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Mechanistic Investigations of Cp-Loss Reactions in an Early–Late Heterobimetallic Complex. Isolation of a Cationic Tantalum–Palladium Compound with a Free Cyclopentadienyl Counteranion

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This paper reports the synthesis of the early–late heterobimetallic complex $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1) and its reactivity with phosphines, including the preparation, structural characterization, and reactivity of a Ta–Pd cationic complex bearing a naked cyclopentadienyl counteranion. Complex 1 was prepared by the reaction of $Cp_2Ta(CH_2)(CH_3)$ with $CpPd(C_3H_5)$. Treatment 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 $Cp_2(CH_2)$. Mechanistic studies indicated that the first step in these transformations is the formation of the respective bis(phosphine) adducts $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(PR_3)_2]Cl$. 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**). Complex **6** was characterized by X-ray crystallography. 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**), which again proceeded through a bis(phosphite) adduct. Each of these reactions of 1 with phosphorus compounds implicates the presence of intermediates bearing a free cyclopentadienide ligand. The 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 anionic Cp and the bimetallic fragment is 3.46(3) Å; the bonding distances in the bimetallic cation are identical with those of **6**. The free Cp anion in **8** undergoes slow deuterium exchange with CD_3CN solvent. Reactions of **8** with electrophilic reagents are similar to those observed for sodium cyclopentadienide. Thus, the 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**.

Introduction

The strength of the metal–cyclopentadienyl (η^5-C_5H_5; Cp) interaction is a practical feature of organometallic Cp complexes that has allowed the extensive study of the chemistry of such compounds. Many Cp transition-metal complexes, however, undergo loss of the Cp ligand when treated with certain reagents.[1-5] While in most cases the fate of the lost ring is unknown,[6-9] there have been reports of 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. Some of these complexes have been isolated and characterized by X-ray diffraction.[10-13] The first example of this class of com-pounds was reported by Casey in 1985. The addition of excess PMe_3 to $CpRe(Me)(NO)(CO)$ resulted in the formation of the isolable, although thermally unstable, $[MeRe(NO)(PMe_3)_4]Cp$.[10] The addition of phosphines to η^5-Cp compounds has been the most common route to isolated complexes containing a cyclopentadienyl counterion,[14] although the reaction of cationic metal complexes with LiCp has also led to such species.[11]

This paper describes the nucleophile-induced extrusion of a cyclopentadienyl ligand from the early–late heterobimetallic (ELHB) complex $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (**1**) under various reaction conditions and a study of the mechanism of Cp loss involved. The product of one of the reactions in this study was isolated as a heterobimetallic complex with an unbound cyclopentadienide counterion, which was characterized by X-ray crystallography. As there appears to be no transition-metal cyclopentadienide salt in which the inherent reactivity of the free Cp^- ligand has been studied, the reactivity of this complex with a number of electrophilic reagents was investigated. A preliminary account of this work has been published.[15]

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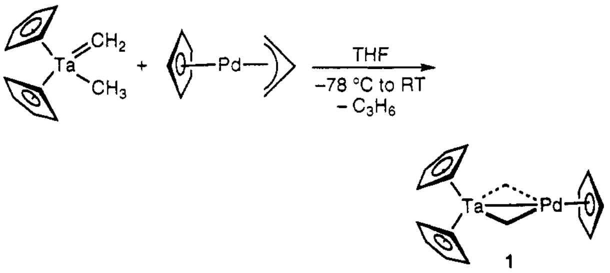
Results

Synthesis of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1). Our recent development of a generalized route to ELHB complexes joining tantalum and various late metals through methylene bridges[16-18] was successfully extended to the synthesis of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1). Allowing $Cp_2Ta(CH_2)(CH_3)$[19] and $CpPd(\eta^3\text{-}C_3H_5)$[20] to react at −78 °C in THF with slow warming to room temperature resulted in the formation of 1 with loss of 1 equiv of propylene (eq 1).

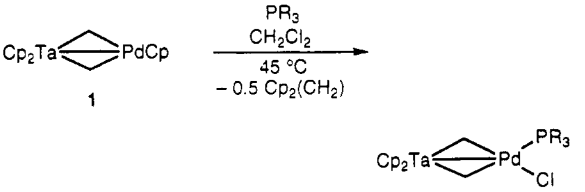


(1)

1

Complex 1 was isolated in 70% yield as an orange crystalline solid from CH_2Cl_2 at −35 °C. The structure of 1 denoted in eq 1 is assigned on the basis of its NMR spectroscopic properties. The Cp rings bound to Ta are equivalent by both ^1H (5.19 ppm) and $^{13}C\{^1H\}$ (97.4 ppm) NMR spectroscopy in CD_2Cl_2. The signal for the chemically equivalent bridging methylene hydrogens appears as a singlet in the ^1H NMR spectrum at 6.24 ppm and that for the bridging carbons at 118.1 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The ^1H and $^{13}C\{^1H\}$ NMR spectra include singlets at 5.66 and 95.9 ppm, respectively, for the Pd-bound Cp.

Reactions of 1 with Phosphorus Ligands: Cp Displacement. Complex 1 underwent a series of Cp displacement reactions at palladium upon addition of phosphorus ligands. Reaction of 1 with 1 equiv of either PMe_3 or $P(OMe)_3$ at 45 °C in CH_2Cl_2 resulted in loss of the Cp ring and formation of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)(Cl)$ (2) or $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(Cl)$ (3) (eq 2). Complexes 2 and 3 were isolated as white crystalline solids in 85% and 66% yield, respectively. NMR spectroscopic data indicate that the geometry at Pd is square planar in both complexes. For example, the Ta-bound Cp rings of 2 are equivalent by both ^1H (5.36 ppm) and $^{13}C\{^1H\}$ (98.6 ppm) NMR spectroscopy in CD_2Cl_2. The ^1H NMR spectrum also includes two resonances for inequivalent bridging methylene hydrogens at 7.19 and 5.19 ppm, both of which are coupled to phosphorus (J = 8.7 and 5.1 Hz, respectively). The bridging carbons are inequivalent by $^{13}C\{^1H\}$ NMR spectroscopy, one resonance appearing at 118.8 ppm as a singlet and the other at 159.6 ppm as a doublet due to trans coupling to phosphorus (J = 45.9 Hz). The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at −16.8 ppm for the PMe_3 ligand. Similar spectroscopic observations were made for 3 in CD_2Cl_2. The coproduct in the reactions of 1 forming 2 and 3 was $^1/_2$ equiv of $Cp_2(CH_2)$, identified by gas chromatography and GCMS by comparison with an authentic sample.[21,22]



1

(2)

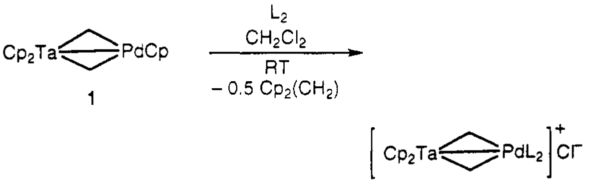
2: R = Me
3: R = OMe

To obtain additional information about the formation of 2, the reaction of 1 and 1 equiv of PMe_3 was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. This indicated that the first observable step is the formation of the bis(phosphine) salt $\{Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)_2]Cl$ (4, see below), which occurred quickly at room temperature. This complex was slowly consumed as the remaining second half of 1 reacted, and thus the overall result was the formation of 1 equiv of 2. The same type of reactivity was observed for the reaction of 1 and $P(OMe)_3$ to form 3.

