DOI 10.5012/bkcs.2010.31.12.3745

Palladium(II) *p*-Tolylamide and Reaction with CO_2 to Generate a Carbamato Derivative

Jung Min Seul and Soonheum Park*

*Department of Chemistry, Dongguk University, Gyeongju 780-714, Korea. *E-mail: shpark@dongguk.ac.kr*
Received October 18, 2010, Accepted October 21, 2010

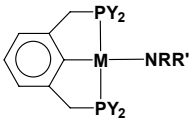
Pd(II) *p*-tolylamide Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)(NH(C_6H_4Me-*p*)) (**1**) was metathetically prepared by the reaction of Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)Cl with NaNH(C_6H_4Me-*p*). Treatment of **1** with carbon dioxide affords the palladium(II) carbamate Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)(OC(O)NH(C_6H_4Me-*p*)) (**2**), quantitatively. Complex **2** reacts with HX (X = Cl, OTf) to give Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)X, NH_2(*p*-Tol) and CO_2. Reaction of the palladium(II) carbamate with MeI produced Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)I along with generation of methyl *N*-tolylcarbamate MeOC(O)NH(C_6H_4Me-*p*), exclusively.

Key Words: Palladium arylamide, Palladium carbamate, Insertion of CO_2, Methyl *N*-aryl carbamate

Introduction

Transition metal carbamates are of importance as potential intermediates in catalytic syntheses of ureas[1] and carbamic esters[2] from amine and CO_2. However such complexes have scarcely 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 generate carbamato complexes.[4] In the reactions, free amines have been shown to promote reactions 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* net insertion of CO_2 into M-NR_2 bond is rare.[5] In the 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 (Scheme 1).[5b] This result suggests a pathway neither coordinated CO_2 nor free amine be involved. Metathetical reaction of metal halides with $Ag(O_2CNR_2)$ to afford carbamato complexes was also reported.[6] Carbamato complexes derived from net insertion of phenylisocyanate (PhNCO) into the M-O bond were studied by several groups, reporting the products *N*-coordinated cabamato complexes (M-NPhC(O)OR) (M = Pt, Pd, Ni, Ir, Mn, Re, Mo).[5a,7]

We have been interested in amido complexes of Pd(II) and Pt(II), particularly having PCP 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 (Figure 1).[8] 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 various electrophiles. In this paper, of relevance to utilizing carbon dioxide as an environmentally benign carbonyl source, we wish to report a new complex of palladium(II) arylamide and its reaction with carbon dioxide to yield a carbamato complex *via* net insertion of carbon dioxide into the Pd-N bond. A stoichiometric reaction of the Pd(II) carbamate with methyl iodide to generate methyl *N*-tolylcarbamate is also reported.

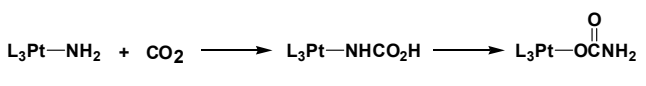


M = Pt, Pd; Y = Ph, Cy

Figure 1

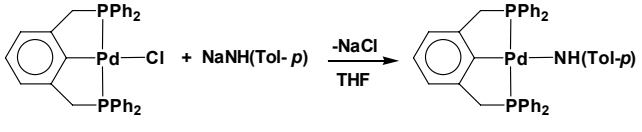
Results and Discussion

Preparation of *p*-tolylamido complex, Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)(NHC_6H_4Me-*p*) (1). Reaction of Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)Cl with an excess of NaNH(C_6H_4Me-*p*) (*ca*. 2 equivalents) in tetrahydrofuran afforded the Pd(II) *p*-toluidinide Pd(2,6-$(Ph_2PCH_2)_2C_6H_3$)(NHC_6H_4Me-*p*) (**1**) in 75% yield (Scheme 2). The formulation of **1** can be readily verified by the ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. In the ^{1}H-NMR spectrum of **1** in d_6-benzene, the N*H* resonance of the amide moiety N*H*(C_6H_4Me-*p*) has been observed at δ 2.43 as a broad signal. The methyl resonance of the *p*-tolyl group exhibits a single peak at δ 2.29. The resonance for the methylene protons (PCH_2) displays at δ 3.62 as a pseudo-triplet due to "virtual trans phosphorus coupling" ($|^2J(PH) + {}^4J(PH)| = 9.0$ Hz).[9] In the ^{31}P{^{1}H}-NMR spectrum of **1** in d_6-benzene, a sharp single resonance at δ 31.1 was observed, indicating no competing side product formed from the reaction.



