J. Am. Chem. Soc. **1994**, *116*, 4999-5000

Direct Approach to Palladium-Mediated Cycloaddition. First Single-Crystal Structure and Convenient Synthesis of Zwitterionic η^3-Trimethylenemethane–Palladium from Nucleophilic Addition of Carbanions to an Allenyl Complex

Chung-Chi Su, Jwu-Ting Chen,* Gene-Hsiang Lee, and
Yu Wang

Department of Chemistry, National Taiwan University
Taipei, Taiwan, 106 Republic of China

Received January 18, 1994

Zwitterionic η^3-trimethylenemethane (TMM) complexes have been considered to be a useful agent for contributing a branched four-carbon building block in organic synthesis and have been proposed as the fleeting intermediates in Pd-mediated cycloaddition reactions.[1] Theoretical and mechanistic studies of such reactions have suggested that such TMM–palladium species are likely in an asymmetric η^3 mode,[2] which exhibits distinguishable chemistry from the much better-studied η^4-TMM complexes.[3] Trost et al. have been elaborating to design a variety of organic bifunctional conjunctive reagents, reacting with Pd(0) to provide η^3-TMM–palladium complexes in situ. However, a well-characterized example of such important organometallic species is still lacking, since the salient development of its chemistry over one decade. We have recently discovered that the unsubstituted allenyl and propargyl complexes are remarkably susceptible to nucleophilic addition at the central carbon of their organic ligands, peculiarly by soft carbonucleophiles. Therefore, it opens a feasible avenue for the preparation of the η^3-TMM and η^3-allyl complexes.[4] Wojcicki obtained a η^3-TMM derivative of platinum essentially by the same synthetic strategy, but did not report its reactivity toward cycloaddition.[5] Herein, we report a convenient synthesis and the first structural confirmation of the novel η^3-TMM–palladium complexes that afford direct evidence of a stoichiometric approach to Pd-mediated [3 + 2] cycloaddition.

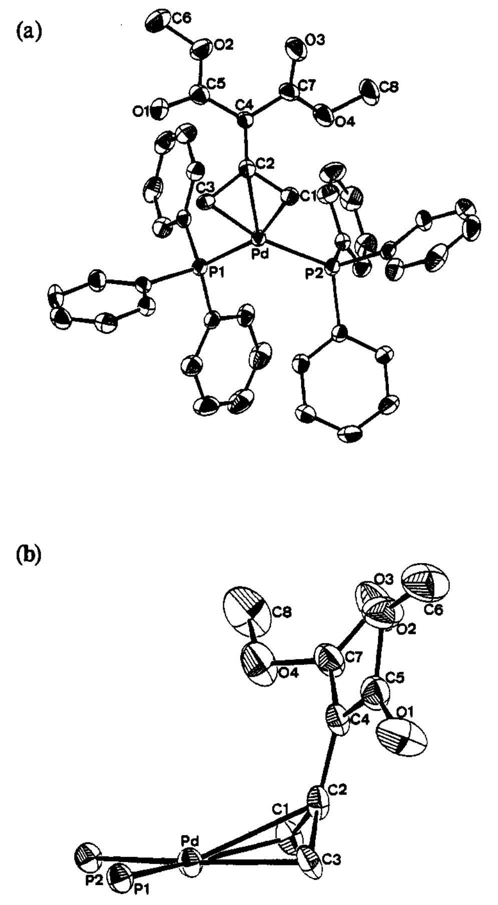


Figure 1. ORTEP drawing of complex **2a**: (a) top view (all hydrogen atoms are omitted for clarity); (b) side view (the phosphino phenyl groups and all hydrogen atoms are omitted for clarity).

