4500 *Organometallics* **2005,** *24,* 4500−4502

Insertion of Carbon Dioxide into (PCP)Pd^{II}−Me Bonds

Roger Johansson, Martin Jarenmark, and Ola F. Wendt*

Organic Chemistry, Department of Chemistry, Lund University, P.O. Box 124,
S-221 00 Lund, Sweden

Received July 4, 2005

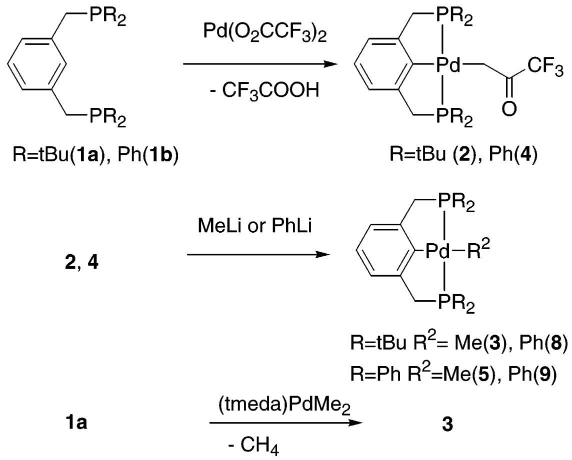
Summary: A (PCP)PdMe complex has been synthesized and structurally characterized, displaying a very long Pd−Me bond. It is reactive toward CO$_2$ insertion, giving the corresponding acetate in quantitative yield. The methyl complex can be regenerated using ZnMe$_2$, and catalytic carboxylation is possible in benzene.

With the increasing awareness of the world's finite petroleum reserves, carbon dioxide has become interesting as a feedstock for the synthesis of useful organic molecules.[1] The formation of C−C bonds would be of particular value, but of course this poses difficulties, since CO$_2$ is an inert molecule that does not react readily under most conditions. There are examples of a number of transition-metal carbon bonds that undergo insertion,[2] and there are also examples of catalytic reactions that form new C−C bonds.[3]

To develop new reactions for catalysis, we decided to investigate the insertion into Pd−C σ-bonds. Palladium is known to activate C−H bonds in hydrocarbons,[4] which are interesting substrates to react with CO$_2$ in a C−C bond-forming reaction. Also, palladium−allyl complexes are known to undergo insertion reactions with CO$_2$;[5] however, there are no known examples of insertions into Pd−C σ-bonds. Furthermore, Fujiwara and co-workers have reported palladium-catalyzed direct carboxylations of arenes, albeit with low conversions. There is no information about a stoichiometric insertion step, but such a step seems likely.[6] Our earlier investigations of Pd−Me complexes with the methyl group trans to nitrogen or phosphorus show that they are either inert or, in the presence of small amounts of water, give carbonate complexes.[7] We therefore decided to try to labilize the Pd−C bond, and our main focus has been on PCP-type complexes which combine high thermal stability with a reactive site trans to the trans-labilizing in-plane aryl ring. PCP complexes of palladium have been shown to catalyze a large number of C−C bond forming reactions.[8] Here we report the synthesis of (PCP)Pd complexes with hydrocarbyl ligands in the fourth position and their reactivity toward CO$_2$. We also report the structural characterizations of (PCP)Pd methyl and acetate complexes.

The free (PCP)H (**1**) ligands were synthesized according to literature methods[9] and reacted with Pd(TFA)$_2$ to give the TFA complexes **2** and **4** (cf. Scheme 1). These undergo reaction with methyllithium in diethyl ether to give the corresponding palladium methyl compounds, which display a characteristic high-field virtual triplet around 0.4 ppm in C$_6$D$_6$ and a single ^{31}P{^{1}H} resonance, in line with a trans geometry. Reactions were sluggish and **5** could not be isolated, since the reaction mixture

Scheme 1



---

* To whom correspondence should be addressed. E-mail: ola.wendt@organic.lu.se.