L_3 = $Ph(PCy_3)_2$

Scheme 1



1

Scheme 2

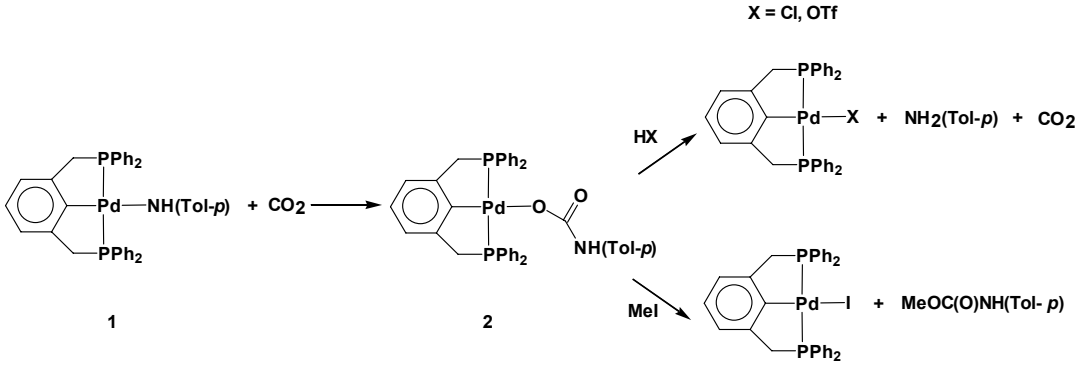
Complex **1** gave satisfactory microanalytical data (see Experimetal Section). The palladium tolylamide is extremely air and moisture sensitive immediately to decompose. It is worthy to note that complex **1** can be readily prepared from the palladium chloride, metathetically. In comparison with the platinum analog, the amido complex could not be obtained from the platinum chloride. Thus, for promising synthesis of the platinum amide, the employed starting compound for metathesis has to bear a more labile ligand such as triflate.[8c]

This monomeric amido complex of palladium with a terminal amide ligand is of particular interest because the complex would demonstrate that the metal-amide bond should selectively involve in the reaction with carbon dioxide; the ancillary PCP pincer would inhibit competing reactions of C-C(aryl) bond formation and C-N bond reductive elimination, likely arising from the *trans*-aryl ligand in the complex.

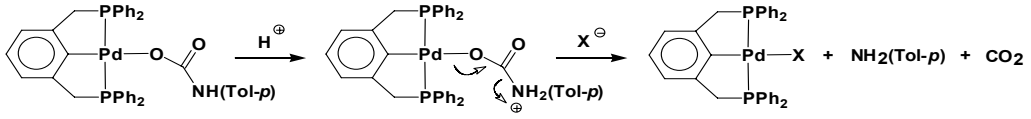
Preparation of carbamato complex, Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OC(O)NH(C$_6$H$_4$Me-*p*)) (2). When carbon dioxide was bubbled through a d_6-benzene solution of Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(NH(Tol-*p*)) (**1**) in a 5-mm screw capped NMR tube for *ca.* 2 min, the carbamato complex Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OC(O)NH(C$_6$H$_4$Me-*p*)) (**2**) was readily formed (Scheme 3). The reaction was nearly quantitative as judged by the ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. In the ^{1}H-NMR spectrum, the N*H* proton of the Pd-OC(O)N*H*(C$_6$H$_4$Me-*p*) moiety resonates at δ 7.48 as a broad signal, which is a fairly large shift to downfield due to the functionality at the electron withdrawing group as compared to that of amido complex **1** at δ 2.43. The ^{31}P{^{1}H}-NMR spectrum of **2** in d_6-benzene shows single resonance at δ 34.5. The addition of a strong coordinating ligand such as PPh$_3$ or pyridine into a d_6-benzene solution of **2** resulted in no signal changes in the ^{1}H- and ^{31}P{^{1}H}-NMR spectra, indicating that *N*- or *O*-chelation of the carbamate moiety to palladium in the complex can be apparently excluded. The ^{13}C{^{1}H}-NMR spectral data for **2** was not available due to instability of the palladium carbamate in solution for a relatively long period of scanning time (> 12 h). In comparison with platinum analogs, palladium carbamates are relatively unstable to slowly undergo decomposition *via* deinsertion of CO_2 (*vide infra*).[4,5]

