bpy})]$ [5]. Recently we studied the first examples of thermally stable palladium(II) alkoxide complexes containing bidentate N -donor ligands [6,7], but these studies failed to provide routes to palladium methoxide complexes. We report here the in situ generation of new palladium methoxides of the type $[\text{Pd}(\text{Me})(\text{OMe})(\text{N}\sim\text{N})]$ ($\text{N}\sim\text{N} = \text{tmeda}$ or

bpy) and describe the carbonylation reactions of these new species.

The ^1H NMR spectra of $[\text{Pd}(\text{Me})(\text{OR})(\text{tmeda})]$ ($\text{R} = \text{CH}(\text{CF}_3)_2$, **1a**; C_6H_5 , **1b**) or $[\text{Pd}(\text{Me})(\text{OR})(\text{bpy})]$ ($\text{R} = \text{CH}(\text{CF}_3)_2$, **2a**; C_6H_5 , **2b**) [7] in CD_3OD reveal the equilibrium shown in Scheme 1. Dissolution of **1a** or **1b** (ca. 15.0 mg) in CD_3OD (0.50 ml) leads to the appearance of new PdMe and tmeda resonances together with the formation of free $(\text{CF}_3)_2\text{CHOH}$ or $\text{C}_6\text{H}_5\text{OH}$, respectively. Similarly, a new set of bpy resonances and a new PdMe signal appear when **2a** or **2b** is dissolved in CD_3OD . These results are consistent with the in situ formation of new palladium methoxide complexes formulated, as shown in Scheme 1, as $[\text{Pd}(\text{Me})(\text{OCD}_3)(\text{N}\sim\text{N})]$ ($\text{N}\sim\text{N} = \text{tmeda}$, **3-d**₃; bpy , **4-d**₃) [8].

The stability of the latter complexes under these conditions could be due to the formation of adducts of the type $[\text{Pd}(\text{Me})(\text{OCD}_3)(\text{N}\sim\text{N})]\cdot\text{HOCD}_3$ involving $\text{O}\cdots\text{H}\text{--}\text{O}$ interactions (several alcohol adducts have been reported in palladium alkoxide chemistry [7,9]). However, the stability of **3** and **4** could also arise from the fact that exchange of coordinated methoxide and methanol is much faster than β -hydrogen elimination from the $\text{Pd}\text{--}\text{OMe}$ unit [5]. The equilibrium depicted in Scheme 1 lies almost completely over to the side of the palladium alkoxide or aryloxy complex, and so in order to achieve a significant concentration of complexes **3-d**₃ or **4-d**₃ a large excess of CD_3OD is needed.

* Corresponding author.



Scheme 1. Formation of palladium methoxide complexes via alkoxide/aryloxide-methanol exchange.

We also explored the possibility of trapping these in situ generated methoxide complexes with CO and of isolating the carbonylated species. When CO was bubbled through a solution of $[\text{Pd}(\text{Me})(\text{OCH}(\text{CF}_3)_2)(\text{bpy})]$ (**2a**; 0.38 g, 1.16 mmol) in a minimum of MeOH (ca. 15 ml) at -60°C the methyl(methoxycarbonyl) complex $[\text{Pd}(\text{Me})(\text{CO}_2\text{Me})(\text{bpy})]$ **5** separated out, and was isolated at low temperatures as a yellow solid in 78% yield (see Scheme 2) [8]. Recently, Tóth reported the in situ generation of the related phosphine ligated methoxycarbonyl complex $[\text{Pd}(\text{Me})(\text{CO}_2\text{Me})\{(S, S)\text{-bdpp}\}]$ [4]. In the ^{13}C NMR spectrum of **5** (CD_2Cl_2 , 243 K) the carbonyl carbon resonance is at 196.5 ppm, a value similar to that of 201.9 ppm found for the corresponding carbon atom in $[\text{Pd}(\text{Me})(\text{CO}_2\text{CH}(\text{CF}_3)_2)(\text{dppe})]$ (CD_2Cl_2 , 213 K) [10]. There was no evidence for insertion of CO into the Pd–OCH(CF₃)₂ bond; i.e. the formation of **5** indicates that insertion into the Pd–OMe bond is kinetically preferred.

When CO was bubbled through a solution of **2a** in MeOH at -25°C , in a procedure similar to that used for obtaining **5** at -60°C , an acyl(methoxycarbonyl) complex $[\text{Pd}(\text{COMe})(\text{CO}_2\text{Me})(\text{bpy})]$ **6** was formed, and was isolated as an orange solid in 43% yield (see Scheme 2) [8]. The ^{13}C NMR spectrum of **6** (CD_2Cl_2 , 243 K) shows the carbonyl carbon atoms at 192.3 and 246.8 ppm. The presence of the latter resonance along with a signal at 42.22 ppm points to the presence of an acylpalladium unit; such units have expected $\delta(^{13}\text{C})$ values of ca. 250–210 ppm (COCH_3) and ca. 45–30 ppm (COCH_3) [11]. Furthermore, the $\delta(^{13}\text{C})$ value of 192.3 ppm for the CO_2CH_3 unit in **6** is similar to that of 196.5 ppm found for this unit in **5**. Bubbling CO through a solution of **5** in MeOH at -25°C also to

generated complex **6** and after 15 min the conversion of **5** into **6** was ca. 75% complete.

