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Reactivity of an early-late heterobimetallic complex toward phosphines: synthesis, structure, and reactivity of a cationic tantalum-palladium compound with a free cyclopentadienyl counteranion

Matthew D. Butts, and Robert G. Bergman

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Reactivity of an Early–Late Heterobimetallic Complex toward Phosphines: Synthesis, Structure, and Reactivity of a Cationic Tantalum–Palladium Compound with a Free Cyclopentadienyl Counteranion

Matthew D. Butts and Robert G. Bergman*

Department of Chemistry, University of California, Berkeley, California 94720

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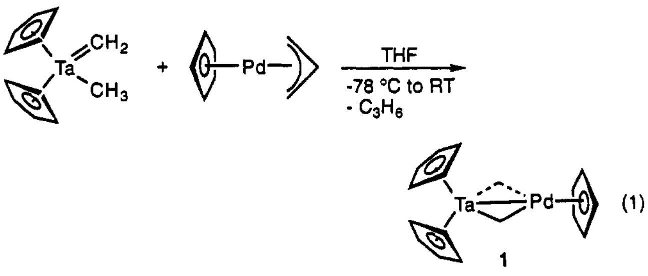
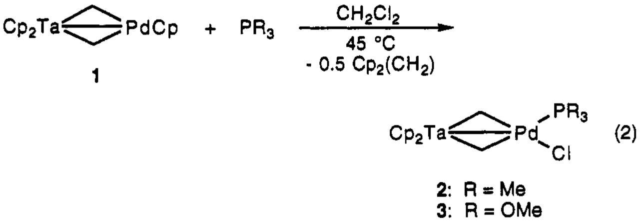
Summary: Treatment of $Cp_2Ta(CH_2)(CH_3)$ with $CpPd(C_3H_5)$ led to $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1). Reaction of 1 with 1 equiv of either PMe_3 or $P(OMe)_3$ in CH_2Cl_2 resulted in the formation of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(PR_3)(Cl)$ (R = Me, 2; R = OMe, 3) and 0.5 equiv of $Cp_2(CH_2)$. The reaction of 1 with 2 equiv of PMe_3 or $P(OMe)_3$ or 1 equiv of $Me_2P(CH_2)_2PMe_2$ (DMPE) led to the isolation of $[Cp_2Ta(\mu\text{-}CH_2)_2PdL_2]Cl$ (L_2 = 2 PMe_3, 4; L_2 = 2 $P(OMe)_3$, 5; L_2 = DMPE, 6). Addition of $P(OMe)_3$ to 1 in CH_3CN gave the product $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(CH_2CN)$ (7). Each of these reactions of 1 with phosphorus compounds implicates the intermediacy of free cyclopentadienyl anion. In support of this hypothesis, the stable naked Cp complex $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (8) was isolated from the reaction of 1 with DMPE in CH_3CN and was characterized by X-ray crystallography. The shortest distance between the free anionic Cp group and the bimetallic fragment in 8 is 3.46(3) Å. Addition of $FeCl_2$ to 8 resulted in the formation of $^1/_2$ equiv of Cp_2Fe and 6. Treatment of 8 with 1,2-dibromoethane led to the quantitative formation of $^1/_2$ equiv of spiro[2.4]hepta-4,6-diene together with the bromide salt of 8.

Many transition-metal cyclopentadienyl (η^5-C_5H_5; Cp) complexes undergo loss of the Cp ligand when treated with certain reagents.[1-5] In a small number of cases, products in which the extruded Cp (and in one related case, indenyl) ligand remains associated with the metal center as an unbound naked cyclopentadienyl anion[6] have been isolated and characterized by X-ray diffraction.[7-10] In many cases, however, the fate of the lost ring is unknown.[11-13] Furthermore, there appears to be no system in which the inherent reactivity of the free cyclopentadienyl ligand has been studied. In this paper we report (a) the nucleophile-induced extrusion of a cyclopentadienyl ligand from an early–late heterobimetallic transition-metal complex, (b) the isolation and full characterization of the product of one of these reactions as a heterobimetallic complex with an unbound cyclopentadienide counterion, and (c) the reactivity of this transition-metal cyclopentadienide salt with a number of electrophilic reagents.

