

Platinum(II) Carbamate Directly Derived from the Insertion of CO₂ into the Pt(II)-NHR (Amido) Bond: Formation of Methyl N-Tolylcarbamate from the Pt(II) Carbamate

Soonheum Park

Department of Chemistry, Dongguk University, Kyongju 780-714, Korea

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Carbamato complexes of late transition metals are of importance as potential intermediates in catalytic syntheses of ureas¹ and carbamic esters² from amines and CO₂. Such complexes, however, have rarely been isolated probably due to their hydrolytic decomposition.³ Several synthetic methodologies for carbamate complexes have been known. Reactions of cationic metal complexes containing labile ligands with amines and CO₂ commonly resulted in the formation of carbamate complexes.⁴ In the reactions, free amines have been shown to promote the reaction in most cases, implicating a pathway involving ligand exchange with pre-formed carbamic acid HO₂CNR₂ derived from free amine and CO₂. However, synthesis of carbamate complexes *via* direct insertion of CO₂ into M-NR₂ bond is scarce.⁵ In the insertion reaction involving a Pt(II)-NH₂ complex with CO₂, the amido ligand attacks CO₂ to give a metastable carbamic acid derivative Pt-NHC(O)OH, which slowly converts to carbamate complexes Pt-OC(O)NH₂. This result suggests a pathway neither coordinated CO₂ nor free amine be involved.^{5b} Metathetical reaction of metal halides with Ag(O₂CNR₂) to afford carbamate complexes was also reported.⁶

Recently we have been interested in arylamido complexes of palladium(II) and platinum(II), particularly having PCP (PCP = 2,6-(R₃PCH₂)₂C₆H₃; R = Ph, Cy) pincer ligands that not only stabilize such a hard base ligand to be terminal but also offer regioselectivity in stoichiometric and catalytic reactions with olefin.⁷ Since the terdentate ligand inhibits both phosphine dissociation and reductive elimination of the aryl group, consequently the terminal amide ligand would display high reactivity towards many electrophiles. In this paper, of relevance to utilizing carbon dioxide as an environmentally benign carbonyl source, we wish to report a platinum(II)-carbamate derived from the reaction of a tolylamido complex with carbon dioxide, and its stoichiometric reaction with methyl iodide to obtain methyl N-tolyl carbamate.

Experimental Section

All preparations of air sensitive compounds were carried out under a nitrogen or argon atmosphere, using a standard Schlenk line or Vacuum Atmospheres glovebox. A screw capped 5-mm NMR tube equipped with a PTFE septum for a needle puncture (528-TR) was supplied from Wilmad Glass

Company. Benzene and *n*-hexane were distilled from sodium/benzophenone ketyl in the presence of tetraglyme. C₆D₆ was purchased from Aldrich Chemical Company, and used as supplied. CO₂ gas was dried by passing through a glass column (*ca.* 2 × 25 cm) filled with anhydrous CaCl₂. All other reagents were from various commercial companies. Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(NH(C₆H₄Me-*p*)) was synthesized according to the literature method.^{7c}

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), as pressed KBr pellets. ¹H-, ¹³C{¹H}- and ³¹P{¹H}-NMR spectra were measured on a Varian Gemini-2000 spectrometer, using the deuterium signal of the solvent as an internal lock frequency. Chemical shifts for ¹H and ¹³C{¹H}-NMR are reported in ppm (δ) relative to TMS. For ³¹P{¹H}-NMR, chemical shift was measured in ppm relative to external 85% H₃PO₄ (in a sealed capillary). GC/MS analyses were performed using an HP 6890 gas chromatograph equipped with an HP 5973 MSD and an HP-Ultra 1 column (Crosslinked Methyl Silicone Gum, 50 m × 0.2 mm, 0.33 μm film thickness). Elemental analysis was performed at Korea Basic Science Institute in Seoul, Korea.

Reaction of Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(NH(C₆H₄Me-*p*)) (1) with CO₂ to yield Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(OC(O)-NH(C₆H₄Me-*p*)) (2). Reaction of Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(NH(C₆H₄Me-*p*)) (*ca.* 10 mg) with carbon dioxide was carried out in a screw capped 5-mm NMR tube equipped with a PTFE septum for a needle puncture (Wilmad, 528-TR). Carbon dioxide was bubbled through a *d*₆-benzene solution of **2** for *ca.* 2 min *via* a 7-inch long needle connected with a silicone tube to a CO₂ cylinder. The complex Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(OC(O)NH(C₆H₄Me-*p*)) (**2**) was quantitatively formed in solution as monitored by ¹H- and ³¹P{¹H}-NMR spectroscopy. The carbamate complex **2** can be isolated from *n*-hexane and recrystallized from benzene/*n*-hexane to give an analytically pure compound. Yield 8 mg (75%). IR (KBr): ν(CO) = 1629 cm⁻¹. ¹H-NMR (C₆D₆): δ 2.11 s (3H, CH₃), δ 3.42 t (4H, CH₂; |²J(PH) + ⁴J(PH)| = 8.4 Hz, ³J(PtH) = 29.4 Hz), δ 6.88 d (2H, CH, ³J(HH) = 8.4 Hz), δ 7.37 d (2H, CH, ³J(HH) = 8.4 Hz), δ 7.73 br (1H, NH), δ 6.98-8.00 m (23H, Ph). ¹³C{¹H}-NMR (*d*₆-benzene): δ 20.84 (Pt-OC(O)NH(C₆H₄CH₃-*p*)), δ 42.93 t (P-CH₂; |¹J(PC) + ³J(PC)| = 35.7 Hz), δ 160.2 (Pt-OC(O)NH(C₆H₄CH₃-*p*)). ³¹P{¹H}-NMR (C₆D₆): δ 36.8 s (¹J(PtP) = 3097 Hz). Anal. Calc. for C₄₀H₃₅NO₂P₂Pt: C, 58.7; H, 4.31; N, 1.71. Found:

C. 58.4; H, 4.26; N, 1.83%.

Reaction of Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(OC(O)NH(C₆H₄-Me-*p*)) (2) with HCl to yield (2,6-(Ph₂PCH₂)₂C₆H₃)PtCl, NH₂(C₆H₄-Me-*p*) and CO₂. Reaction of Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OC(O)NH(C₆H₄-Me-*p*)) with HCl in *d*₆-benzene generated Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)Cl, *p*-toluidine, and CO₂. For Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)Cl: ³¹P{¹H}-NMR (C₆D₆): δ 33.2 s (¹J(PtP) = 2968 Hz).

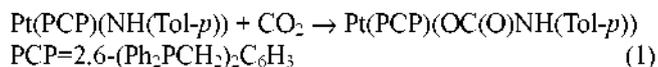
Reaction of Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(OC(O)NH(C₆H₄-Me-*p*)) (2) with HOSO₂CF₃ to yield Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OTf), NH₂(C₆H₄-Me-*p*) and CO₂. Reaction of Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OC(O)NH(C₆H₄-Me-*p*)) with HOSO₂CF₃ in *d*₆-benzene generated Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OTf), *p*-toluidine, and CO₂. For Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OTf): ³¹P{¹H}-NMR (C₆D₆): δ 39.2 s (¹J(PtP) = 3007 Hz).

Reaction of Pt(2,6-(Ph₂PCH₂)₂C₆H₃)(OC(O)NH(C₆H₄-Me-*p*)) (2) with MeI to yield Pt(2,6-(Ph₂PCH₂)₂C₆H₃)I and MeOC(O)NH(C₆H₄-Me-*p*). Reaction of Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OC(O)NH(C₆H₄-Me-*p*)) and MeI in *d*₆-benzene slowly (*ca.* 12 h) generated Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)I and MeOC(O)NH(C₆H₄-Me-*p*), which were identified by NMR and GC/MS spectroscopy. For Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)I: ¹H-NMR (C₆D₆): δ 3.55 t (4H, CH₂; |²J(PH) + ⁴J(PH)| = 9.0 Hz, ³J(PtH) = 25.4 Hz), δ 7.0-7.9 m (23H, Ph), ³¹P{¹H}-NMR (C₆D₆): δ 35.4 s (¹J(PtP) = 2860 Hz). For MeOC(O)NH(C₆H₄-Me-*p*): GC/MS: *m/z* = 165, 133, 120, 106, 77.

Results and Discussion

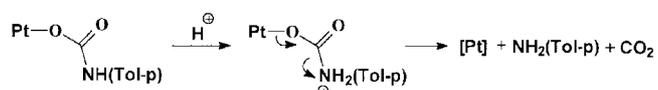
When carbon dioxide was bubbled through a *d*₆-benzene solution of Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(NH(Tol-*p*)) (1) in a 5-mm screw capped NMR tube for *ca.* 2 min, the carbamate complex Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OC(O)NH(C₆H₄-Me-*p*)) (2) was readily formed (Eq 1). The reaction was nearly quantitative as judged by the ¹H-, ³¹P{¹H}- and ¹³C{¹H}-NMR spectroscopy. The ³¹P{¹H}-NMR spectrum of 2 in *d*₆-benzene shows single resonance at δ 36.8 accompanied with ¹⁹⁵Pt satellites (¹J(PtP) = 3097 Hz). In the ¹³C{¹H}-NMR spectrum, the carbonyl carbon resonance of the Pt-OC(O)-NH(C₆H₄-Me-*p*) moiety was observed at δ 160.2, as commonly found in Pt(II) carbamate complexes at about δ 160.^{4a,c,5} The NH proton of the Pt-OC(O)NH(C₆H₄-Me-*p*) moiety resonates at δ 7.73 as a broad signal in the ¹H-NMR spectrum, which largely shifted to downfield due to the functionality at the electron withdrawing group. The addition of a strong coordinating ligand such as PPh₃ into a *d*₆-benzene solution of 2 resulted in no signal changes in the ¹H-NMR spectrum, indicating that N- or O-chelation of the carbamate moiety to platinum in the complex can be apparently excluded. Complex 2 was isolated in 75% yield from the *d*₆-benzene solution by reducing the volume of the solution under high vacuum followed by addition of *n*-hexane. The carbamate complexes are characterized by an intense absorption band of the ν(CO) around 1600 cm⁻¹ associated with the Pt-OC(O)NR₂ moiety. The ν(CO) at 1629 cm⁻¹ observed for complex 2 is in good agreement with the literature data for *trans*-PtH(OC(O)NHPh)(PET₃)₂^{5a}

and *trans*-PtPh(OC(O)NH₂)(PCy₃)₂^{5b} reporting its respective ν(CO) at 1626 and 1616 cm⁻¹. The analytically pure complex of 2 was synthesized in a preparative scale by the reaction of 1 with CO₂ in benzene (see Experimental).