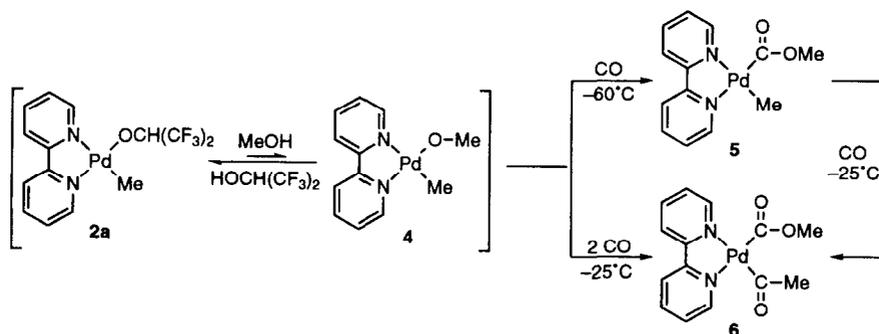
Carbonylation of the methylpalladium(II) methoxides shows that insertion of CO can take place either into the Pd–OMe bond or into the Pd–Me bond (depending upon the temperature used) to give rare examples of isolable methylpalladium(II) or acylpalladium(II) methoxycarbonyl species, which can be observed as intermediates in methoxycarbonylation reactions. The relevance of these model complexes to catalytic processes is the subject of further study.

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- [7] For synthesis and properties of $[\text{Pd}(\text{Me})(\text{OR})(\text{N-N})]$ (R = CH(CF₃)₂, C₆H₅; N-N = tmeda, bpy), see: G.M. Kapteijn, A. Dervisi, D.M. Grove, H. Kooijman, M.T. Lakin, A.L. Spek, G. van Koten, *J. Am. Chem. Soc.*, (1995) submitted.
- [8] Selected spectroscopic data: NMR data recorded at 300.13 MHz (^1H) or 75.04 MHz (^{13}C) and given as δ relative to SiMe₄. Methoxide complexes: NMR data for **3-d₃**: ^1H NMR (CD_3OD): δ 2.64–2.48 (m, 4H, CH₂), 2.54 (s, 6H, NMe₂), 2.50 (s, 6H, NMe₂), 0.34 (s, 3H, Pd–Me). NMR data for **4-d₃**: ^1H NMR (CD_3OD): δ 8.72 (broad, 1H, H₆), 8.65 (d, 1H, H₆), 8.37 (d,



Scheme 2. Carbonylation of N-ligated methylpalladium(II) methoxide complexes.

2H, H₃, H_{3'}), 8.12 (t, 2H, H₄, H_{4'}), 7.69 (t, 1H, H₅), 7.59 (t, 1H, H_{5'}), 0.86 (s, 3H, Pd–Me). Owing to the fact that CD₃OD was used there is no ¹H NMR signal for the palladium methoxide group in **3**-d₃ and **4**-d₃.

Carbonylated complexes: Data for **5**: ¹H NMR (CD₂Cl₂, 243 K): δ 8.55 (d, 1H, H(6)), 8.46 (d, 1H, H(6)), 8.16 (d, 1H, H(3)), 8.13 (d, 1H, H(3)), 8.01 (t, 1H, H(4)), 7.96 (t, 1H, H(4)), 7.49 (t, 1H, H(5)), 7.43 (t, 1H, H(5)), 3.60 (s, 3H, OMe), 0.32 (s, 3H, Pd–Me). ¹³C NMR (CD₂Cl₂, 243 K): δ 196.54 (CO), 155.08, 152.28, 150.61, 147.65, 138.90, 138.43, 126.54, 125.87, 122.14, 121.94 (bpy), 49.61 (OCH₃), –8.41 (Pd–CH₃). IR(KBr) for **5**: ν(CO) 1630 cm⁻¹. Data for **6**: ¹H NMR (CD₂Cl₂, 243 K): δ 8.53 (d, 1H, H(6)), 8.23 (d, 1H, H(6)), 8.20 (d, 1H, H(3)), 8.10 (d, 1H, H(3)), 8.00 (t, 1H, H(4)), 7.98 (t, 1H, H(4)), 7.36–7.32

(m, 2H, H(5)), 3.52 (s, 3H, OCH₃), 2.40 (s, 3H, COCH₃). ¹³C NMR (CD₂Cl₂, 243 K): δ 246.80 (COMe), 192.31 (CO₂Me), 153.70, 152.89, 150.50, 150.14, 139.29, 139.21, 126.17, 126.01, 122.40, 122.16 (bpy), 48.71 (OCH₃), 42.22 (Pd–CH₃). IR(KBr) for **6**: ν(CO) 1641, 1620 cm⁻¹.

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