Allowing $Cp_2Ta(CH_2)(CH_3)$[14] and $CpPd(\eta^3\text{-}C_3H_5)$[15] to react at −78 °C in THF with slow warming to room temperature resulted in the formation of $Cp_2Ta(\mu\text{-}CH_2)_2$-PdCp (1)[16] with loss of 1 equiv of propylene (eq 1).



Complex 1 was isolated in 70% yield as an orange crystalline solid from CH_2Cl_2 at −35 °C.[17] Reaction of 1 with 1 equiv of either PMe_3 or $P(OMe)_3$ at 45 °C in CH_2Cl_2 resulted in displacement of the Cp ring[3,18,19] and formation of **2** (R = Me) and **3** (R = OMe) (eq 2).



Complexes **2** and **3** were isolated in 85% and 66% yield, respectively, as white crystalline solids; NMR spectroscopic data indicate that the geometry at Pd is square planar in both complexes.[20] The coproduct in these reactions was $^1/_2$ equiv of $Cp_2(CH_2)$, identified by gas chromatography

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(1) Werner, H. *J. Organomet. Chem.* **1980**, *200*, 335.

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(5) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870.

(6) Such free cyclopentadienide groups have been referred to earlier (see, e.g., ref 7) as "η^0-Cp" ligands. We have avoided this nomenclature in response to the strenuous objections of a reviewer.

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(8) Lilga, M. A.; Sohn, Y. S.; Ibers, J. A. *Organometallics* **1986**, *5*, 766.

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(13) Roth, S.; Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1990**, *29*, 3345.

(14) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(15) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1991**, *28*, 343.

(16) ^1H NMR (CD_2Cl_2, 400 MHz): δ 6.24 (s, 4H, CH_2), 5.66 (s, 5H, PdCp), 5.19 (s, 10H, TaCp). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 118.1 (s, CH_2), 97.4 (s, Cp), 95.9 (s, Cp).

(17) Satisfactory elemental analyses have been obtained on all organometallic complexes described here except for 7.

(18) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1502.

(19) Werner, H.; Küln, A.; Tune, D. *J. Chem. Ber.* **1977**, *110*, 1763.

(20) NMR spectroscopic data for **2**: ^1H NMR (CD_2Cl_2, 400 MHz) δ 7.19 (d, J = 8.7 Hz, 2H, CH_2), 5.36 (s, 10H, Cp), 5.19 (d, J = 5.1 Hz, 2H, CH_2), 1.42 (d, J = 8.3 Hz, 9H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz) δ 159.6 (d, J = 45.9, CH_2), 118.8 (s, CH_2), 98.6 (s, Cp), 16.0 (d, J = 22.4, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz) δ −16.8 (s).

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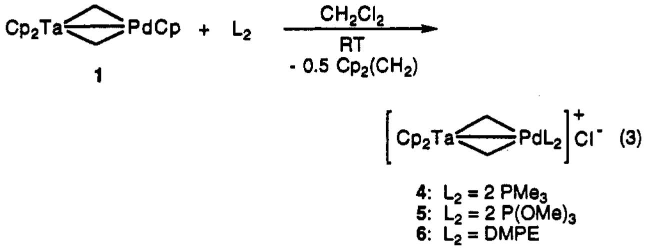
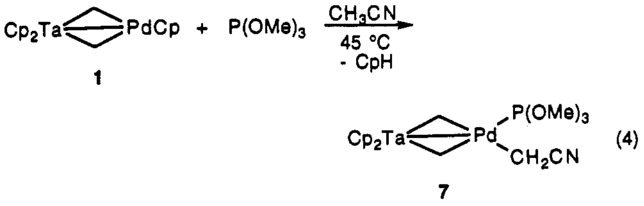
and GCMS as compared to an authentic sample.[21,22] The fact that this material had been prepared earlier by treatment of methylene chloride with sodium cyclopentadienide[22] suggested strongly that the ring is extruded from 1 as $[C_5H_5]^-$.