The rate of formation of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)(Cl)$ (2) was significantly accelerated in the presence of an excess (PPN)Cl (PPN = bis(triphenylphosphine)nitrogen(1+)), while the formation of the intermediate bis(phosphine) salt was still observed at early reaction times. For example, the addition of 1 equiv of PMe_3 to 1 at room temperature resulted in the ratios (1:bis(phosphine) salt:2) 44:44:12 after 4.5 min, 37:38:25 after 20 min, and 33:34:33 after 34 min. When 21.6 equiv of (PPN)Cl was added to a reaction mixture containing the same concentrations of 1 and PMe_3, the ratios observed were 27:38:35, 10:18:72, and 7:10:83 after 4.5, 20, and 34 min, respectively. Even when the solution was saturated with (PPN)Cl (94 equiv), the reaction mixture still contained 35% bis(phosphine) salt after 4.5 min.

It is interesting to note that 3 disproportionated completely on dissolution in CD_3CN to produce $^1/_2$ equiv of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)_2]Cl$ (see below) at room temperature, as determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The fate of the remaining organometallic species was not determined. Disproportionation of 2 was also observed at room temperature in CD_3CN to produce a final 2:bis(phosphine) salt ratio of 85:15.

Treatment of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1) with 2 equiv of phosphine or phosphite or 1 equiv of $Me_2P(CH_2)_2PMe_2$ (DMPE) caused complete conversion (as expected on the basis of the observations summarized above) to the cationic complexes 4–6, which were isolated in 70, 63, and 81% yield, respectively (eq 3). Once again, $^1/_2$ equiv of $Cp_2(CH_2)$ was formed in each reaction, which was identified by GC and GCMS. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2) of 4–6 are quite similar and indicate a high degree of symmetry in these compounds. In each



1

(3)

4: $L_2 = 2\ PMe_3$
5: $L_2 = 2\ P(OMe)_3$
6: L_2 = DMPE

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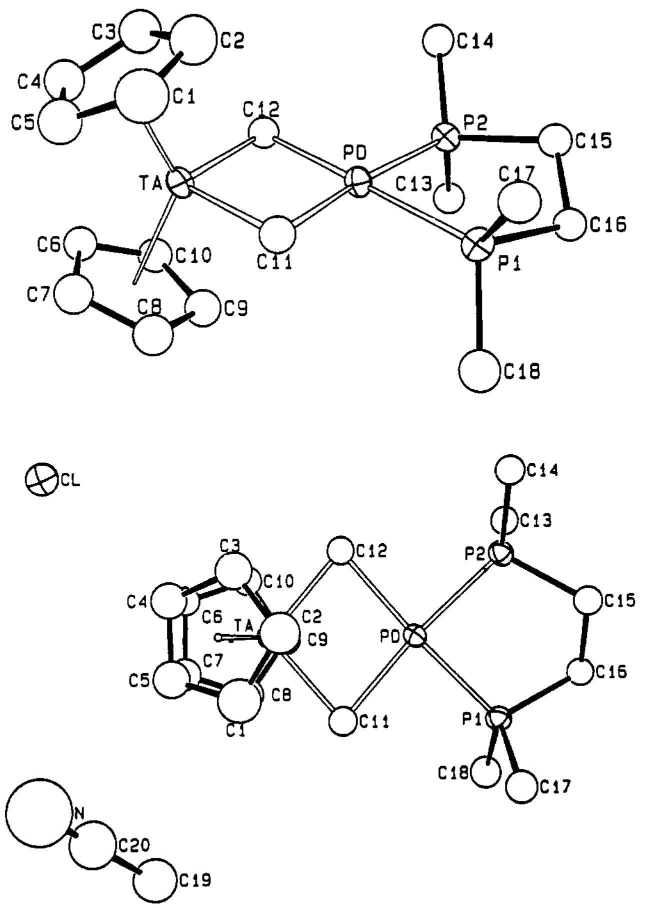


Figure 1. ORTEP diagrams of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cl$ (**6**).

Table 1. Crystal and Data Collection Parameters for $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cl$ (6)

(A) Crystal Parameters at 103 °C[a,b]

$a = 11.1298(13)$ Å
$b = 20.2296(25)$ Å
$c = 11.7262(15)$ Å
$\alpha = 90.0°$
$\beta = 116.140(10)°$
$\gamma = 90.0°$
$V = 2370.8(10)$ Å^3
size: 0.30 × 0.40 × 0.50 mm
space group: $P2_1/c$
fw = 672.2
$Z = 4$
d(calcd) = 1.88 g cm^{-3}
μ(calcd) = 55.6 cm^{-1}

(B) Data Measurement Parameters

radiation: Mo Kα ($\lambda = 0.710\,73$ Å)
monochromator: highly oriented graphite ($2\theta = 12.2°$)
diffractometer: Enraf-Nonius CAD-4
rflns measd: $+h,+k,\pm l$
2θ range: 3–45°
scan type: ω
scan width: $\Delta w = 0.90 + 0.35 \tan\theta$
scan speed: 5.49 (w, deg min^{-1})
bkgd: measd over $0.25(\Delta w)$ added to each end of the scan
vert aperture: 4.0 mm
horiz aperture: $2.5 + 1.0 \tan\theta$ mm
no. of rflns collected: 3195

(C) Data Reduction and Refinement

intensity stds: measd every 1 h of X-ray exposure time
max cor for cryst decay: 3.1% on F
empirical abs cor based on azimuthal scan data:
$T_{max} = 0.997$, $T_{min} = 0.647$
no. of atoms in least squares: 26
no. of unique rflns: 3080
no. of rflns with $F^2 > 3\sigma(F^2)$: 2784
final residuals: $R = 3.4\%$, $R_w = 4.8\%$, GOF = 2.50,
$R_{all} = 3.8\%$, p factor: 0.03, no. of params 130 difference
Fourier: +0.92, −0.35 e$^-$ Å^{-3}

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 28 and 32°. [b] In this table the esd's of all parameters are given in parentheses, right justified to the least significant digit(s) of the reported value.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cl$ (6)

Ta–Pd	2.832(1)	Cp1–Ta–C11	105.9
Ta–C11	2.145(9)	Cp2–Ta–C11	104.3
Ta–C12	2.136(8)	Cp1–Ta–C12	104.9
		Cp2–Ta–C12	105.5
Ta–Cp1	2.093	Cp1–Ta–Cp2	133.4
Ta–Cp2	2.093	C11–Ta–C12	97.1(3)
Pd–P1	2.277(2)	P1–Pd–P2	86.85(8)
Pd–P2	2.275(2)	P1–Pd–C11	87.1(3)
Pd–C11	2.130(9)	P1–Pd–C12	174.8(2)
Pd–C12	2.152(8)	P2–Pd–C11	173.9(3)
		P2–Pd–C12	89.0(2)
P1–C16	1.850(8)	C11–Pd–C12	97.1(3)
P1–C17	1.833(9)		
P1–C18	1.830(10)	Pd–P1–C16	107.7(3)
P2–C13	1.832(9)	Pd–P2–C15	106.6(3)
P2–C14	1.816(8)		
P2–C15	1.856(9)		
C15–C16	1.551(12)		

complex the Cp rings are equivalent by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, as are each of the bridging methylene hydrogens in the ^1H NMR spectra and the bridging carbons in the $^{13}C\{^1H\}$ NMR spectra. The phosphorus nuclei in each complex are equivalent and appear as singlets in the $^{31}P\{^1H\}$ NMR spectra. These data indicate that the Cl counterion is noncoordinating in solution in each compound. In support of this conclusion, **6** was found to be a 1:1 electrolyte in acetonitrile in conductivity studies (see Experimental Section).

The Cl counterion of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cl$ (**6**) is also noncoordinating in the solid state, as determined in an X-ray crystallographic study performed by Dr. F. J. Hollander. X-ray-quality crystals were obtained by vapor diffusion of Et_2O into a saturated CH_3CN solution of **6**. ORTEP diagrams of **6** are shown in Figure 1. Tables 1–3 include crystal and data collection parameters, selected bond lengths and bond angles, and positional parameters. The unit cell contains a CH_3CN molecule. The four-membered ring of **6** is completely planar with a Ta–Pd distance of 2.832(1) Å. The average Ta–CH_2 bond length of 2.140(9) Å is essentially equal to that of Pd–CH_2 (2.141(9) Å).

