Platinum(II) Carbamate Directly Derived from the Insertion of CO_2 into the Pt(II)-NHR (Amido) Bond: Formation of Methyl N-Tolylcarbamate from the Pt(II) Carbamate

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Carbamato complexes of late transition metals are of importance as potential intermediates in catalytic syntheses of ureas[1] and carbamic esters[2] from amines and CO_2. Such complexes, however, have rarely been isolated probably due to their hydrolytic decomposition.[3] Several synthetic methodologies for carbamato complexes have been known. Reactions of cationic metal complexes containing labile ligands with amines and CO_2 commonly resulted in the formation of carbamato 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 HO_2CNR_2 derived from free amine and CO_2. However, synthesis of carbamato complexes *via* direct insertion of CO_2 into M-NR_2 bond is scarce.[5] In the insertion reaction involving a Pt(II)-NH_2 complex with CO_2, the amido ligand attacks CO_2 to give a metastable carbamic acid derivative Pt-NHC(O)OH, which slowly converts to carbamato complexes Pt-OC(O)NH_2. This result suggests a pathway neither coordinated CO_2 nor free amine be involved.[5b] Metathetical reaction of metal halides with $Ag(O_2CNR_2)$ to afford carbamato 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-$(R_2PCH_2)_2C_6H_3$; 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. C_6D_6 was purchased from Aldrich Chemical Company, and used as supplied. CO_2 gas was dried by passing through a glass column (*ca.* 2 × 25 cm) filled with anhydrous $CaCl_2$. All other reagents were from various commercial companies. Pt(2,6-$(Ph_2PCH_2)_2C_6H_3$)(NH(C_6H_4Me-*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. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-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 ^{1}H and ^{13}C{^{1}H}-NMR are reported in ppm (δ) relative to TMS. For ^{31}P{^{1}H}-NMR, chemical shift was measured in ppm relative to external 85% H_3PO_4 (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-$(Ph_2PCH_2)_2C_6H_3$)(NH(C_6H_4Me-*p*)) (1) with CO_2 to yield Pt(2,6-$(Ph_2PCH_2)_2C_6H_3$)(OC(O)NH(C_6H_4Me-*p*)) (2). Reaction of Pt(2,6-$(Ph_2PCH_2)_2C_6H_3$)(NH(C_6H_4Me-*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 CO_2 cylinder. The complex Pt(2,6-$(Ph_2PCH_2)_2C_6H_3$)(OC(O)NH(C_6H_4Me-*p*)) (**2**) was quantitatively formed in solution as monitored by ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. The carbamato 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}. ^{1}H-NMR (C_6D_6): δ 2.11 s (3H, CH_3), δ 3.42 t (4H, CH_2; $|^2J$(PH) + ^4J(PH)$|$ = 8.4 Hz, ^3J(PtH) = 29.4 Hz), δ 6.88 d (2H, C*H*, ^3J(HH) = 8.4 Hz), δ 7.37 d (2H, C*H*; ^3J(HH) = 8.4 Hz), δ 7.73 br (1H, N*H*), δ 6.98-8.00 m (23H, Ph). ^{13}C{^{1}H}-NMR (d_6-benzene): δ 20.84 (Pt-OC(O)NH(C_6H_4CH_3-*p*)), δ 42.93 t (P-CH_2; $|^1J$(PC) + ^3J(PC)$|$ = 35.7 Hz), δ 160.2 (Pt-OC(O)NH($C_6H_4CH_3$-*p*)). ^{31}P{^{1}H}-NMR (C_6D_6): δ 36.8 s (^1J(PtP) = 3097 Hz). *Anal.* Calc. for $C_{40}H_{35}NO_2P_2Pt$: C, 58.7; H, 4.31; N, 1.71. Found:

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

Reaction of Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(OC(O)NH($C_6H_4$-Me-*p*)) (2) with HCl to yield (2,6-(Ph_2PCH_2)$_2$$C_6H_3$)PtCl, NH_2(C_6H_4Me-*p*) and CO_2. Reaction of Pt(2,6-(Ph_2PCH_2)$_2$-C_6H_3)(OC(O)NH(C_6H_4Me-*p*)) with HCl in d_6-benzene generated Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)Cl, *p*-toluidine, and CO_2. For Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)Cl: $^{31}P\{^1H\}$-NMR (C_6D_6): δ 33.2 s (^1J(PtP) = 2968 Hz).

Reaction of Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(OC(O)NH($C_6H_4$-Me-*p*)) (2) with $HOSO_2CF_3$ to yield Pt(2,6-(Ph_2PCH_2)$_2$-C_6H_3)(OTf), NH_2(C_6H_4Me-*p*) and CO_2. Reaction of Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(OC(O)NH($C_6H_4$Me-*p*)) with $HOSO_2CF_3$ in d_6-benzene generated Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(OTf), *p*-toluidine, and CO_2. For Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(OTf): $^{31}P\{^1H\}$-NMR (C_6D_6): δ 39.2 s (^1J(PtP) = 3007 Hz).