[1] Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953 and references therein.

[2] (a) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27. (b) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37. (c) Darensbourg, D. J.; Kudaroski Hankel, R.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463. (d) Darensbourg, D. J.; Grötsch, G.; Wiegreffe, P.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3827. (e) Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191.

[3] (a) Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257. (b) Shimizu, K.; Takimoto, M.; Sato, Y.; Mori, M. *Org. Lett.* **2005**, *7*, 195 and references therein. (c) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188.

[4] (a) Boele, M. D. K.; von Strijdonk, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuven, P. W. N. M. *J. Am. Chem. Soc.* **2002**, *124*, 1586. (b) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (c) Zaitsev, V. G.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 4156. (d) Orito, K.; Horibata, A.; Nakamura, T.; Ushito, H.; Nagasaki, H.; Yuguchi, M.; Yamashita, S.; Tokuda, M. *J. Am. Chem. Soc.* **2004**, *126*, 14342. (e) Yokota, T.; Tani, M.; Sakagushi, S.; Ishii, Y. *J. Am. Chem. Soc*. **2003**, *125*, 1476. (f) Periana, R. A.; Mironov, O.; Taube, D.; Bhalla, G.; Jones, C. J. *Science* **2003**, *301*, 814. (g) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550.

[5] (a) Santi, R.; Marchi, M. *J Organomet. Chem.* **1979**, *182*, 117. (b) Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5.

[6] (a) Sugimoto, H.; Kawata, I.; Taniguchi, H.; Fujiwara, Y. *J. Organomet. Chem.* **1984**, *266*, C44. (b) Fujiwara, Y.; Tabaki, K.; Taniguchi, Y. *Synlett* **1996**, 591. (c) Fuchita, Y.; Hiraki, K.; Kamogawa, Y.; Suenaga, M.; Tohgoh, K.; Fujiwara, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1081.

[7] Pushkar, J.; Wendt, O. F. *Inorg. Chim. Acta* **2004**, *357*, 1295.

[8] (a) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (b) Cotter, W. D.; Barbour, L.; McNamara, K. L.; Hechter, R.; Lachcotte, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 11016.

[9] Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Y. *Organometallics* **2000**, *19*, 1734.

10.1021/om0505561 CCC: $30.25

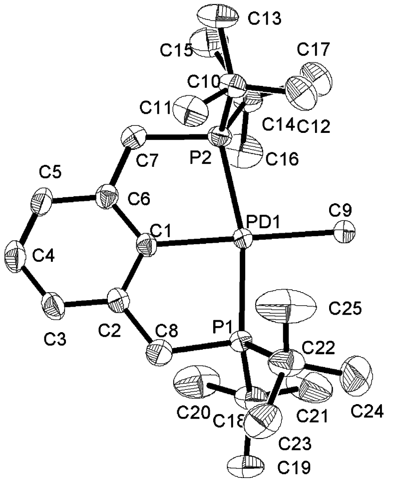


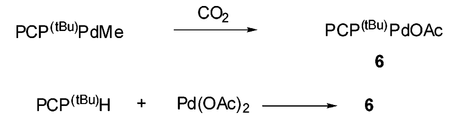
Figure 1. DIAMOND[19] drawing of **3**. For clarity hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Pd1−P1 = 2.2927(8); Pd1−P2 = 2.2885(7); Pd1−C1 = 2.076(2); Pd1−C9 = 2.199(3); P1−Pd1−P2 = 165.48(3); P1−Pd1−C1 = 83.24(7); P1−Pd1−C9 = 97.16(8); P2−Pd1−C1 = 82.74(7); P2−Pd1−C9 = 97.01(8).