In addition to the method shown in eq 3, complexes **4** and **5** were also produced on the addition of 1 equiv of PMe_3 or $P(OMe)_3$ to **2** and **3**, respectively, in CD_2Cl_2, as determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. These reactions are reversible, as demonstrated in the thermal decomposition reaction of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)_2]Cl$ (**4**) monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Heating **4** in CD_2Cl_2 for 5 days at 93 °C resulted in a **4**:**2** ratio of 36:64. Thermal decomposition of **4** was accelerated in the presence of (PPN)Cl. Thus, the addition of 15 equiv of (PPN)Cl to **4** in CD_2Cl_2 led to a **4**:**2** ratio of 24:76 after only 44 h at 93 °C; the reaction went to completion within 5 days. The displaced PMe_3 ligand in both cases reacted with solvent to produce $[Me_3PCD_2Cl]Cl$, which was identified by comparison of its ^1H and $^{31}P\{^1H\}$ NMR spectra with those of an authentic sample. In addition to the resonance for the phosphonium salt, after 5 days at 93 °C the ^1H NMR spectrum of the reaction mixture containing (PPN)Cl also included an unidentified doublet at 1.7 ppm.

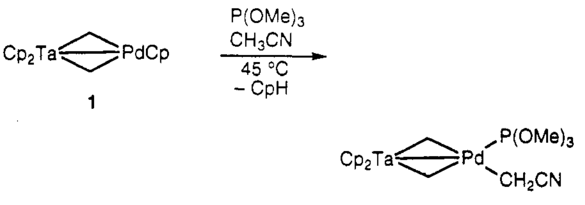
As in the reactions performed in methylene chloride, elimination of the Pd-bound Cp also occurred when Cp_2-

Table 3. Positional Parameters and Their Estimated Standard Deviations for $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cl$ (6)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ta	0.15895(1)	0.15055(1)	0.25924(1)	1.647(7)
Pd	–0.06123(1)	0.08191(1)	0.26268(1)	1.59(1)
Cl	0.4681(2)	0.1706(1)	0.0333(2)	2.83(5)
P1	–0.1875(2)	0.0918(1)	0.3707(2)	1.79(4)
P2	–0.2031(2)	–0.0004(1)	0.1503(2)	1.73(4)
C1	0.338(1)	0.1253(6)	0.465(1)	4.6(2)*
C2	0.293(1)	0.0645(5)	0.3988(9)	4.0(2)*
C3	0.3265(9)	0.0656(5)	0.2964(8)	3.3(2)*
C4	0.3842(9)	0.1272(5)	0.2967(9)	3.2(2)*
C5	0.3928(9)	0.2236(4)	0.1079(7)	2.4(2)*
C7	0.1944(9)	0.2643(5)	0.2155(8)	3.1(2)*
C8	0.0701(9)	0.2619(5)	0.2193(8)	3.1(2)*
C9	–0.0175(8)	0.2216(4)	0.1208(8)	2.8(2)*
C10	0.0526(8)	0.1993(4)	0.0490(7)	2.6(2)*
C11	0.0607(8)	0.1591(4)	0.3802(7)	2.3(2)*
C12	0.0417(8)	0.0706(4)	0.1457(7)	2.1(2)*
C13	–0.3372(8)	0.0255(4)	–0.0024(7)	2.4(2)*
C14	–0.1449(8)	–0.0767(4)	0.1098(7)	2.3(2)*
C15	–0.2919(8)	–0.0273(4)	0.2443(7)	2.2(2)*
C16	–0.3319(7)	0.0352(4)	0.2963(7)	2.0(1)*
C17	–0.1058(8)	0.0717(4)	0.5404(8)	2.6(2)*
C18	–0.2655(9)	0.1717(5)	0.3680(8)	2.9(2)*
C19	0.572(1)	0.1777(5)	0.7764(9)	4.0(2)*
C20	0.689(1)	0.1536(5)	0.773(1)	4.4(2)*
N	0.785(1)	0.1325(6)	0.770(1)	8.5(3)*

[a] Starred values denote atoms included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)(\beta(2,3)]$, where *a*, *b*, and *c* are real cell parameters: and $\beta(i,j)$ values are anisotropic β's.

$Ta(\mu\text{-}CH_2)_2PdCp$ (1) was allowed to react with phosphorus compounds in acetonitrile. For example, $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(CH_2CN)$ (7) was formed in the reaction of $P(OMe)_3$ with 1 in CH_3CN held at 45 °C for 15 h (eq 4).



1

7

(4)

The production of dicyclopentadiene as a coproduct was confirmed by GCMS by comparison with an authentic sample. 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 2% 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, although the same difficulties in purification were encountered. The NMR spectroscopic data for 7, similar to those described for 2, are in agreement with the formulation depicted in eq 4 and indicate a square-planar geometry at palladium. The resonance for the methylene hydrogens of the CH_2CN ligand appears at 2.04 ppm (J_{HP} = 9.5 Hz) in the ^1H NMR spectrum. The methylene carbon signal appears at –9.9 ppm (J_{CP} = 14.0 Hz) and that of the CN carbon at 130.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum in C_6D_6. When the reaction of 1 with $P(OMe)_3$ was performed in CD_3CN, the resonance at 2.04 ppm in the ^1H NMR spectrum disappeared. The infrared spectrum (KBr) contains a strong peak at 2166 cm^{-1}, which is assigned to the CN stretch.

Table 4. Crystal Data and Collection Parameters for $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (8)

(A) Crystal Parameters at T = –118 °C[a,b]

a = 10.451(3) Å
b = 14.619(3) Å
c = 16.308(4) Å
α = 68.918(19)°
β = 85.976(19)°
γ = 88.114(19)°
V = 2318.9(13) Å^3
size: 0.10 × 0.25 × 0.55 mm
space group: $P\bar{1}$
fw = 660.8
Z = 4
d(calcd) = 1.89 g cm^{-3}
μ(calcd) = 55.7 cm^{-1}

(B) Data Measurement Parameters

radiation: Mo Kα (λ = 0.710 73 Å)
monochromator: highly oriented graphite (2θ = 12.2°)
diffractometer: Enraf-Nonius CAD-4
rflns measd:[c] $+h,\pm k,\pm l$
2θ range; 3–46°
scan type: ω
scan width: $\Delta w = 1.50 + 0.35 \tan\theta$
scan speed: 8.24 (w, deg min^{-1})
bkgd: measd over 0.25(Δw) added to each end of the scan
vert aperture: 6.0 mm
horiz aperture: 3.0 + 1.0 tan θ mm
no. of rflns collected: 5302

(C) Data Reduction and Refinement

intensity stds: measd every 1 h of X-ray exposure time
no cor for cryst decay necessary
empirical abs cor based on azimuthal scan data:
T_{max} = 0.999, T_{min} = 0.624
no. of atoms in least squares: 54
no. of unique rflns: 5302
no. of rflns with $F^2 > 3\sigma(R^2)$: 3774
final residuals: R = 5.4%, R_w = 6.9%, GOF = 2.59,
R_{all} = 10.1%, p factor 0.03, no. of params 257 difference
Fourier: +1.74, –0.36 e$^-$ Å^{-3}

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 24 and 30°. [b] In this table the esd's of all parameters are given in parentheses, righ justified to the least significant digit(s) of the reported value. [c] Data were only collected from h = 0 to h = 7 due to interruption of the data set and loss of orientation. The maximum value of h was expected to be h = 11.