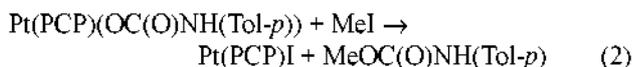
The platinum carbamate reacts with HX (diluted with *d*₆-benzene, X = Cl, OTf) in *d*₆-benzene to give the corresponding platinum(II) complex Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)X along with elimination of CO₂ and *p*-toluidine as evidenced by the ¹H-, ³¹P{¹H}-NMR and GC/MS spectroscopy. The resulting platinum(II) complexes Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)Cl and Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(OTf) were verified by the observation of single ³¹P resonance at δ 33.2 (¹J(PtP) = 2968 Hz) and δ 39.2 (¹J(PtP) = 3007 Hz), respectively. The released *p*-toluidine and CO₂ were identified by ¹H-NMR and/or GC/MS spectroscopy. In the reactions, either *N*-tolyl carbamic acid HOC(O)NH(Tol-*p*) or tolyl isocyanate OCN(Tol-*p*) likely arising from dehydration from the carbamic acid was not generated. These results can be indisputably explained by a sequence of reactions involving preferential protonation at the amine nitrogen rather than at the oxygen atom (Pt-O) in the carbamate moiety, and then subsequent elimination of free CO₂ along with *p*-toluidine *via* deinsertion (see Scheme 1). In precedents, facile reactions of carbamate complexes with protic reagents such as H₂S, H₂O, acetic acid, and hydrogen halides to give respective sulfido,^{8a} oxo,^{8b,c} acetato,^{8d} and halogeno complexes^{8d,e} with evolution of CO₂ were reported. Recently Calderazzo and his co-workers have reported the use of *N,N*-dialkylcarbamato complexes of Pd(II) and Pt(II) as precursors for chemical implantation of metal ions and reduced metal nanoparticles on a silica support by reacting with an acidic silanol group.⁹

On the contrary to protonolysis, treatment of the platinum (II) carbamate with MeI exclusively generated methyl *N*-tolyl carbamate MeOC(O)NH(C₆H₄-Me-*p*) and the Pt(II) iodide Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)I which was verified by single ³¹P-NMR resonance at δ 35.4 (¹J(PtP) = 2860 Hz) (Eq 2).¹⁰ The formation of MeOC(O)NH(C₆H₄-Me-*p*) was confirmed by GC/MS analysis. The fragmentation pattern of the released aryl carbamate was in good accordance with that of an authentic sample (*m/z* = 165, 133, 120, 106, 77). The reaction proceeded fairly slowly but quantitatively for *ca.* 12h. In this reaction, NHMe(Tol-*p*) was not produced, precluding a reaction pathway involving *N*-methylation in the carbamate moiety followed by CO₂ elimination. This result is of interest as compared with our previous report pertinent to methylation of a toluidinoalkyl Pt(II) complex with MeI, resulting in *N*-methylated products.^{7b,c} In the precedent, reaction of Pt(2,6-(Ph₂PCH₂)₂-C₆H₃)(CH(CN)-



Scheme 1

CH₂NH(C₆H₄Me-*p*) with MeI underwent preferential N-methylation followed by deinsertion to generate NHMe(Tol-*p*) and free CH₂=CHCN along with the platinum iodide. This incompatible reactivity of both aminated derivatives of Pt(II) towards MeI can be explained by relative nucleophilicity of the tolylamino group due to different functionality. The lack of nucleophilicity of the carbamato nitrogen bound to the electron withdrawing group disfavors N-methylation, resulting in the O-methylated product MeOC(O)NH(C₆H₄-Me-*p*). In the reaction, O-methylation to release MeOC(O)-NH(C₆H₄Me-*p*) likely proceeds *via* facile oxidative addition of MeI to Pt(II) leading to a transient Pt(IV) species followed by C-O reductive elimination.



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- Few examples for synthesis of carbamic esters from reactions of carbamato complexes with methyl iodide have been known. One precedent for the formation of carbamic methyl ester RR'NC(O)OMe from the reaction of palladium carbamate PdMe(OC(O)NRR')(PPh₃)₂ with methyl iodide was reported. In the precedent, however, the reaction involves more complicated manners to produce competing side products such as MeOC(O)OMe and CO₂, which implies hydrolytic decomposition of the carbamato complexes proceeded; see ref. 4(d).