The carbamate moiety in complex **2**, however, is well characterized by observation of the ν(CO) absorption band at 1632 cm^{-1} in the IR spectrum, which is well consistent with those of previously reported Pt(II) and Pd(II) carbamates.[5] Carbamato complexes are characterized by an intense absorption band of the ν(CO) around 1600 cm^{-1} associated with the M-OC(O)NR$_2$ moiety. The ν(CO) at 1632 cm^{-1} observed for **2** is in good agreement with the literature data for *trans*-PdPh(OC(O)NHPh)(PMe$_3$)$_2$ at 1630 cm^{-1}.[5c] For Pt(II) complexes *trans*-PtH(OC(O)NHPh)(PEt$_3$)$_2$[5a] and *trans*-PtPh(OC(O)NH$_2$)(PCy$_3$)$_2$,[5b] the ν(CO) was reported at 1626 and 1616 cm^{-1}, respectively. A preparative scale of complex **2** was synthesized in benzene by the reaction of **1** with CO_2 in 82% yield (see Experimental Section). The mass of molecular ion (729.19) observed in the FAB/MS spectrum of **2** is in good accordance with the calculated isotopic molecular mass (729.12).

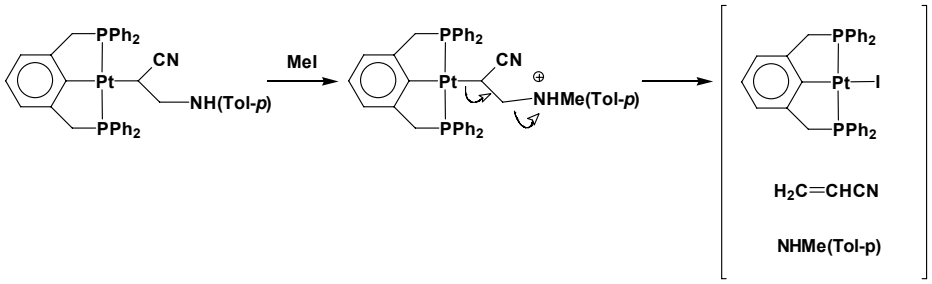
Complex **2** reacts with HX (diluted with d_6-benzene, X = Cl, OTf) in d_6-benzene to give the corresponding palladium(II) complex Pt(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)X along with elimination of CO_2 and *p*-toluidine as evidenced by the ^{1}H-, ^{31}P{^{1}H}-NMR and GC/MS spectroscopy (Scheme 3). The resulting palladium(II) species Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)Cl and Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf) were verified by the observation of a single ^{31}P-NMR resonance at δ 32.6 and δ 36.4, respectively. The released *p*-toluidine and CO_2 were identified by ^{1}H-NMR and GC/MS spectroscopy. In the reactions, either *N*-tolylcarbamic 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 unambiguously explained by a sequence of reactions involving preferential protonation at the amine nitrogen rather than at oxygen atom (Pt-*O*) in the carbamate moiety, and then subsequent elimination of free CO_2 along with *p*-toluidine *via* deinsertion (Scheme 4). In precedents, facile reactions of carbamato complexes with protic reagents such as H_2S, H_2O, acetic acid, and hydrogen halides to give



Scheme 3



Scheme 4



Scheme 5

respective sulfido,[10] oxo,[11] acetato,[12a] and halogeno complexes[12] with evolution of CO_2 were reported. *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 acidic silanol group were reported.[13] Carbamato complexes commonly undergo hydrolytic cleavages in the presence of H_2O as well as by treatment of acidic proton sources.

In stark contrast to protonolysis, treatment of complex **2** with MeI exclusively generated methyl *N*-tolylcarbamate MeOC(O)NH(C_6H_4Me-*p*) and the Pd(II) iodide Pd(2,6-(Ph_2PCH_2)$_2C_6H_3$)I which was verified by single ^{31}P-NMR resonance at δ 37.3 (Scheme 3). 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 dialkylcarbamate PdMe(OC(O)NRR')(PPh_3)$_2$ with methyl iodide was previously reported.[4a] 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 carbamate complexes proceeded.