Like the reactions of 1 with monodentate phosphorus ligands in CD_2Cl_2, monitoring the course of the reaction of 1 and $P(OMe)_3$ in CD_3CN at room temperature indicated that the first observable step was the immediate formation of $^1/_2$ equiv of a bis(phosphite) salt, which reacted slowly with the remaining 1 to produce 7. The ^1H and $^{31}P\{^1H\}$ NMR spectra of this intermediate are consistent with the formulation of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)_2]Cp$. In the ^1H NMR spectrum the Cp rings bound to Ta are equivalent (5.44 ppm, singlet). The resonance for the equivalent bridging methylene hydrogens appears at 6.27 ppm, and that for the methyl groups is found at 3.60 ppm; both signals are multiplets due to phosphorus coupling. A singlet resonance at 5.48 ppm which integrated to 5H is assigned to the free cyclopentadienyl anion. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 28.3 ppm for the equivalent phosphite ligands.

Similar spectroscopic observations were made in the reaction of 1 with PMe_3 in CD_3CN, although this reaction failed to go to completion even after 3 days at 45 °C. Allowing 1 to react with 1 equiv of $P(OMe)_3$ in the presence of benzonitrile in THF at 45 °C led to the formation of a product analogous to 7, as determined by ^1H NMR spectroscopy. Unfortunately, the product was not stable to the reaction conditions required to drive it to completion.

Synthesis, Structure, and Reactivity of the Free-Cp Complex 8. Each of the above reactions of 1 with phosphorus ligands implicate the intermediacy of complexes containing a free cyclopentadienide anion. Therefore, an isolable analogue was prepared by treating 1 with

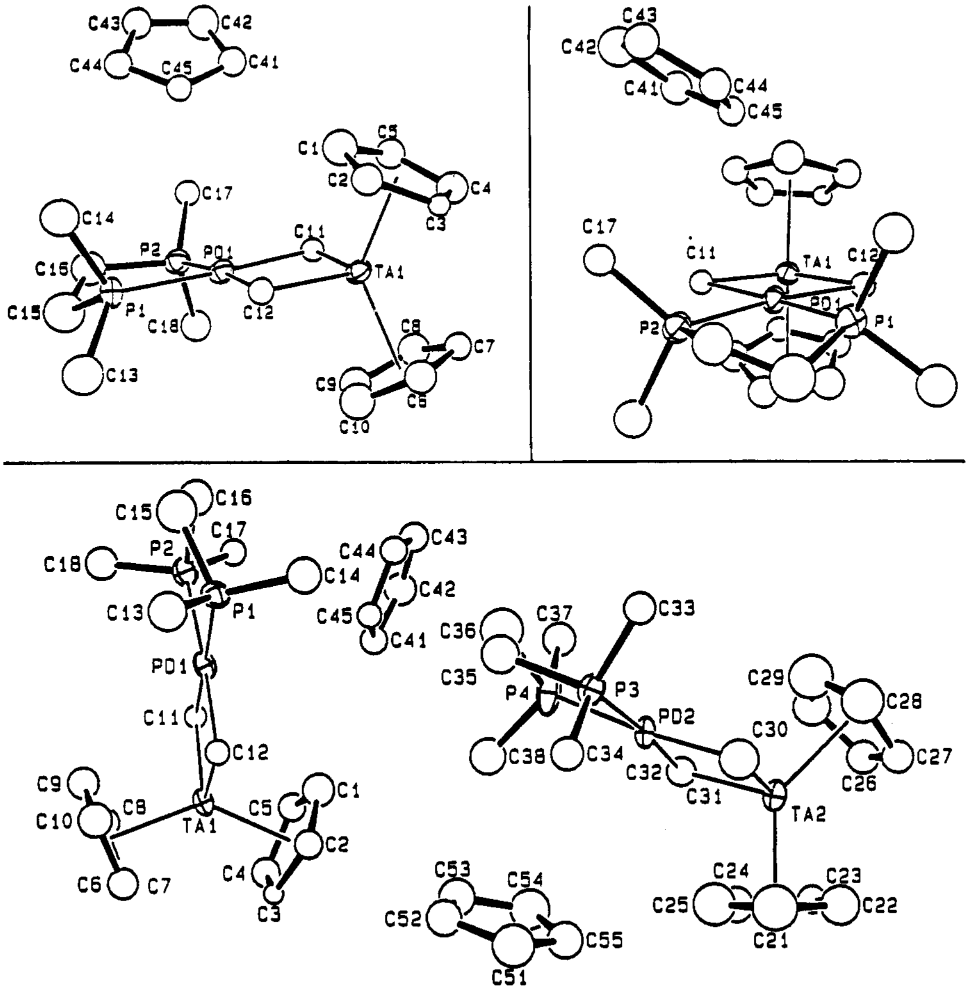
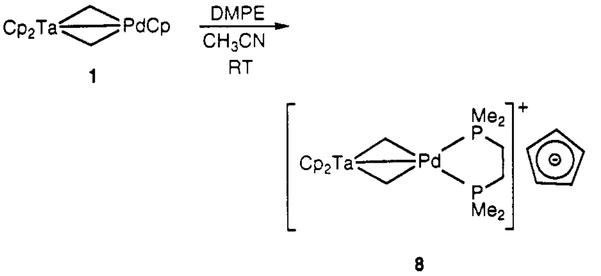


Figure 2. ORTEP diagrams of [$Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)$]Cp (8).

DMPE in CH_3CN at room temperature. Pale orange crystals of the free Cp^- complex [$Cp_2Ta(\mu\text{-}CH_2)_2Pd$-(DMPE)]Cp (8) were isolated directly from the reaction mixture by diethyl ether diffusion at room temperature in 85% yield (eq 5). The ^1H and $^{13}C\{^1H\}$ NMR spectra of



(5)

8 in CD_3CN include singlets at 5.48 and 104.2 ppm, respectively, which were assigned to the cyclopentadienide counterion. Over the course of several hours at room temperature in CD_3CN, both of these resonances disappeared, with the concomitant growth of a signal at 5.48 ppm in the ^2H NMR spectrum. This indicates that deuterium exchange occurs between the unbound Cp and the solvent. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the cation portion of 8 in CD_3CN are identical to those of the chloride salt 6 in this solvent. Conductivity studies showed that 8 is a 1:1 electrolyte in acetonitrile (see Experimental Section).

In order to confirm the structure of 8, an X-ray crystallographic study was performed by Dr. F. J. Hollander. ORTEP diagrams are shown in Figure 2, and crystal and data collection parameters, selected bond lengths and bond angles, and positional parameters can be found in Tables 4–7. Unfortunately, an incomplete data set was collected due to accidental interruption of the data collection and loss of crystal orientation. The structure, however, which contains two molecules in the unit cell, clearly illustrates the lack of bonding between the Cp anion and the cationic portion of the molecule. The shortest distance between the cyclopentadienide counterion and the bimetallic fragment is 3.46(3) Å, which is that between the Cp ring and a methyl carbon of the DMPE ligand. The average C–C distance in the planar

Table 5. Selected Bond Lengths (Å) for [$Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)$]Cp (8)

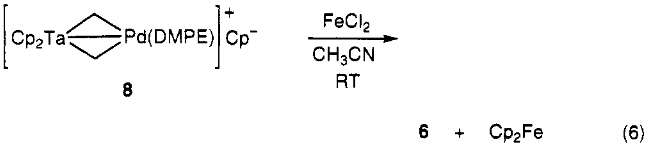
Ta1–Pd1	2.829(2)	Ta2–Pd2	2.830(2)
Ta1–C11	2.13(2)	Ta2–C31	2.18(3)
Ta1–C12	2.15(2)	Ta2–C32	2.14(2)
Ta1–Cp1	2.078	Ta2–Cp3	2.043
Ta1–Cp2	2.116	Ta2–Cp4	2.109
Pd1–P1	2.264(6)	Pd2–P3	2.275(6)
Pd1–P2	2.269(6)	Pd2–P4	2.263(6)
Pd1–C11	2.16(2)	Pd2–C31	2.12(3)
Pd1–C12	2.11(2)	Pd2–C32	2.17(2)
P1–C15	1.82(3)	P3–C35	1.85(3)
P2–C16	1.84(3)	P4–C36	1.86(3)
C15–C16	1.45(3)	C35–C36	1.46(4)
C41–C42	1.46(3)	C5–C52	1.41(3)
C41–C45	1.40(3)	C51–C55	1.42(3)
C42–C43	1.38(3)	C52–C53	1.40(3)
C43–C44	1.42(3)	C53–C54	1.42(3)
C44–C45	1.39(3)	C54–C55	1.40(3)