Reaction of Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(OC(O)NH($C_6H_4$-Me-*p*)) (2) with MeI to yield Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)I and MeOC(O)NH($C_6H_4$Me-*p*). Reaction of Pt(2,6-(Ph_2P-CH_2)$_2$$C_6H_3$)(OC(O)NH($C_6H_4$Me-*p*)) and MeI in d_6-benzene slowly (*ca.* 12 h) generated Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)I and MeOC(O)NH($C_6H_4$Me-*p*), which were identified by NMR and GC/MS spectroscopy. For Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)I: ^{1}H-NMR ($C_6D_6$): δ 3.55 t (4H, CH_2; $|\,^2J(PH) + {}^4J(PH)\,| = 9.0$ Hz, ^3J(PtH) = 25.4 Hz), δ 7.0-7.9 m (23H, Ph). $^{31}P\{^1H\}$-NMR (C_6D_6): δ 35.4 s (^1J(PtP) = 2860 Hz). For MeOC(O)NH-(C_6H_4Me-*p*): GC/MS: m/z = 165, 133, 120, 106, 77.

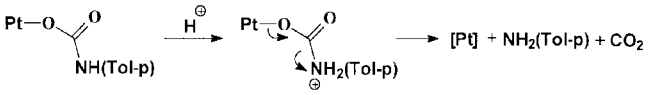
Results and Discussion

When carbon dioxide was bubbled through a d_6-benzene solution of Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(NH(Tol-*p*)) (**1**) in a 5-mm screw capped NMR tube for *ca.* 2 min, the carbamato complex Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(OC(O)NH($C_6H_4$Me-*p*)) (**2**) was readily formed (Eq 1). The reaction was nearly quantitative as judged by the ^{1}H-, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectroscopy. The $^{31}P\{^1H\}$-NMR spectrum of **2** in d_6-benzene shows single resonance at δ 36.8 accompanied with ^{195}Pt satellites (^1J(PtP) = 3097 Hz). In the $^{13}C\{^1H\}$-NMR spectrum, the carbonyl carbon resonance of the Pt-O*C*(O)-NH(C_6H_4Me-*p*) moiety was observed at δ 160.2, as commonly found in Pt(II) carbamato complexes at about δ 160.[4a,c,5] The N*H* proton of the Pt-OC(O)N*H*(C_6H_4Me-*p*) moiety resonates at δ 7.73 as a broad signal in the ^{1}H-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 PPh_3 into a d_6-benzene solution of **2** resulted in no signal changes in the ^{1}H-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 carbamato complexes are characterized by an intense absorption band of the ν(CO) around 1600 cm^{-1} associated with the Pt-OC(O)NR_2 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)(PEt_3)$_2$[5a] and *trans*-PtPh(OC(O)NH_2)(PCy_3)$_2$[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 CO_2 in benzene (see Experimental).

$$\text{Pt(PCP)(NH(Tol-}p\text{))} + CO_2 \rightarrow \text{Pt(PCP)(OC(O)NH(Tol-}p\text{))} \quad \text{PCP=2,6-(}Ph_2PCH_2\text{)}_2C_6H_3 \qquad (1)$$

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-(Ph_2PCH_2)$_2$$C_6H_3$)X along with elimination of CO_2 and *p*-toluidine as evidenced by the ^{1}H-, $^{31}P\{^1H\}$-NMR and GC/MS spectroscopy. The resulting platinum(II) complexes Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)Cl and Pt-(2,6-($Ph_2PCH_2$)$_2$$C_6H_3$)(OTf) were verified by the observation of single ^{31}P resonance at δ 33.2 (^1J(PtP) = 2968 Hz) and δ 39.2 (^1J(PtP) = 3007 Hz), respectively. The released *p*-toluidine and CO_2 were identified by ^{1}H-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 CO_2 along with *p*-toluidine *via* deinsertion (see Scheme 1). In precedents, facile reactions of carbamato complexes with protic reagents such as H_2S, H_2O, acetic acid, and hydrogen halides to give respective sulfido,[8a] oxo,[8b,c] acetato,[8d] and halogeno complexes[8d,e] with evolution of CO_2 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(C_6H_4Me-*p*) and the Pt(II) iodide Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)I which was verified by single ^{31}P-NMR resonance at δ 35.4 (^1J(PtP) = 2860 Hz) (Eq 2).[10] The formation of MeOC(O)NH(C_6H_4Me-*p*) was confirmed by GC/MS analysis. The fragmentation pattern of the released aryl carbamate was in good accordance with that of an authentic sample (m/z = 165, 133, 120, 106, 77). The reaction proceeded fairly slowly but quantitatively for *ca.* 12h. In this reaction, NHMe(Tol-*p*) was not produced, precluding a reaction pathway involving N-methylation in the carbamate moiety followed by CO_2 elimination. This result is of interest as compared with our previous report pertinent to methylation of a toluidinoalkyl Pt(II) complex with MeI, resulting in N-methylated products.[7b,c] In the precedent, reaction of Pt(2,6-(Ph_2PCH_2)$_2$$C_6H_3$)(CH(CN)-