In our study, complex **2** bearing a terdentate PCP pincer as an ancillary ligand, Pd(2,6-(Ph_2PCH_2)$_2C_6H_3$)(OC(O)NH(C_6H_4Me-*p*)) selectively reacts with MeI to produce MeOC(O)NH(C_6H_4Me-*p*), exclusively. No side product has been observed from the reaction. The formation of MeOC(O)NH(C_6H_4Me-*p*) was confirmed by GC/MS analysis. The fragmentation pattern of generated methyl *N*-tolylcarbamate is in good agreement with that of an authentic sample (*m*/*z* = 165, 133, 120, 106, 77). The reaction proceeded fairly slowly but quantitatively for *ca.* 12 h. In the reaction, amine derivative NHMe(Tol-*p*) was not produced, clearly ruling out a reaction pathway involving *N*-methylation 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.[8c] In our previous study, reaction of Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(CH(CN)CH_2NH(C_6H_4Me-*p*)) with MeI underwent preferential *N*-methylation followed by deinsertion of olefin to generate NHMe(Tol-*p*) and free CH_2=CHCN along with the platinum(II) iodide (Scheme 5). This incompatible reactivity of aminated derivatives of Pt(II) and Pd(II) towards MeI can readily be explained by relative nucleophilicity of tolylamino group due to different functionality. The lack of nucleophilicity of the carbamato nitrogen attached with electron withdrawing group disfavors *N*-methylation, resulting in the *O*-methylated product MeOC(O)NH(C_6H_4Me-*p*). In the reaction, *O*-methylation to produce MeOC(O)NH(C_6H_4Me-*p*) likely proceeds *via* facile oxidative addition of MeI to Pd(II) leading to a transient Pd(IV) species followed by C-O reductive elimination.

Experimental Section

All preparations of air sensitive compounds were carried out on a standard Schlenk line or in an inert atmosphere glovebox under argon. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone ketyl under nitrogen, and then stored over molecular sieve. Benzene, *n*-pentane and *n*-hexane were distilled from sodium/benzophenone ketyl with tetraglyme (tetraethylene glycol dimethyl ether). CH_2Cl_2 was dried by refluxing over sodium hydride under nitrogen. $PdCl_2$ was supplied by Kojima Chemicals Co., Ltd., and used without purification. Potassium diphenylphosphide, 1,5-cyclooctadiene, α,α'-dibromo-*m*-xylene and C_6D_6 were purchased from Aldrich Chemical Company, and used as supplied. *p*-Toluidine was purified by subliming in vacuo at 50 °C. CO_2 gas was dried by passing through a column (Drierite gas-drying unit: Aldrich Z11,287-9) filled with anhydrous $CaSO_4$. A screw capped 5-mm NMR tube equipped with a PTFE septum for a needle puncture (528-TR) was supplied from Wilmad Glass Company. All other reagents were from various commercial companies. NaNH(C_6H_4Me-*p*) was prepared from the reaction of NaH and *p*-toluidine in refluxing THF solution for 24 hours, and isolated from diethyl ether. Pd(2,6-(Ph_2PCH_2)$_2C_6H_3$)Cl and Pd(2,6-(Ph_2PCH_2)$_{2\,6}H_3$)(OTf) were synthesized according to the literatures.[8ab,14]

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), as pressed KBr pellets. ^{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-NMR are reported in ppm (δ) relative to TMS. For ^{31}P{^{1}H}-NMR, chemical shifts were measured in ppm relative to external 85% H_3PO_4 (in a sealed capillary). GC/MS analyses were carried out 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 and FAB/MS analyses were performed at Korea Basic Science Institute in Seoul, Korea.