Monitoring the course of the reaction of 1 and 1 equiv of PMe_3 by ^1H NMR spectroscopy indicated that the first observable step is the formation of the bis(phosphine) adduct $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)_2]Cl$ (see below), which occurred quickly at room temperature. This complex was slowly consumed as the remaining half of 1 reacted, with the overall result being the formation of 1 equiv of **2**. The same type of reactivity was observed for the reaction of 1 and $P(OMe)_3$, forming **3**. Treatment of 1 with 2 equiv of phosphine or phosphite or 1 equiv of $Me_2P(CH_2)_2PMe_2$ (DMPE) led, as expected, to complexes **4**–**6** (eq 3).



Complex **6** was characterized by X-ray crystallography;[23] an ORTEP diagram of the cation portion is shown in Figure 1.[24–27] The chloride counterion is noncoordinating in the solid state, a feature which is also true of the solution structure, as determined by NMR spectroscopy.[28] In agreement with this observation, complex **6** was found in conductivity studies to be a 1:1 electrolyte in CH_3CN. In each of the reactions illustrated in eq 3, the Pd-bound Cp in 1 reacted with solvent to produce 0.5 equiv of $Cp_2(CH_2)$; no intermediates were observed.

Further evidence for the elimination of $[C_5H_5]^-$ from 1 is provided by the reaction of 1 with phosphorus compounds in acetonitrile. For example, complex **7** is formed in the reaction of $P(OMe)_3$ with 1 in CH_3CN at 45 °C (eq 4).[29] Although this is a fairly clean reaction (approximately 90% NMR yield), separation from side products is exceedingly difficult, and **7** could be isolated in only 3% yield as a pure (>97%) compound. It is possible, though, to synthesize **7** independently by treating **3** with $NaCH_2CN$ in CH_3CN at room temperature. We conclude that in reaction 4 $[C_5H_5]^-$ is again expelled and abstracts a proton from acetonitrile to generate $[CH_2CN]^-$. Even though the cyanomethide ion is undoubtedly generated reversibly in low concentration (in view of the relative pK_a's of cyclopentadiene and acetonitrile), apparently it can be trapped rapidly by an unsaturated cationic palladium center.[30] As in the reactions of 1 with monodentate phosphines in CH_2Cl_2, the first step in the reaction of 1 and $P(OMe)_3$ at room temperature is the immediate formation of $^1/_2$ equiv of a bis(phosphine) adduct. The ^1H and ^{13}C NMR spectra of this intermediate are consistent with the formulation $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)_2]Cp$.[31]



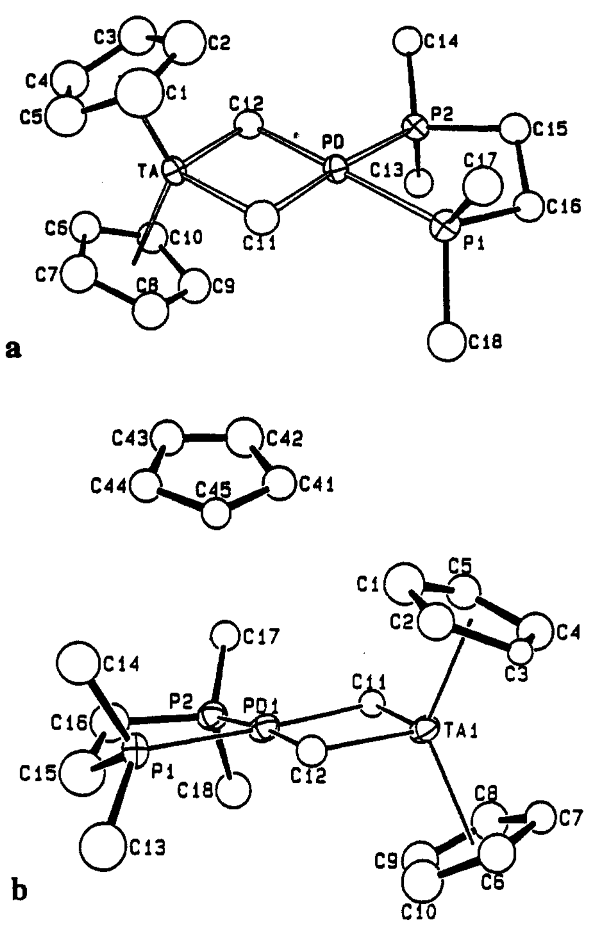


Figure 1. (a) ORTEP diagram of the cation portion of **6**. Selected bond distances (Å) and bond angles (deg): Ta–Pd, 2.832(1); Ta–CH_2, 2.136(8), 2.145(9); Pd–CH_2, 2.152(8), 2.130(9); Ta–CH_2–Pd, 82.7(3), 83.0(3); CH_2–Ta–CH_2, 97.1(3); CH_2–Pd–CH_2, 97.1(3). (b) ORTEP diagram of **8**. The bond distances and angles of the cation are identical with those of **6** within experimental error.

