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

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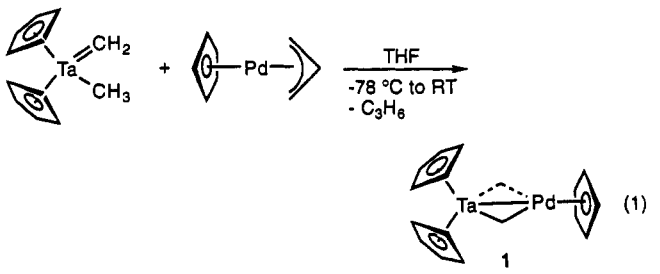
Summary: Treatment of $Cp_2Ta(CH_2)(CH_3)$ with $CpPd(C_3H_5)$ led to $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1). Reaction of 1 with 1 equiv of either PMe_3 or $P(OMe)_3$ in CH_2Cl_2 resulted in the formation of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(PR_3)(Cl)$ (R = Me, 2; R = OMe, 3) and 0.5 equiv of $Cp_2(CH_2)$. The 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.

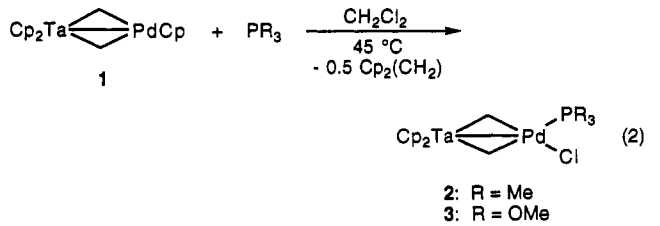
Allowing $Cp_2Ta(CH_2)(CH_3)$[14] and $CpPd(\eta^3\text{-}C_3H_5)$[15] to react at −78 °C in THF with slow warming to room temperature resulted in the formation of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1)[16] with loss of 1 equiv of propylene (eq 1).



(1)

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).



1

(2)

2: R = Me
3: R = OMe

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.
(2) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155.
(3) Anderson, G. K.; Cross, R. J.; Fallis, S.; Rocamora, M. *Organometallics* **1987**, *6*, 1440.
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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.
(7) Casey, C. P.; O'Conner, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241.
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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) ^{1}H 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.; Kühn, A.; Tune, D. *J. Chem. Ber.* **1977**, *110*, 1763.
(20) NMR spectroscopic data for 2: ^{1}H 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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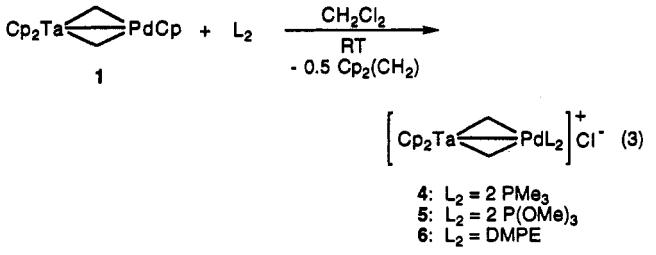
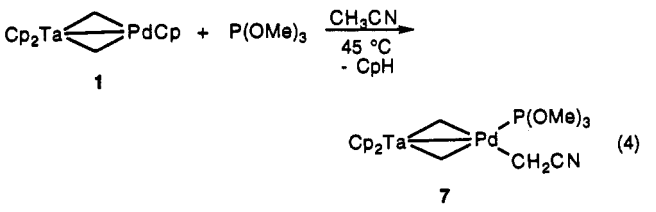
and GCMS as compared to an authentic sample.[21,22] The fact that this material had been prepared earlier by treatment of methylene chloride with sodium cyclopentadienide[22] suggested strongly that the ring is extruded from **1** as $[C_5H_5]^-$.

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



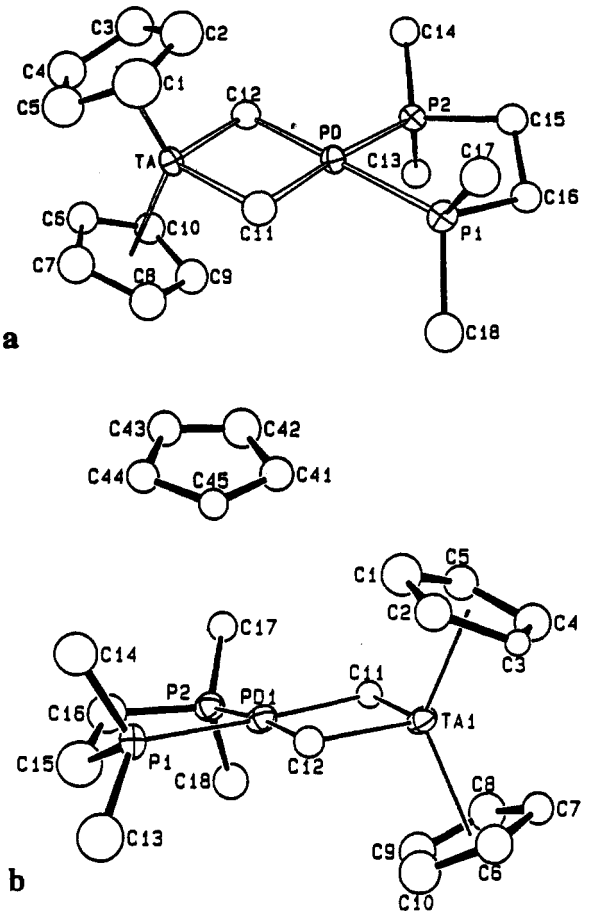


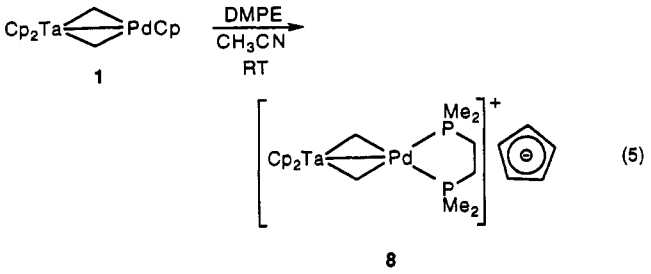
Figure 1. (a) ORTEP diagram of the cation portion of **6**. Selected bond distances (Å) and bond angles (deg): Ta–Pd, 2.832(1); Ta–CH_2, 2.136(8), 2.145(9); Pd–CH_2, 2.152(8), 2.130(9); Ta–CH_2–Pd, 82.7(3), 83.0(3); CH_2–Ta–CH_2, 97.1(3); CH_2–Pd–CH_2, 97.1(3). (b) ORTEP diagram of **8**. The bond distances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

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]

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

(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, CH_2CN). $^{31}P\{^1H\}$ 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).

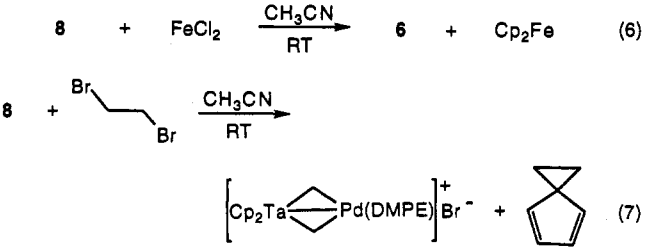
anionic Cp complex 8 were isolated directly from the reaction mixture by diethyl ether diffusion at room temperature in 85% yield (eq 5).[32] The structure of 8 was



(5)

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.

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



(6)

(7)

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.

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.

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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]