also contained starting material. Compound **3** was fully characterized and gave crystals suitable for X-ray crystallography.[10] The molecular structure, together with selected distances and angles, is given in Figure 1. It consists of discrete molecules packed by dispersive forces. The coordination geometry is distorted square-planar with the typical "bent-back" P−Pd−P angle of 165.48(3)°. It displays a very long Pd−Me bond of 2.199(3) Å, the longest reported Pd−C σ-bond in a mononuclear complex. This is in line with the high trans influence of the aryl ring and confirms our assumption that the methyl group should have an enhanced reactivity. The methyl group of course also exerts a high trans influence, giving rise to a rather long palladium−aryl bond of 2.076(2) Å, in the same range as has been observed trans to a σ(C)-bonded furyl group.[11]

As described by Hughes and co-workers[12] for the corresponding (PCP)PtR^F complex, (PCP)^{tBu}H can also be reacted with Pd(tmeda)Me$_2$ to give compound **3**. On an NMR scale this reaction was quantitative, generating methane as the only byproduct, but it was not amenable to upscaling (cf. Scheme 1). The corresponding phenyl complexes **8** and **9** could be obtained similarly from the reaction of **2** and **4** with PhLi. Also in this case the reactions were sluggish and none of the phenyl complexes could be isolated, but they were characterized in situ using ^{1}H and ^{31}P NMR spectroscopy. Using Grignard or organotin reagents did not improve this reaction.

Treating the methyl complexes **3** and **5** in C$_6$D$_6$ with approximately 30 equiv of CO$_2$ in a sealable NMR tube gave no reaction at room temperature. The mixture was then heated to 80 °C and the reaction followed by NMR. Only **3** was reactive: within 2 days all of the starting material was consumed and the sole product was the normally inserted complex **6** (cf. Scheme 2). Isolation of this product was unsuccessful, but it could be independently synthesized according to Scheme 2. The insertion product was characterized by comparison with the synthesized sample of PCPPdOAc (**6**), which was fully characterized. We also obtained crystals of **6** suitable for X-ray diffraction.[13] The molecular structure is shown in Figure 2. The acetate is η^1 coordinated, as expected in a pincer complex. The P−Pd−P angle is again substantially lower than 180°. The Pd−C distance is 2.014 Å, in line with a lower trans influence of the acetate compared to the methyl, and the Pd−O distance is similar to those found in other examples of acetates trans to aryl groups.[14]

Scheme 2



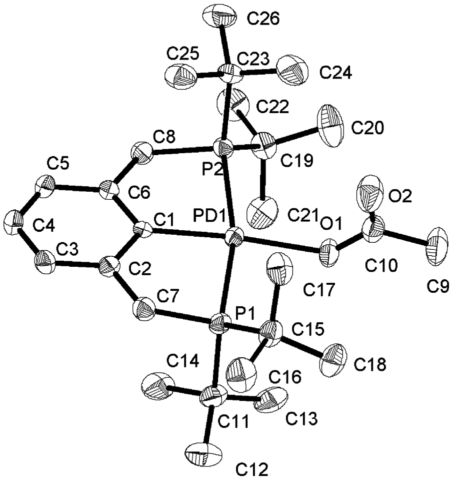
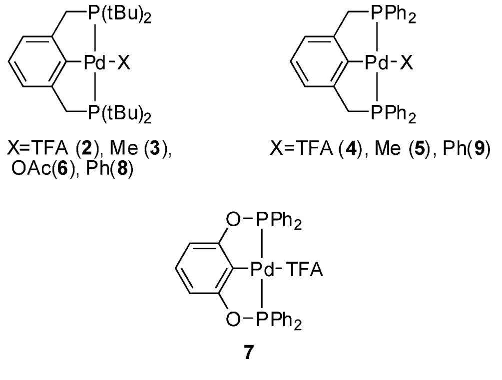


Figure 2. DIAMOND[19] drawing of **6**. For clarity hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Pd1−P1 = 2.3058(8); Pd1−P2 = 2.3118(8); Pd1−C1 = 2.014(2); Pd1−O1 = 2.1279(19); O1−C10 = 1.252(3); O2−C10 = 1.227(3); P1−Pd1−P2 = 165.94(3); P1−Pd1−C1 = 83.17(7); P1−Pd1−O1 = 96.24(6); P2−Pd1−C1 = 82.77(7); P2−Pd1−O1 = 97.71(6), O2−C10−O1 = 126.0(3).