Table 6. Selected Bond Angles (deg) for [$Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)$]Cp (8)

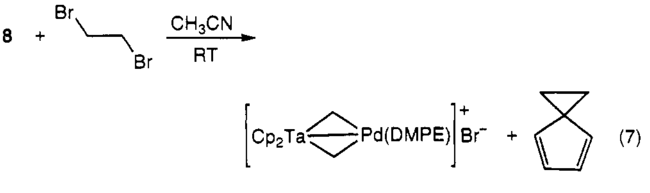
Cp1–Ta1–C11	104.8	Cp3–Ta2–C31	105.2
Cp2–Ta1–C11	102.9	Cp4–Ta2–C31	105.6
Cp1–Ta1–C12	106.1	Cp3–Ta2–C32	104.0
Cp2–Ta1–C12	105.8	Cp4–Ta2–C32	104.8
Cp1–Ta1–Cp2	134.3	Cp3–Ta2–Cp4	134.1
C11–Ta1–C12	97.0(7)	C31–Ta2–C32	97.3(9)
P1–Pd1–P2	86.11(22)	P3–Pd2–P4	85.66(23)
P1–Pd1–C11	173.0(5)	P3–Pd2–C31	87.2(8)
P1–Pd1–C12	89.5(6)	P3–Pd2–C32	174.2(6)
P2–Pd1–C11	87.1(5)	P4–Pd2–C31	171.6(7)
P2–Pd1–C12	174.3(6)	P4–Pd2–C32	89.3(6)
C11–Pd1–C12	97.4(8)	C31–Pd2–C32	98.0(9)
Ta1–C11–Pd1	82.3(7)	Ta2–C31–Pd2	82.5(9)
Ta1–C12–Pd1	83.2(7)	Ta2–C32–Pd2	82.1(8)
Pd1–P1–C15	106.5(9)	Pd2–P3–C35	109.1(8)
Pd1–P2–C16	106.6(8)	Pd2–P4–C36	106.9(9)
C42–C41–C45	105.7(19)	C52–C51–C55	107.4(23)
C41–C42–C43	107.2(21)	C51–C52–C53	106.9(23)
C42–C43–C44	110.0(20)	C52–C53–C54	110.5(23)
C43–C44–C45	106.4(19)	C53–C54–C55	105.4(23)
C41–C45–C44	110.6(18)	C51–C55–C54	109.8(23)

displaced Cp ligand of 1.41(3) Å is in agreement with data previously observed for other complexes containing a dissociated cyclopentadienide ligand.[10,13] The bonding distances and angles in the bimetallic cation are, within experimental error, identical with those of the chloride salt 6.

Stoichiometric reactions of [$Cp_2Ta(\mu\text{-}CH_2)_2Pd$-(DMPE)]Cp (8) with added electrophiles are strongly reminiscent of those observed earlier with sodium cyclopentadienide. The addition of 8 to $FeCl_2$ in acetonitrile, for example, led to the immediate formation of $^1/_2$ equiv of Cp_2Fe (eq 6),which was isolated in 80% yield by



sublimation and identified by ^1H NMR spectroscopy and GC.[23] No reaction was observed between the chloride salt 6 and $FeCl_2$ under the same conditions. 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 (2 equiv of Cp^- is required to form the product) after 19.5 h, as determined by ^1H NMR spectroscopy (eq 7). The addition of 1 equiv of $LiN(SiMe_3)_2$ to the reaction



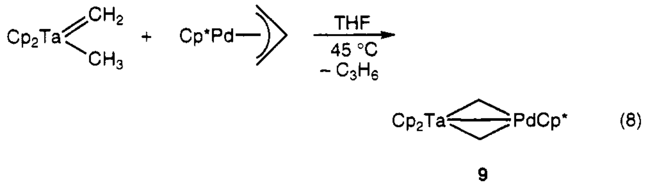
mixture increased the yield of spiro[2.4]hepta-4,6-diene to 85% after 21 h at room temperature. The organic product in these reactions was identified by comparison of ^1H NMR, GC, and GCMS data with those of an authentic sample.[24] In the reactions of 8 with $FeCl_2$ and 1,2-dibromoethane the halide salt of the bimetallic cation was formed, although the bromide salt was not fully characterized.

Table 7. Positional Parameters and Their Estimated Standard Deviations for [$Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)$]Cp (8)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ta1	0.37174(9)	0.20654(1)	0.57561(1)	1.82(2)
Ta2	–0.0438(1)	0.29326(1)	–0.07394(1)	1.92(2)
Pd1	0.6076(2)	0.2546(1)	0.47446(9)	1.84(4)
Pd2	0.1762(2)	0.2567(1)	0.02530(9)	1.76(4)
P1	0.7482(6)	0.1879(4)	0.3993(3)	2.2(1)
P2	0.7526(6)	0.3764(4)	0.4438(3)	2.3(1)
P3	0.3419(6)	0.1471(4)	0.0542(3)	1.9(1)
P4	0.2773(7)	0.3282(4)	0.1046(4)	3.2(2)
C1	0.273(2)	0.286(2)	0.437(1)	3.4(5)*
C2	0.225(2)	0.188(1)	0.476(1)	2.5(4)*
C3	0.155(2)	0.184(1)	0.557(1)	1.2(4)*
C4	0.155(2)	0.272(1)	0.567(1)	2.8(5)*
C5	0.233(2)	0.338(1)	0.492(1)	2.6(5)*
C6	0.341(2)	0.067(1)	0.709(1)	2.8(5)*
C7	0.294(2)	0.148(1)	0.729(1)	2.0(4)*
C8	0.403(2)	0.210(2)	0.719(1)	3.3(5)*
C9	0.514(2)	0.164(2)	0.699(1)	3.1(5)*
C10	0.474(2)	0.077(2)	0.694(1)	3.5(5)*
C11	0.487(2)	0.334(1)	0.540(1)	1.6(4)*
C12	0.489(2)	0.132(1)	0.505(1)	1.8(4)*
C13	0.798(2)	0.057(2)	0.445(2)	4.0(6)*
C14	0.710(2)	0.203(2)	0.288(1)	3.5(5)*
C15	0.902(3)	0.247(2)	0.391(2)	4.6(6)*
C16	0.882(2)	0.351(2)	0.372(1)	3.7(5)*
C17	0.710(2)	0.503(1)	0.386(1)	2.2(4)*
C18	0.836(2)	0.377(2)	0.539(1)	3.4(5)*
C21	–0.156(3)	0.139(2)	–0.003(2)	5.3(7)*
C22	–0.236(3)	0.209(2)	–0.074(2)	4.2(6)*
C23	–0.260(2)	0.285(1)	–0.049(1)	2.1(4)*
C24	–0.214(2)	0.270(2)	0.036(1)	3.6(5)*
C25	–0.145(3)	0.185(2)	0.059(2)	4.7(6)*
C26	–0.110(2)	0.435(2)	–0.199(1)	3.2(5)*
C27	–0.084(2)	0.356(1)	–0.230(1)	2.8(5)*
C28	0.053(3)	0.334(2)	–0.222(2)	4.9(6)*
C29	0.097(3)	0.397(2)	–0.187(2)	5.3(7)*
C30	0.008(2)	0.456(2)	–0.175(2)	4.0(6)*
C31	0.109(3)	0.184(2)	–0.054(2)	4.1(6)*
C32	0.021(2)	0.363(1)	0.010(1)	2.5(4)*
C33	0.450(2)	0.147(1)	–0.041(1)	2.4(4)*
C34	0.313(2)	0.017(1)	0.114(1)	2.6(5)*
C35	0.449(2)	0.175(2)	0.127(1)	3.8(6)*
C36	0.445(3)	0.280(2)	0.113(2)	5.2(7)*
C37	0.309(2)	0.460(2)	0.059(1)	3.4(5)*
C38	0.209(3)	0.308(2)	0.215(2)	4.0(6)*
C41	0.430(2)	0.497(1)	0.279(1)	2.5(5)*
C42	0.472(2)	0.592(2)	0.215(1)	3.5(5)*
C43	0.567(2)	0.574(1)	0.160(1)	2.7(5)*
C44	0.594(2)	0.472(1)	0.188(1)	2.3(4)*
C45	0.509(2)	0.427(1)	0.260(1)	1.9(4)*
C51	0.090(3)	–0.114(2)	0.279(2)	4.4(6)*
C52	0.160(2)	–0.085(2)	0.337(1)	3.1(5)*
C53	0.129(2)	0.013(2)	0.321(1)	3.6(5)*
C54	0.042(3)	0.049(2)	0.253(2)	4.2(6)*
C55	0.017(2)	–0.032(2)	0.229(1)	3.3(5)*