Synthesis of zwitterionic η^3-TMM complexes is conducted by ready nucleophilic addition of carbanion to the metal–allenyl complexes. The reactions of *trans*-Pd(η^1-CHCCH$_2$)(Br)(PPh$_3$)$_2$ (**1**) with an equimolar amount of Na[CH(X)(Y)] in dry CH_2Cl_2 at 25 °C generate Pd(η^3-CH$_2$C(CXY)CH$_2$)(PPh$_3$)$_2$ (X = Y = CO$_2$Me (**2a**); X = CO$_2$Me, Y = SO$_2$Ph (**2b**)).[6] In the ^{1}H-coupled ^{13}C NMR spectrum of **2a**, two singlets at δ 81.6 and 149.9 belong to the quaternary carbons. The downfield resonance, which suggests possible bond interaction with the metal, is assigned to the central carbon of the η^3-TMM.[7] The high-field resonance agrees with the data of the corresponding carbanionic carbon in its Pt analogue and evidences the zwitterionic character of **2a**.[5] The two terminal metal-bound carbons are located at δ 66.7 as a triplet with J_{C-H} = 156.4 Hz which suggests that the hybridization at these carbons is intermediate between sp^2 and sp^3, in support of the TMM characteristic. Providing additional spectral evidence for the η^3 structure are the separated ^{1}H NMR resonances for the syn and anti hydrogens, appearing at δ 4.38 and 2.64, respectively. The NMR data of **2b** show the equivalency of the phosphino and terminal methylene groups even at −50 °C, indicating that such a η^3-TMM might be close to an allyl group and able to freely rotate along the C=C bond.[4]

The X-ray analysis unequivocally confirms the structure of **2a**.[8] Its ORTEP drawing is shown in Figure 1. The most characteristic features of this TMM complex are as follows: (1) the three C–C bond distances (<1.45 Å) indicate substantial π-delocalization on the TMM moiety, and (2) palladium is only bonded to three TMM carbons with $D(\text{Pd–C}_{\text{terminal}})$ = 2.143(7), 2.170(7) Å and $D(\text{Pd–C}_{\text{central}})$ = 2.324(6) Å. These data are

---

(1) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6432; **1981**, *103*, 5972; **1983**, *105*, 2315. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (c) Trost, B. M. *Pure Appl. Chem.* **1988**, *60*, 1615. (d) Trost, B. M.; King, S. A.; Schmidt, J. *J. Am. Chem. Soc.* **1989**, *111*, 5902. (e) Trost, B. M.; King, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 408. (f) Trost, B. M.; Marrs, C. H. *J. Am. Chem. Soc.* **1993**, *115*, 6636.

(2) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1980**, *102*, 6359. (b) Gordon, D. J.; Fenske, R. F.; Nanninga, T. N.; Trost, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 5974. (c) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2326.

(3) (a) Almenningen, A.; Haaland, A.; Wahl, K. *Acta Chem. Scand.* **1969**, *23*, 1145. (b) Allen, S. R.; Barnes, S. G.; Green, M.; Moran, G.; Murrall, N. W.; Welch, A. J.; Sharaiha, D. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1157, 1175. (c) Churchill, M. R.; Gold, K. *Inorg. Chem.* **1969**, *8*, 401. (d) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1973**, *12*, 525. (e) Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* **1989**, *27*, 279. (f) Yang, G.-M.; Su, G.-M.; Liu, R.-S. *Organometallics* **1992**, *11*, 3444. (g) Wu, I.-Y.; Cheng M.-C.; Lin, Y.-C.; Wang, Y. *Organometallics* **1993**, *12*, 1686.

(4) (a) Chen, J.-T.; Huang, T.-M.; Cheng, M.-C.; , Lin, Y.-C.; Wang, Y. *Organometallics* **1992**, *11*, 1761. (b) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170.

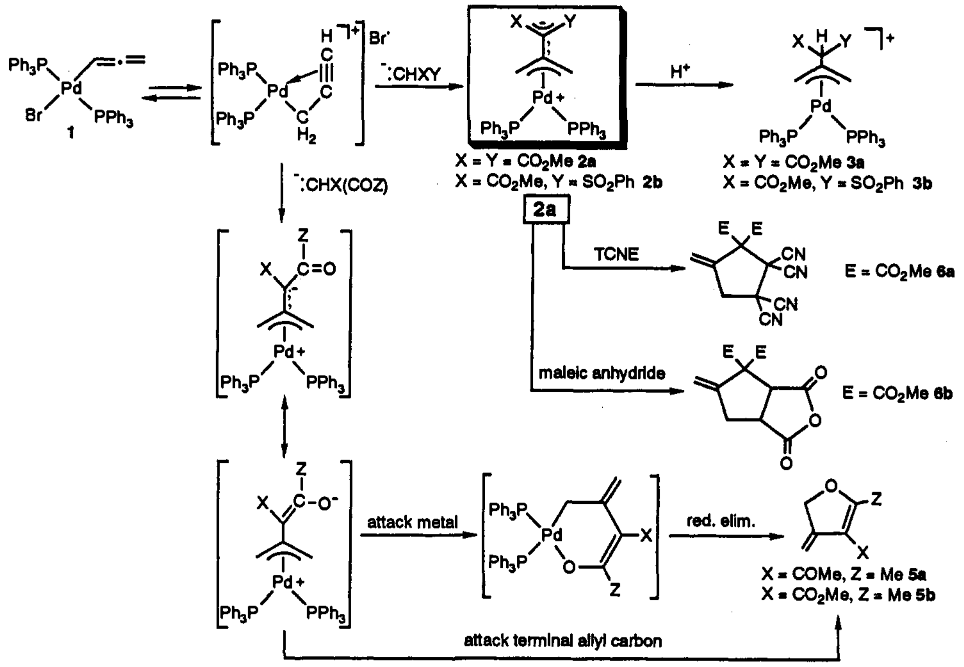
(5) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993.