Chart 1



X=TFA (**2**), Me (**3**), OAc(**6**), Ph(**8**)

X=TFA (**4**), Me (**5**), Ph(**9**)

7

---

[10] Crystal data: C$_{25}$H$_{46}$P$_2$Pd, M_r = 514.96, orthorhombic, a = 11.156(2) Å, b = 15.780(3) Å, c = 30.671(6) Å, V = 5399.7(19) Å^3, space group $Pbca$, Z = 8. A total of 53 129 reflections were measured, 8802 of which were unique (R_{int} =0.067) and were used in all calculations. The final $R_w(F^2)$ value was 0.1262 (all data), and the $R(F)$ value was 0.0424 ($I > 2\sigma(I)$) using 254 parameters. CCDC reference number: 277322.

[11] Cotter, W. D.; Barbour, L.; McNamara, K. L.; Hechter, R.; Lachicotte, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 11016.

[12] Hughes, R. P.; Williamson, A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2001**, *20*, 4741.

Compound **3** was the only palladium hydrocarbyl complex that displayed any reactivity toward CO_2. Thus, all phenyl complexes were unreactive, presumably due to the stronger σ bond that sp^2-hybridized carbon atoms form with transition metals, as seen for example in the bond distances in Figure 1. It is also clear that the ancillary ligands play a crucial role. Substituting bulky and electron-releasing *tert*-butyl groups on the phosphorus atoms for phenyl groups results in loss of reactivity of the Pd−Me bond. It seems clear that the combination of a fairly weak Pd−C bond and a nucleophilic metal center is crucial for the reaction.

We were interested in incorporating the insertion reaction in some catalytic context and investigated the possibility of re-forming **3** from **6** using various nucleophiles. Obviously MeLi is not interesting, because it undergoes an uncatalyzed reaction with CO_2.[15] Carboxylation of allyl tin reagents has been shown to be catalyzed by palladium complexes,[16] presumably due to the easy insertion into palladium allyl complexes. We therefore investigated the reactivity of **6** (and **2** and **4**) versus various aryl, alkyl, and vinyl tin reagents, but no transmetalation activity was observed. This is in line with the results from our investigation of compounds such as **4** as catalysts in Stille cross-coupling.[17] We then turned our attention to dimethylzinc, which reacts with **6** to form **3** within 3 h at room temperature.

To test this reaction in a catalytic fashion, we reacted an excess of CO_2 with $ZnMe_2$ in dry benzene with a catalyst load of 3−23% (cf. Table 1). The reactivity of dimethylzinc toward CO_2 can be enhanced by stoichiometric amounts of *N*-methylimidazole and other organic nitrogen donors,[18] but in benzene there is no reaction in the absence of catalyst. Only **2**, **3**, and **6** are active catalysts for this transformation, as expected if an insertion−transmetalation cycle is operating. In this case it would be expected that **3** and **6** would display similar reactivities and that these would not be higher than those of any of the stoichiometric reactions. This is also the case. The unexpectedly high activity of compound **2** is somewhat puzzling. Both **2** and **6** undergo transmetalation with $ZnMe_2$ to form **3**, and a possible explanation would be a faster transmetalation of **2** compared to **6** and an even more rapid equilibrium between these two. However, the stoichiometric reactions indicate that the insertion reaction is rate determining and so the reactivity of **3** must somehow be altered. To probe this, we studied the reactivity of **3** toward CO_2 in the presence of 10% **2**, but in the absence of organozinc reagent. Indeed, the methyl peak disappears much faster than in the absence of **2**, but we do not see a corresponding increase of the acetate peak. We do not fully understand this, but it seems to indicate that the fast catalysis by **2** does lie in the insertion step and does not involve any activation of or by the zinc reagents, as observed by Inoue in the activation of Et_2Zn by base.[18] Perhaps the weakly coordinated triflouroacetate is substituted by CO_2, which becomes activated by this and in the presence of a weak Pd−Me bond gives rise to a fast reaction. It seems unlikely, though, that the enhanced reactivity in the catalysis is due to general Lewis acid catalysis by the transition metal, since our results clearly indicate that the activity is very specific; numerous other metal complexes have been tested (cf. Table 1) and none were active in this catalysis. Attempts to fully understand the mechanism for these transformations are underway in our laboratory.