[a] Starred values denote atoms included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$, where *a*, *b*, and *c* are real cell parameters and $\beta(i,j)$ values are anisotropic β's.

As an analogue of 1, $Cp_2Ta(\mu\text{-}CH_2)_2PdCp^*$ (9) was synthesized in the reaction of $Cp_2Ta(CH_2)(CH_3)$ with $Cp^*Pd(\eta^3\text{-}C_3H_5)$[25] at 45 °C (eq 8). Complex 9 was isolated



in 50% yield as a dark red crystalline compound. No

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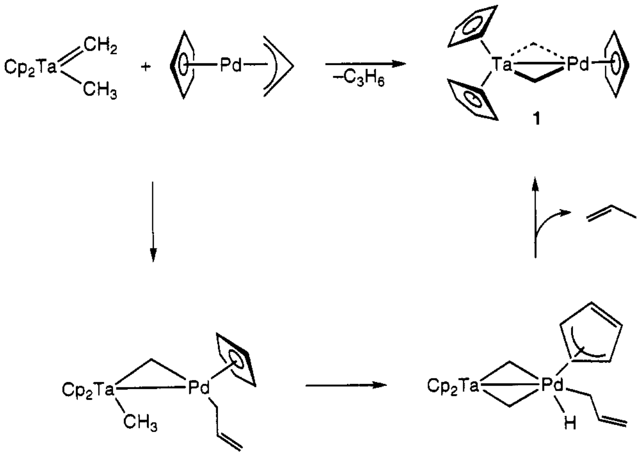
(23) Wilkinson, G. *Org. Synth.* **1956**, *36*, 31.

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

Scheme 1



intermediates were observed when the reaction was monitored by ^{1}H NMR spectroscopy. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **9** indicate a structure analogous to that described for **1**. Preliminary studies showed that **9** reacted with phosphines to give metal-containing products identical with those observed in the reactions of **1** with phosphines. However, these transformations required harsher conditions and were not as clean. For example, **9** reacted with PMe_3 in CD_2Cl_2 at 45 °C to form **2**, as determined by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. The addition of DMPE to **9** in CD_2Cl_2 at 45 °C led to the chloride salt **6** as the major product. Only slow decomposition was observed in the reaction of **9** with DMPE in CD_3CN at 68 °C. In each case, no organic product could be identified.

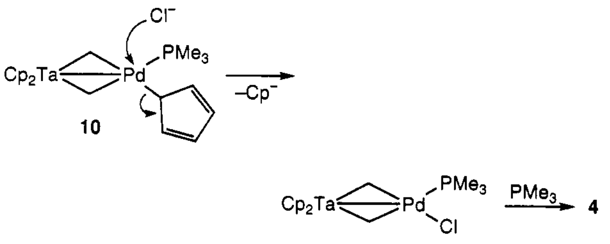
Discussion

Synthesis of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1). The complex $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (**1**) was isolated from the reaction of $Cp_2Ta(CH_2)(CH_3)$ with $CpPd(\eta^3\text{-}C_3H_5)$ at low temperatures, which also produced 1 equiv of propylene (eq 1). We believe that this reaction proceeds by a mechanism similar to that proposed for the reaction of $Cp_2Ta(CH_2)(CH_3)$ with $(indenyl)Ir(CO)_2$ to form $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ and indene.[16] As shown in Scheme 1, the attack of $Cp_2Ta(CH_2)(CH_3)$ on $CpPd(\eta^3\text{-}C_3H_5)$ could occur together with $\eta^3 \rightarrow \eta^1$ isomerization of the allyl ligand. Intramolecular oxidative addition of the C–H bond of the Ta–CH_3 group to the Pd center would then proceed with Cp ring slip from η^5 to η^3 in order to maintain an 18 e^- count at palladium. Reductive elimination of propylene from this intermediate gives **1**. Unfortunately, no intermediates were observed when this reaction was monitored at low temperature by ^{1}H NMR spectroscopy.

Reactions of 1 with Phosphorus Ligands in CH_2Cl_2: Mechanism of Cp Loss. Reactions of **1** with phosphorus compounds indicated that the Pd-bound Cp of **1** is quite labile. As a result of this lability, the addition of PMe_3 or $P(OMe)_3$ to **1** in methylene chloride led to the formation of the phosphine-substituted complexes $Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)(Cl)$ (**2**) and $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(Cl)$ (**3**) (eq 2) together with $^1/_2$ equiv of $Cp_2(CH_2)$.

The overall reaction of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (**1**) with PMe_3, investigated by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, proceeded with the immediate formation of the bis(phosphine) chloride salt **4** at room temperature. The second half of **1** then slowly reacted as this intermediate was consumed, forming 1 equiv of **2**. The proposed mechanism for the first stage of the reaction is shown in the top part of Scheme 2. Initial attack of PMe_3 on **1** could proceed with Cp ring slip to form **10**. The immediate formation of the bis(phosphine) adduct **4** observed at room temperature would suggest that free PMe_3 reacts with **10** faster than with starting material **1**. We propose that PMe_3 reacts with **10** to displace the Cp ligand, forming the intermediate **11**, which contains an unbound cyclopentadienide anion, although this is not observed directly. The displaced cyclopentadienide ligand of **11** then reacts rapidly with solvent to produce **4** and $^1/_2$ equiv of $Cp_2(CH_2)$. The fact that $Cp_2(CH_2)$ was prepared earlier by the treatment of CH_2Cl_2 with NaCp strongly suggests that the ring is extruded as $[C_5H_5]^-$.

It is not possible to determine at which point the Cp ligand is displaced from the palladium center in this reaction, although it is clear that the spectroscopically observed bis(phosphine) intermediate does not include the Cp ring. It is conceivable that adventitious Cl^- ions could catalyze the conversion of **10** directly to **2**, which would then react with free PMe_3 to form **4** (eq 9). The displaced Cp^- would react with solvent to regenerate the Cl^- ion. The observation that isolated **2** reacted rapidly with PMe_3 at room temperature to form **4** is in agreement with this alternative pathway.



(9)

Although the formation of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)_2]Cl$ (**4**) undoubtedly proceeds through a mono(phosphine) complex, this intermediate could not be trapped by the addition of excess (PPN)Cl. The bis(phosphine) complex **4** was observed at early reaction times even when 94 equiv of (PPN)Cl was added to the reaction.