(6) The reaction of 0.59 g (0.79 mmol) of **1** with equimolar Na[CH(CO$_2$Me)$_2$] in degassed CH_2Cl_2 at 25 °C generated **2a** in 82% isolated yields. Selected spectral data: IR (KBr pellet) ν_{CO} 1694, 1637 cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 27.2 (s); ^{1}H NMR (CDCl$_3$) δ 4.38 (2H, d, J_{H-P} = 2.4 Hz, H$_{syn}$), 3.44 (6H, s, CO$_2$CH_3), 2.64 (2H, ddd, J_{H-H} = 2.7, 2.7 Hz, J_{H-P} = 10.2 Hz, H$_{anti}$); ^{13}C NMR (CDCl$_3$) δ 170.4 (q, J_{C-H} = 3.8 Hz, CO$_2$Me), 149.9 (t, J_{C-P} = 4.3 Hz, H$_2$CC), 81.6 (s, C(CO$_2$Me)$_2$), 66.7 (m, J_{C-H} = 156.4 Hz, CCH$_2$), 49.9 (q, J_{C-H} = 145.0 Hz, CO$_2$$CH_3$); FAB MS (*m*/*z*) 800 (M$^+$). Anal. Calcd for $PdC_{44}H_{40}O_4P_2 \cdot CH_2Cl_2$: C, 61.00; H, 4.78. Found: C, 61.18; H, 4.72. For **2b**: IR (KBr pellet) ν_{CO} 1642, ν_{SO} 1383, 1135 cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 27.1 (s); ^{1}H NMR (CDCl$_3$) δ 4.59 (2H, d, J_{H-P} = 2.1 Hz, H$_{syn}$), 3.30 (3H, s, CO$_2$CH_3), 2.63 (2H, ddd, J_{H-H} = 2.4, 3.1 Hz, J_{H-P} = 10.1 Hz, H$_{anti}$); ^{13}C NMR (CDCl$_3$) δ 166.6 (s, CO$_2$Me) , 147.0 (t, J_{C-P} = 4.8 Hz, H$_2$CC), 87.5 (s, C(CO$_2$Me)$_2$), 66.4 (m with C–P virtual coupling, CCH$_2$), 49.4 (s, CO$_2$$CH_3$); FAB MS (*m*/*z*) 882 (M$^+$). Anal. Calcd for $PdC_{48}H_{42}SO_4P_2 \cdot CH_2Cl_2$: C, 60.79; H, 4.58. Found: C, 60.89; H, 4.55.

(7) Carfagna, C.; Galarini, R.; Linn, K.; Løpez, J. A.; Mealli, C.; Musco, A. *Organometallics* **1993**, *12*, 3019.

0002-7863/94/1516-4999$04.50/0

Scheme 1



quite comparable to those of the platinum analogue.[11] The dihedral angle between the C1–C2–C3 and C1–Pd–C2 planes is 62.5(1)°, which falls in the boundary region between those of the hetero-η^3-TMM and of the β-substituted allyl complexes[4,9] and is in agreement with the NMR results. The fourth carbon atom of η^3-TMM, which is 3.38(6) Å distant from Pd, does not show any bonding interaction with the metal. The central TMM carbon C2 is slightly out of the C1–C3–C4 plane (0.8(1) Å in the opposite direction from Pd). The palladium and the four donor atoms are disposed in a distorted square plane with Pd slightly out of the plane at a distance of 0.043(3) Å, ∠P1–Pd–P2 and ∠C1–Pd–C3 being 104.25(7)° and 65.3(3)°, respectively. The β-diketonate moiety on TMM also shows π-electron delocalization.