Pd(2,6-(Ph_2PCH_2)$_2C_6H_3$)(NH(C_6H_4Me-*p*)) (1). A THF solution of NaNH(C_6H_4Me-*p*) (39 mg, 0.30 mmol) was slowly added to a stirred solution of Pd(2,6-(Ph_2PCH_2)$_2C_6H_3$)Cl (100

mg, 0.16 mmol) in THF. The reaction mixture was stirred for *ca*. 2 h. The color of solution gradually changed from pale yellow to deep greenish orange during the course of reaction. Removal of volatiles from the solution under high vacuum resulted in a greenish orange residue, which was washed with *n*-hexane (2 × 10 mL) and then extracted with benzene (2 × 10 mL) to give an orange solution. The volume of the solution was reduced to *ca*. 3 mL under high vacuum. Addition of *n*-hexane (*ca.* 15 mL) to the concentrated solution resulted in orange precipitates, which were filtered and dried in vacuo for 12 h gave an analytically pure orange compound. Yield 82 mg (75%). ^{1}H-NMR (d_6-benzene) δ 2.29 s (3H, C*H*$_3$), δ 2.43 br (1H, N*H*), δ 3.62 t (4H, C*H*$_2$, $|^2$J(PH) + ^{4}J(PH)$|$ = 9.0 Hz), δ 6.7-7.8 m (27H, phenyl). ^{31}P{^{1}H}-NMR (d_6-benzene) δ 31.1 s. *Anal.* Calc. for $C_{39}H_{35}N_1P_2Pd_1$: C, 68.28; H, 5.14; N, 2.04. Found: C, 68.13; H, 5.14; N, 2.11%.

Reaction of 1 with CO_2 to yield Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OC(O)NH(C$_6$H$_4$Me-*p*)) (2). Reaction of Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(NH(C$_6$H$_4$Me-*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 complex **1** for *ca.* 2 min *via* a 7-inch long needle connected with a silicone tube to a CO_2 cylinder. The color of solution immediately changes from orange to yellow upon treatment of CO_2. The complex Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OC(O)NH(C$_6$H$_4$Me-*p*)) (**2**) was quantitatively formed in solution as monitored by ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. The carbamato complex **2** in a pale yellowish solid can be isolated from *n*-hexane. Complex **2** can be obtained in a preparative scale by the reaction of **1** (100 mg, 0.15 mmol) with CO_2 in benzene. Recrystallization from benzene/*n*-hexane gave an analytically pure compound. Yield 87 mg (82%). IR (KBr Pellet): ν(CO) = 1632 cm^{-1}. ^{1}H-NMR (d_6-benzene) δ 2.14 s (3H, C*H*$_3$), δ 3.41 t (4H, C*H*$_2$, $|^2$J(PH) + ^{4}J(PH)$|$ = 8.9 Hz), δ 6.8-8.0 m (27H, phenyl), δ 7.48 (1H, N*H*). ^{31}P{^{1}H}-NMR (d_6-benzene) δ 34.5 s. FAB/MS: Calcd. for $C_{40}H_{35}N_1O_2P_2Pd_1$: 729.12. Found: 729.19.

Reaction of 2 with HCl to yield Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)Cl, NH$_2$(C$_6$H$_4$Me-*p*) and CO_2. Reaction of Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OC(O)NH(C$_6$H$_4$Me-*p*)) with HCl in d_6-benzene generated Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)Cl and (NH$_2$C$_6$H$_4$Me-*p*)·HCl.

Reaction of 2 with HOSO$_2$CF$_3$ to yield Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf), NH$_2$(C$_6$H$_4$Me-*p*) and CO_2. Reaction of Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OC(O)NH(C$_6$H$_4$Me-*p*)) with a triflic acid (HOSO$_2$CF$_3$) in d_6-benzene generated Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf) and (NH$_2$C$_6$H$_4$Me-*p*)·HOSO$_2$CF$_3$.

Reaction of 2 with MeI to yield Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)I and MeOC(O)NH(C$_6$H$_4$Me-*p*). Reaction of Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)(OC(O)NH(C$_6$H$_4$Me-*p*)) and MeI in d_6-benzene generated Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)I and MeOC(O)NH(C$_6$H$_4$Me-*p*), which were identified by NMR and GC/MS spectroscopy. For Pd(2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$)I: ^{1}H-NMR (d_6-benzene) δ 3.62 t (4H, C*H*$_2$), δ 7.1-7.8 m (23H, Ph). ^{31}P{^{1}H}-NMR (C$_6$D$_6$) δ 37.3 s. For MeOC(O)NH(C$_6$H$_4$Me-*p*): GC/MS: *m*/*z* 165, 133, 120, 106, 77.

Acknowledgments. This work was supported, in part, by Korea Research Foundation Grant (R05-2003-000-10486-0) and Dongguk University through the Research Fund Program.