Scheme 1

$CH_2NH(C_6H_4Me$-*p*)) with MeI underwent preferential N-methylation followed by deinsertion to generate NHMe(Tol-*p*) and free CH_2=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 $MeOC(O)NH(C_6H_4$-Me-*p*). In the reaction, O-methylation to release $MeOC(O)$-$NH(C_6H_4Me$-*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.

$$Pt(PCP)(OC(O)NH(Tol\text{-}p)) + MeI \rightarrow Pt(PCP)I + MeOC(O)NH(Tol\text{-}p) \quad (2)$$

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References

1. (a) McGhee, W. D.; Riley, D. P.; Christ, M. E.; Christ, K. M. *Organometallics* **1993**, *12*, 1429. (b) Fournier, J.; Bruneau, C.; Dixneuf, P. H.; Lecolier, S. *J. Org. Chem.* **1991**, *56*, 4456. (c) Aresta, M.; Quaranta, E. *ChemTech* **1997**, *27*, 32.
2. (a) Mahe, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518. (b) McGhee, W. D.; Riley, D. P. *Organometallics* **1992**, *11*, 900. (c) Aresta, M.; Dibenedetto, A.; Quaranta, E. *J. Chem. Soc., Dalton Trans.* **1995**, *20*, 3359. (d) Walther, D.; Geßler, S.; Ritter, U.; Schmidt, A.; Hamza, K.; Görls, H.; Sieler, J. *Chem. Ber.* **1995**, *128*, 281.
3. (a) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*, vol. 8; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; chapter 50.4, p 225. (b) Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257. (c) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37. (d) Yin, X.; Moss J. R. *Coord. Chem. Rev.* **1999**, *181*, 27.
4. (a) Anillo, A.; Dell'Amico, D. B.; Calderazzo, F.; Nardelli, M.; Pelizzi, G.; Rocchi, L. *J. Chem. Soc., Dalton Trans.* **1991**, 2845. (b) Belforte, A.; Dell'Amico, D. B.; Calderazzo, F. *Chem. Ber.* **1988**, *121*, 1891. (c) Abram, U.; Dell'Amico, D. B.; Calderazzo, F.; Marchetti, L.; Strähle, J. *J. Chem. Soc., Dalton Trans.* **1999**, 4093. (d) Ozawa, F.; Ito, T.; Yamamoto, A. *Chem. Lett.* **1979**, 735. (e) Srivastava, R. S.; Singh, G.; Nakano, M.; Osakada, K.; Ozawa, F.; Yamamoto, A. *J. Organomet. Chem.* **1993**, *451*, 221.
5. (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (b) Park, S.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* **1991**, *10*, 615. (c) Boncella, J. M.; Villanueva, L. A. *J. Organomet. Chem.* **1994**, *465*, 297.
6. (a) Alessio, R.; Dell'Amico, D. B.; Calderazzo, F.; Englert, U.; Guarini, A.; Labella, L.; Strasser, P. *Helv. Chim. Acta* **1998**, *81*, 219. (b) Alessio, R.; Dell'Amico, D. B.; Calderazzo, F.; Englert, U. *Gazz. Chim. Ital.* **1993**, *123*, 719.
7. (a) Ryu, S. Y.; Kim, H.; Kim, H. S.; Park, S. *J. Organomet. Chem.* **1999**, *592*, 194. (b) Park, S. *Bull. Korean Chem. Soc.* **2001**, *22*, 15. (c) Seul, J. M.; Park, S. *J. Chem. Soc., Dalton Trans.* in press.
8. (a) Bacchi, A.; Dell'Amico, D. B.; Calderazzo, F.; Giurlani, U.; Pelizzi, G.; Rocchi, L. *Gazz. Chim. Ital.* **1992**, *122*, 429. (b) Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Maichle-Mössmer, C.; Strähle, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1555. (c) Abram, U.; Dell'Amico, D. B.; Calderazzo, F.; Kaskel, S.; Labella, L.; Marchetti, F.; Rovai, R.; Strähle, J. *Chem. Commun.* **1997**, 1941. (d) Dell'Amico, D. B.; Calderazzo, F.; Marchetti, F.; Perego, G. *J. Chem. Soc., Dalton Trans.* **1983**, 483. (e) Dell'Amico, D. B.; Calderazzo, F.; Giurlani, U.; Pelizzi, G. *Chem. Ber.* **1987**, *120*, 955.
9. (a) Abis, L.; Dell'Amico, D. B.; Busetto, C.; Calderazzo, F.; Caminiti, R.; Ciofi, C.; Garbassi, F.; Masciarelli, G. *J. Mater. Chem.* **1998**, *8*, 751. (b) Abis, L.; Dell'Amico, D. B.; Busetto, C.; Calderazzo, F.; Caminiti, R.; Garbassi, F.; Tomei, A. *J. Mater. Chem.* **1998**, *8*, 2855.
10. 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 $PdMe(OC(O)NRR')(PPh_3)_2$ 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 CO_2, which implies hydrolytic decomposition of the carbamato complexes proceeded: see ref. 4(d).