The zwitterionic character of **2a** and **2b** is also supported by their chemical reactivity. Protonation of **2a** and **2b** with HBF_4 leads to the cationic β-substituted η^3-allyl complexes $[Pd(\eta^3\text{-}(CH_2)_2CCH(X)(Y))(PPh_3)_2](BF_4)$ (X = Y = CO_2Me (**3a**); X = CO_2Me, Y = SO_2Ph (**3b**)). When $Na[CH(COMe)_2]$ or $Na[CH(COMe)(CO_2Me)]$ was allowed to react with **1**, hydrofuran derivative **5a** or **5b** resulted (Scheme 1). Such results afford direct evidence that the η^3-TMM palladium is likely a crucial intermediate in the Pd-catalyzed reactions of propargyl carbonates with carbonucleophiles.[10] A plausible mechanism is preceded by addition of carbonucleophile to the σ-allenyl complex, forming the η^3-TMM–palladium species. Subsequent intramolecular cyclization between the enol oxygen and a terminal allyl carbon accomplishes furan formation. Another possible pathway for the ring closure might be coordination of the carbonyl oxygen to metal, followed by reductive elimination to construct the C–O bond. In addition, complex **2a** is readily coupled with an electron-deficient olefin such as tetracyanoethylene (TCNE) or maleic anhydride (MA) to form cyclopentanoids **6a** and **6b**, providing the first direct stoichiometric examples of palladium-mediated [3 + 2] cycloaddition. These two specific cases were not obtained by the catalytic process; since TCNE and MA are such good π-acceptors, they may react with Pd(0) before formation of the TMM intermediate.

In viewing that *trans*-$Pt(\eta^1\text{-}CHCCH_2)(Br)(PPh_3)_2$ is not reactive, whereas $[Pt(\eta^3\text{-}CHCCH_2)(PPh_3)_2]^+$ is highly reactive to carbanions under the same conditions,[12] the Pd–TMM complexes are likely formed via nucleophilic addition of $^-$:CHXY to a η^3-propargyl species which may be the result of release of a ligand from **1**. The synthetic route to the η^3-TMM complexes from the reactions of carbanions and allenyl (and/or propargyl) complexes is feasible. It allows introduction of substituents to the TMM ligand and eventually to the cyclopentanoids. The electron-withdrawing substituents that we used are certainly crucial for the stabilization of such η^3-TMM complexes. Investigations of the variation of carbanions for preparing the η^3-TMM complexes and the reactivity of such η^3-TMM complexes are in progress.

Acknowledgment. We are grateful to the National Science Council, Taipei, Taiwan, ROC, for their financial support.

Supplementary Material Available: Experimental data and an ORTEP drawing, complete crystal data, bond distances and angles, atomic coordinates, and thermal parameters of **2a** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[8] Crystal data of **2a**: $C_{44}H_{40}P_2O_4Pd{\cdot}CHCl_3$, FW = 920.52 $P\bar{1}$, a = 11.336(2) Å, b = 13.077(4) Å, c = 16.800(8) Å, α = 86.10(3)°, β = 71.24(3)°, γ = 65.81(3)°, V = 2145(1) Å^3, Mo Kα radiation λ = 0.7107 Å, Z = 2, μ = 7.279 cm^{-1}, 5619 total reflections, 4433 observed reflections ($I > 2.0\sigma(I)$), R = 0.049, R_w = 0.049. Selected bond distances (Å) and angles (deg): Pd–P1 = 2.336(2), Pd–P2 = 2.317(2), Pd–C1 = 2.143(7), Pd–C2 = 2.324(6), Pd–C3 = 2.170(7), C1–C2 = 1.42(1), C2–C3 = 1.45(1), C2–C4 = 1.42(1), C4–C5 = 1.43(1), C4–C7 = 1.45(1); P1–Pd–P2 = 104.25(7), C1–Pd–C3 = 65.3(3), C1–C2–C3 = 108.5(6).

[9] (a) Jones, M. D.; Kemmit, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279 (b) Fawcett, J.; Henderson, W.; Jones, M. D.; Kemmit, R. D.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, *8*, 1991 and references therein.

[10] (a) Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. (b) Tsuji, J.; Shimizu, I.; Ohashi, Y. *Tetrahedron Lett.* **1984**, *25*, 5183.

[11] Wojcicki and associates, in addition to having prepared a platinum complex similar to **2a**, more recently, also have determined its structure. The platinum analogue is, however, less reactive than **2a** toward cycloaddition.

[12] Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. Submitted for publication.