The second stage in the reaction of **1** with PMe_3 is that in which the remaining **1** and the bis(phosphine) chloride salt **4** are converted to the final product $Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)(Cl)$ (**2**). The overall balanced reaction, shown in the lower part of Scheme 2, expends 1 equiv of **1** and 2 equiv of **4** to form 2 equiv of **2** and 1 new equiv of **4**. Complex **2** is generated on phosphine dissociation from **4** with binding of the chloride counterion. Starting material **1** reacts with the dissociated phosphine, where 2 equiv of free PMe_3 is required to form new **4** by the same route shown in the top part of Scheme 2. The mechanism in the lower part of Scheme 2 predicts that the concentrations of **1** and **4** remain equivalent (decrease at the same rate) throughout the reaction, as was, in fact, observed.

The rate-determining step in the reaction of **1** with PMe_3 is proposed to be phosphine loss from **4** to generate **2**. Although it is true that (PPN)Cl would be expected to promote the conversion of **10** to **2** in the first stage of the reaction (eq 9, see below), the overall rate enhancement observed in the presence of added (PPN)Cl is attributed to chloride attack on the bis(phosphine) adduct **4** which

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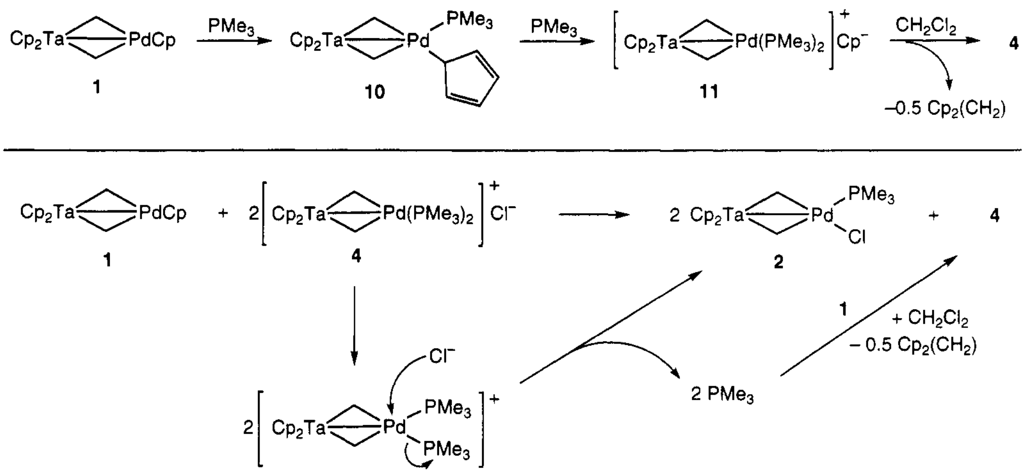
(25) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.; Krüger, C. *Organometallics* **1983**, *2*, 1369.

Scheme 2



accelerates the rate of phosphine loss to produce **2**. This conclusion is supported by studies on the thermal decomposition of **4** in CD_2Cl_2.

Heating isolated $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)_2]Cl$ (**4**) in CD_2Cl_2 at 93 °C led to the slow formation of **2** and PMe_3 which subsequently reacted with solvent to produce $[Me_3PCD_2Cl]Cl$. The rate-determining step in this reversible decomposition appears to be scavenging of PMe_3 by CD_2Cl_2, as this entire thermal decomposition reaction is significantly slower (28% complete after 19 h at 93 °C) than the reaction of the same concentration of **1** (29.6 mM) with PMe_3, which proceeds through the same bis(phosphine) complex (33% complete after 34 min at 25 °C) as discussed above. In agreement with the proposed role of (PPN)Cl described above in the reaction presented in Scheme 2, the addition of (PPN)Cl strongly enhanced the rate of thermal decomposition of **4**.

Observations analogous to those which led to the proposal of Scheme 2 for the reaction of **1** with PMe_3 were made in the reaction of **1** with $P(OMe)_3$ at room temperature, i.e. the immediate formation of $^1/_2$ equiv of the bis(phosphite) chloride salt **5** which slowly reacted as the second half of **1** was consumed to form **3**. An analogous mechanism is proposed for this system.

Both the bis(phosphine) and the bis(phosphite) chloride salts **4** and **5** were prepared independently from the reactions of **1** with 2 equiv of either PMe_3 or $P(OMe)_3$, respectively, in methylene chloride at room temperature together with $^1/_2$ equiv of $Cp_2(CH_2)$ (eq 3). Both reactions are believed to occur according to the steps outlined in the top part of Scheme 2 for the formation of the bis(phosphine) intermediate **4**.

In a similar reaction, the addition of DMPE to **1** in methylene chloride led to the isolation of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cl$ (**6**; eq 3). Complex **6** was characterized by X-ray crystallography. The structure, shown in Figure 1, reveals that the chloride counterion is noncoordinating in the solid state, as was found in solution at 25 °C by NMR spectroscopy (CD_2Cl_2 and CD_3CN) and in room-temperature conductivity studies (CH_3CN). The presence of a planar four-membered metallacycle in this complex is not surprising. This structural feature was also observed in a series of other $Ta(\mu\text{-}CH_2)_2M$ (M = Co, Rh, Ir, Pt) complexes.[16-18] The average $Ta-CH_2$ bond length of 2.140(9) Å is also quite consistent with previous observations in $Ta(\mu\text{-}CH_2)_2M$ compounds and is approximately intermediate in length between the $Ta-CH_2$ (2.039(1) Å) and $Ta-CH_3$ (2.268(1) Å) bonds in $Cp_2Ta(CH_2)(CH_3)$.[26] With a Ta–Pd distance of 2.832(1) Å, bonding between metal centers cannot be ruled out.[27]

It should be noted that reactions of Pd–Cp compounds in chlorinated solvents resulting in Cp loss have been reported previously. For example, the addition of excess PEt_3 to CpPd[2-(arylazo)phenyl] complexes in $CDCl_3$ resulted in loss of the Cp ring and formation of a phosphine-substituted Pd chloride complex. Intermediates containing unbound cyclopentadienide counterions were suggested, although none were detected nor were any organic products identified.[8,28]

Mechanism of Formation of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(CH_2CN)$ (7) in CH_3CN. Extrusion of the Pd-bound Cp of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (**1**) was not limited to reactions performed in methylene chloride. Treatment of **1** with $P(OMe)_3$ in acetonitrile at 45 °C led to the isolation of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(CH_2CN)$ (**7**) with the formation of $^1/_2$ equiv of dicyclopentadiene (eq 4). Complex **7** was synthesized independently in the reaction of **3** with $NaCH_2CN$.

The reaction of **1** with $P(OMe)_3$ in CD_3CN was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and appeared to be similar to the reactions of **1** with monodentate phosphorus ligands in methylene chloride in many respects. The first observable step was the immediate formation of $^1/_2$ equiv of a bis(phosphite) intermediate at room temperature. As found for the reactions generating **2** and **3**, this intermediate and the second half of **1** were slowly consumed with the formation of 1 equiv of **7** and $^1/_2$ equiv of dicyclopentadiene. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the bis(phosphite) intermediate are consistent with the formulation $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)_2]Cp$ (**12**). The observation of **12** in acetonitrile lends support to the suggestion that the analogous complexes $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(PR_3)_2]Cp$ are viable intermediates in the reactions of **1** with PMe_3 and $P(OMe)_3$ in methylene chloride, as shown in Scheme 2.