Because the above results implicate the intermediacy of complexes containing free cyclopentadienyl anions, an isolable analogue was sought by treating 1 with DMPE in CH_3CN at room temperature. Pale orange crystals of the

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(21) Katz, T. J.; Acton, N.; Martin, G. *J. Am. Chem. Soc.* **1973**, *95*, 2934.

(22) Bryndza, H. Ph.D. Thesis, University of California, Berkeley, CA, 1981.

(23) Crystal parameters for **6** at −103 °C: monoclinic, $P2_1/c$, a = 11.130(1) Å, b = 20.230(2) Å, c = 11.726(2) Å, V = 2370.8(10) Å^3, Z = 4, d(calc) = 1.88 g cm^{-3}, R = 3.4%, R_W = 4.8%.

(24) Jacobsen, E. N.; Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3706.

(25) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4853.

(26) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *Inorg. Chim. Acta* **1992**, *198–200*, 377.

(27) Butts, M. D.; Bergman, R. G. Manuscript in preparation.

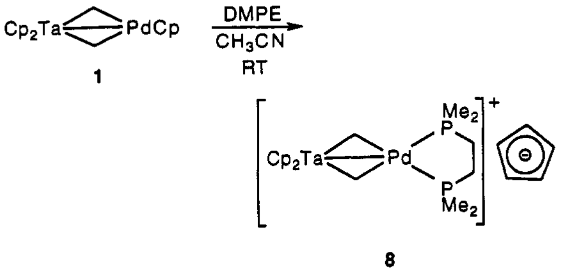
(28) See the supplementary material.

(29) ^1H NMR (C_6D_6, 400 MHz): δ 6.47 (d, J = 11.3 Hz, 2H, CH_2), 5.68 (d, J = 3.6 Hz, 2H, CH_2), 4.69 (s, 10H, Cp), 3.40 (d, J = 12.0 Hz, 9H, CH_3), 2.04 (d, J = 9.5 Hz, 2H, CH_2CN). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz): δ 141.8 (d, J = 6.8 Hz, CH_2 bridge), 130.2 (s, CN), 125.6 (s, CH_2 bridge), 98.1 (s, Cp), 50.8 (d, J = 1.3 Hz, CH_3), −9.9 (d, J = 14.0 Hz, $\mathit{CH_2}$CN). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 52.0 (s).

(30) It appears that a reactive solvent, such as CH_2Cl_2 or CH_3CN, is required to obtain stable products in the reactions of 1 with phosphines. Reactions performed in tetrahydrofuran were not clean and provided no evidence for intermediates containing free cyclopentadienide ions.

(31) ^1H NMR (CD_3CN, 300 MHz, 25 °C): δ 6.27 (m, 4H, CH_2 bridge), 5.48 (s, 5H, Cp), 5.44 (s, 10H, Cp), 3.60 (m, 18H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz): δ 28.3 (s).

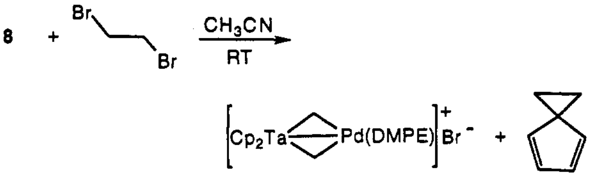
anionic Cp complex 8 were isolated directly from the reaction mixture by diethyl ether diffusion at room temperature in 85% yield (eq 5).[32] The structure of 8 was confirmed in an X-ray crystallographic study (Figure 1).[33] The unit cell contains two molecules. The shortest distance between the cyclopentadienide counterion and the bimetallic fragment is 3.46(3) Å.[34] The average C–C distance in the planar displaced Cp ligand of 1.41(3) Å is in agreement with data previously observed.[7-10] The bonding distances in the bimetallic cation are identical to those in the chloride salt 6. Likewise, the ^1H, ^{13}C, and ^{31}P NMR spectra of the bimetallic portion of 8 in CD_3CN are identical with those of 6, indicating that the cyclopentadienide remains noncoordinating in solution.