Table 1. Catalytic Carboxylation of $ZnMe_2$ in C_6D_6 with Various Metal Complexes as Catalysts

complex	t/h[b]	cat. / %	amt of $ZnMe_2$/ mmol	T/°C	TON	conversn[c]/ %
2	3	12	0.08	room temp	8	100
3		23	0.05	room temp		no reacn
3	2	19	0.06	100	5	100
6	4	11	0.08	100	7	80
$dppePdCl_2$		8	0.15	90		no reacn
5		6	0.15	90		no reacn
$(PPh_3)_3RhCl$		3	0.20	90		no reacn
(PCP)NiCl[a]		11	0.08	110		no reacn
4		7	0.18	110		no reacn
7		9	0.09	110		no reacn
$Pd(PPh_3)_4$		16	0.05	100		no reacn

[a] Refers to [1,3-bis((di-*tert*-butylphosphino)methyl)benzene]nickel chloride. [b] Reactions left overnight unless stated otherwise. Reaction times not optimized. [c] Determined by ^1H NMR.

In conclusion, we have synthesized a (PCP)PdMe complex that undergoes insertion of CO_2 into the Pd−Me bond. A catalytic reaction has been devised which converts $ZnMe_2$ to $Zn(OAc)_2$ with a (PCP)Pd complex as catalyst.

Acknowledgment. Financial support from the Swedish Research Council, the Crafoord Foundation, the Knut and Alice Wallenberg Foundation, and the Royal Physiographic Society in Lund is gratefully acknowledged. We thank Prof. Janis Louie for helpful discussions.

Supporting Information Available: Text and a table giving full experimental procedures and details of the X-ray crystal structure determination and a CIF file giving crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0505561

---

(13) Crystal data: $C_{26}H_{46}O_2P_2Pd$, $M_r = 558.97$, monoclinic, $a = 21.0355(14)$ Å, $b = 12.5322(7)$ Å, $c = 10.9438(6)$ Å, $V = 2822.5(3)$ Å^3, space group $P2_1/c$, $Z = 4$. A total of 25 559 reflections were measured, 9530 of which were unique ($R_{int} = 0.0477$) and were used in all calculations. The final $R_w(F^2)$ value was 0.0727 (all data), and the $R(F)$ value was 0.0423 ($I > 2\sigma(I)$) using 280 parameters. CCDC reference number: 277323.

(14) Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1477.

(15) Volpin, M. E.; Kolomnikov, I. S. *Organomet. React.* **1975**, *5*, 313.

(16) (a) Franks, R. J.; Nicholas, K. M, *J. Am. Chem. Soc.* **1997**, *119*, 5057. (b) Shi, M.; Nicholas, K. M. *Organometallics* **2000**, *19*, 1458.

(17) Olsson, D.; Nilsson, P.; El Masnaouy, M.; Wendt, O. F. *Dalton Trans.* **2005**, 1924.

(18) Inoue, S.; Yokoo, Y. *J. Organomet. Chem.* **1972**, *39*, 11.

(19) Brandenburg, K. DIAMOND, Program for Molecular Graphics; Crystal Impact, Bonn, Germany, 2000.