References

1. (a) Sakakura, T.; Choi, J. C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365. (b) McGhee, W. D.; Riley, D. P.; Christ, M. E.; Christ, K. M. *Organometallics* **1993**, *12*, 1429. (c) Fournier, J.; Bruneau, C.; Dixneuf, P. H.; Lecolier, S. *J. Org. Chem.* **1991**, *56*, 4456. (d) Aresta, M.; Quaranta, E. *ChemTech* **1997**, *27*, 32. (e) Gabriele, B.; Salerno, G.; Mancuso, R.; Costa, M. *J. Org. Chem.* **2004**, *69*, 4741.
2. (a) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, *28*, 2975. (b) Mahe, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518. (c) McGhee, W. D.; Riley, D. P. *Organometallics* **1992**, *11*, 900. (d) Aresta, M.; Dibenedetto, A.; Quaranta, E. *J. Chem. Soc. Dalton Trans.* **1995**, 3359. (e) 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) Ozawa, F.; Ito, T.; Yamamoto, A. *Chem. Lett.* **1979**, 735. (b) Anillo, A.; Dell'Amico, D. B.; Calderazzo, F.; Nardelli, M.; Pelizzi, G.; Rocchi, L. *J. Chem. Soc., Dalton Trans.* **1991**, 2845. (c) Abram, U.; Dell'Amico, D. B.; Calderazzo, F.; Marchetti, L.; Strähle, J. *J. Chem. Soc., Dalton Trans.* **1999**, 4093. (d) Belforte, A.; Dell'Amico, D. B.; Calderazzo, F. *Chem. Ber.* **1988**, *121*, 1891. (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. (d) Boncella, J. M.; Eve, T. M.; Rickman, B.; Abboud, K. *Polyhedron* **1998**, *17*, 725.
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) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371. (b) Glueck, D. S.; Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. (c) Ruiz, J.; Martnez, M. T.; Florenciano, F.; Rodrguez, V.; Lopez, G.; Prez, J.; Chaloner, P. A.; Hitchcock, P. B. *Inorg. Chem.* **2003**, *42*, 3650. (d) Mandal, S. K.; Ho, D. M.; Orchin, M. *Organometallics* **1993**, *12*, 1714. (e) Hevia, E.; Perez, J.; Riera, L.; Riera, V.; delRio, I.; Garcia-Granda, S.; Miguel, D. *Chem. Eur. J.* **2002**, *8*, 4510.
8. (a) Ryu, S. Y.; Kim, H.; Kim, H. S.; Park, S. *J. Organomet. Chem.* **1999**, *592*, 194. (b) Ryu, S. Y.; Yang, W.; Kim, H. S.; Park, S. *Bull. Korean Chem. Soc.* **1997**, *18*, 1183. (c) Seul, J. M.; Park, S. *J. Chem. Soc. Dalton Trans.* **2002**, 1153.
9. (a) Verkade, J. G. *Chem. Rev.* **1972**, *9*, 1. (b) Pregosin, P. S.; Kunz, R. *Helv. Chim. Acta* **1975**, *58*, 423. (c) Verstuyft, A. W.; Nelson, J. H.; Cary, L. W. *Inorg. Chem.* **1976**, *15*, 732. (d) Pregosin, P. S.; Kunz, R. W. *31P- and 13C-NMR of Transition Metal Phosphine Complexes*; Springer: Berlin, 1979; p 65.
10. Bacchi, A.; Dell'Amico, D. B.; Calderazzo, F.; Giurlani, U.; Pelizzi, G.; Rocchi, L. *Gazz. Chim. Ital.* **1992**, *122*, 429.
11. (a) Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Maichle-Mössmer, C.; Strähle, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1555. (b) Abram, U.; Dell'Amico, D. B.; Calderazzo, F.; Kaskel, S.; Labella, L.; Marchetti, F.; Rovai, R.; Strähle, J. *Chem. Commun.* **1997**, 1941.
12. (a) Dell'Amico, D. B.; Calderazzo, F.; Marchetti, F.; Perego, G. *J. Chem. Soc., Dalton Trans.* **1983**, 483. (b) Dell'Amico, D. B.; Calderazzo, F.; Giurlani, U.; Pelizzi, G. *Chem. Ber.* **1987**, *120*, 955.
13. (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.
14. Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, 259, C6. 11.