(5)

The reactivity of 8 is consistent with the intervention of free Cp complexes in the reactions discussed above. First, the unbound Cp ligand undergoes slow deuterium exchange with CD_3CN solvent over several hours at room temperature, as seen in the disappearance of the cyclopentadienide resonance in the ^1H NMR spectrum and the appearance of a corresponding signal in the ^2H NMR spectrum. This supports the existence of an endothermic, but operable, proton-transfer equilibrium between the $[C_5H_5]^-$ group and CH_3CN. It is also possible to carry out stoichiometric reactions between the transition-metal cyclopentadienide complexes and added electrophiles that are strongly reminiscent of those observed earlier with sodium cyclopentadienide. Thus, addition of $FeCl_2$ to 8 in acetonitrile resulted in the immediate formation of $^1/_2$ equiv of Cp_2Fe (eq 6), which was isolated in 80% yield by sublimation.[35] Treatment of 8 with 1,2-dibromoethane at room temperature led to the quantitative formation of $^1/_2$ equiv of spiro[2.4]hepta-4,6-diene over the course of several hours (2 equiv of Cp^- is required to form the product) by ^1H NMR spectroscopy (eq 7). The organic product was identified by ^1H NMR spectroscopy, GC, and GCMS as compared to an authentic sample.[36] In both reactions the halide salt of the bimetallic cation is formed, although the bromide salt was not fully characterized.

$$8 + FeCl_2 \xrightarrow[RT]{CH_3CN} 6 + Cp_2Fe \qquad (6)$$



(7)

In conclusion, an early–late heterobimetallic complex has been prepared which undergoes Cp loss at palladium upon reaction with phosphines, in one case to form a unique example of an early–late cationic heterobimetallic complex containing a free cyclopentadienyl counteranion (8). An interesting aspect of the behavior of 8 is that essentially all of its chemistry is focused at the counterion rather than at either of the metal centers.[37] It is presumably the electron richness of the palladium center of 1, formally an 18-electron complex, that makes Cp loss a facile process upon phosphine addition, despite the potential for the Pd to back-donate electron density to the Ta center.

Acknowledgments. We are grateful for support of this work from the National Science Foundation (Grant No. CHE-9113261). We thank Dr. F. J. Hollander, director of the UC Berkeley X-ray diffraction facility (CHEXRAY), for solving the crystal structures of 6 and 8.

Supplementary Material Available: Spectroscopic and analytical data for complexes 1–8 and X-ray diffraction data (ORTEP diagrams and tables of crystal and data collection parameters, positional and anisotropic thermal parameters, and intramolecular distances and angles) for 6 and 8 (13 pages). This material is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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(32) ^1H NMR (CD_3CN, 400 MHz): δ 5.91 (m, 4H, μ-CH_2), 5.48 (s, 5H, Cp anion), 5.31 (s, 10H, Cp), 1.94 (d, J = 16.9 Hz, 4H, DMPE CH_2), 1.53 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 101 MHz): δ 130.1 (m, μ-CH_2), 104.2 (s, Cp anion), 99.7 (s, Cp), 14.2 (m, DMPE CH_2), 28.9 (dd, J = 23.8, 22.6 Hz, CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN, 162 MHz): δ 28.3 (s).

(33) Crystal parameters for 8 at −118 °C: triclinic, $P\bar{1}$, a = 10.451(3) Å, b = 14.619(3) Å, c = 16.308(4) Å, V = 2318.9(13) $Å^3$, Z = 4, d(calc) = 1.89 g cm^{-3}, R = 5.4%, R_W = 6.9%. An incomplete data set was collected due to interruption of the data set and loss of crystal orientation.

(34) This distance refers to that between the Cp ring and a methyl carbon of the DMPE ligand.

(35) Wilkinson, G. *Org. Synth.* **1956**, *36*, 31.

(36) This compound was prepared by treating NaCp with 1,2-dibromoethane: Wilcox, C. F., Jr.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 3866.

(37) This is in contrast to the behavior of $[Ir(DPPE)_2]Cp$.[8]