The proposed mechanism of the reaction of **1** with $P(OMe)_3$ in acetonitrile, shown in Scheme 3, is quite similar to that offered in Scheme 2. Thus, in the first stage of the reaction **1** reacts with 2 equiv of phosphite to produce **12**,

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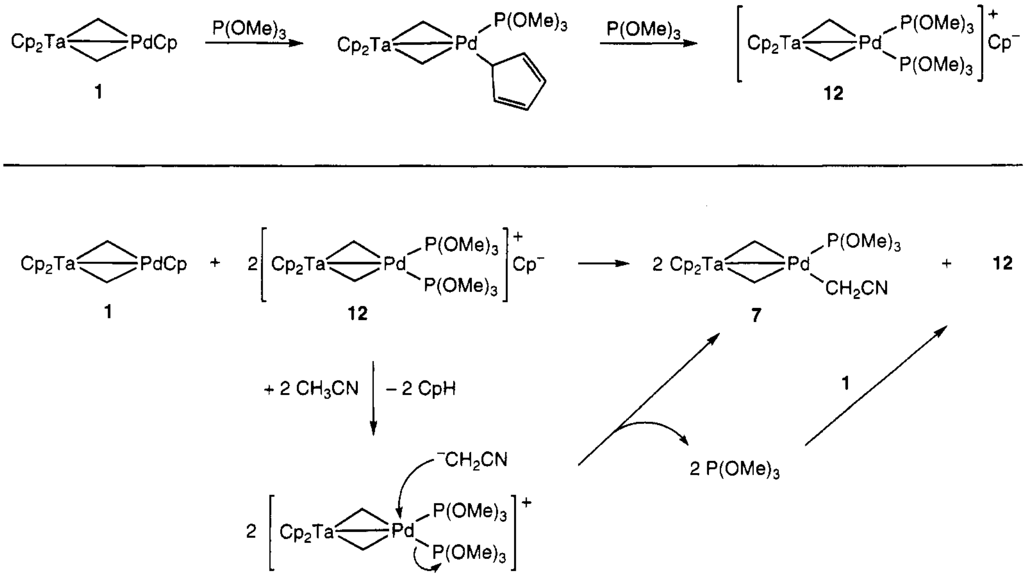
Scheme 3



as shown in the top part of Scheme 3. The final stage (lower part of Scheme 3) involves the overall reaction in which the remaining **1** and 2 equiv of **12** are consumed in the formation of 2 equiv of final product **7** and 1 new equiv of **12**. We believe that in both stages of the reaction the Pd-bound Cp ligand of **1** is extruded as a cyclopentadienide anion which abstracts H^+ from CH_3CN to generate $[CH_2CN]^-$. Even though the cyanomethide ion is undoubtedly generated reversibly in low concentration, it is sufficiently reactive to be trapped by the unsaturated cationic palladium center to form product **7**.

It appears that a reactive solvent such as methylene chloride or acetonitrile is necessary to obtain isolable products in the reactions of **1** with phosphines. Reactions performed in THF gave insoluble products and provided no evidence for intermediates containing a naked cyclopentadiene anion. Complex **1** and each of the salts **4–6** are insoluble in benzene and toluene, barring the use of these solvents.

Synthesis, Structure, and Reactivity of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (8). The participation of intermediates containing an unbound cyclopentadienide anion has been suggested in the reactions of **1** with phosphorus ligands in both CH_2Cl_2 and CH_3CN. In order to investigate the structure and reactivity of such species in greater detail, an isolable analogue was synthesized. Treatment of **1** with DMPE in acetonitrile led to the isolation of the free Cp^- complex $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (**8**) in 85% yield. An X-ray crystallographic study confirmed the absence of bonding between the cyclopentadienide counterion and the Ta–Pd fragment, the smallest distance between which is 3.46(3) Å. Consistent with this, the bond distances and bond angles in the bimetallic cation of **8** were found to be identical with those of the chloride salt **6**. The average C–C bond length of 1.41(3) Å in the dissociated Cp ring is in agreement with that observed previously for $Na(C_5H_5)$(TMEDA) (1.38(2) Å).[29] It is not clear why the free Cp ring exists as a dissociated counterion to **8** rather than as a ligand, perhaps η^1-bound to the Pd center, because the metal center is neither sterically nor electronically (formally 16 e^-) saturated. Although $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (**1**) is stable as an 18 e^- species, the addition of the strong donor DMPE apparently increases the effective charge on Pd to the extent that the 16 e^- naked cyclopentadienide complex is more stable than the 18 e^- η^1-Cp compound. The same peculiarity exists for the previously reported compounds $[Ir(DPPE)_2]Cp$ and $[Ir(DMPE)_2]Cp$.[11]

The cyclopentadienide counterion of **8** remains dissociated in solution. In support of this conclusion, the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the cationic portion of **8** are indistinguishable from those of **6** in CD_3CN at 25 °C. Also, **8** was found to be a 1:1 electrolyte in acetonitrile in conductivity studies.

The unbound Cp of **8** underwent slow deuterium exchange with CD_3CN solvent over the course of a few hours at room temperature, as was previously observed for $[MeRe(NO)(PMe_3)_4]Cp$.[10] This exchange reaction, which occurs by the reversible deprotonation of CD_3CN by the cyclopentadienide counterion, is consistent with the proposed mechanism for the formation of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(CH_2CN)$ (**7**) in which the $[CH_2CN]^-$ ligand is derived from reversible deprotonation of solvent by an intermediate cyclopentadienide counterion (Scheme 3). Although neither sterically nor electronically saturated, the bimetallic cation in **8** is unreactive toward $[CH_2CN]^-$, in contrast to the intermediate **12** in the reaction producing **7** (Scheme 3).

As would be expected, the cyclopentadienide counterion of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (**8**) displayed reactivity similar to that reported earlier for sodium cyclopentadienide. For example, **8** reacted quickly with $FeCl_2$ in acetonitrile at 25 °C to form the chloride salt **6** and $^1/_2$ equiv of Cp_2Fe (eq 6).[23] In a separate experiment the chloride **6** did not react with $FeCl_2$, indicating that the Cp groups transferred to iron in eq 6 were not those bound to the Ta center of **8**. In another reaction analogous to that which can be performed with NaCp, the addition of 1,2-dibromoethane to **8** in acetonitrile led to the formation of $^1/_2$ equiv of spiro[2.4]hepta-4,6-diene (eq 7).[24] Complex **8** cannot be thought of, however, as a completely equivalent replacement for MCp (M = Li, Na, K). For example, **8** does not react with acetone to form 6,6-dimethylfulvene, whereas the addition of cyclopentadienide salts to many ketones (including acetone) to form dialkylfulvene com-

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pounds is well-known.[30-34] Furthermore, 8 is insoluble in THF, a commonly used solvent for reactions of NaCp. An interesting aspect of the behavior of 8 is that essentially all of its chemistry is focused at the Cp counterion rather than at either of the metal centers.

Conclusions

An early–late heterobimetallic complex, $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1), has been prepared which undergoes facile Cp loss at palladium upon reaction with phosphines. Presumably, the lability of the Pd-bound Cp is a consequence of the electron richness of the palladium center of 1 (formally an 18 e^- species), despite the possibility for the Pd to back-donate electron density to the Ta center. Mechanistic studies suggest the participation of intermediates containing unbound cyclopentadienide counterions in several of these Cp-loss reactions. In one case the Ta–Pd complex $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (8) was isolated and structurally characterized. The cyclopentadienide counterion of 8 was found to react in much the same way as sodium cyclopentadienide.

Experimental Section

General Considerations. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere in a Vacuum Atmospheres DC-882 drybox equipped with an MO-40-2 Dri-Train or using standard Schlenk techniques. "Glass bomb" refers to a cylindrical, medium-walled Pyrex vessel joined to a Kontes K-826510 high-vacuum Teflon stopcock.

All ^1H, ^2H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on 300- or 400-MHz instruments at the University of California, Berkeley, NMR facility. One of the 300-MHz instruments was constructed by Mr. Rudi Nunlist and interfaced with a Nicolet 1280 computer. One 300-MHz and the 400-MHz machines were commercial Bruker AM or AMX series spectrometers. IR spectra were obtained on a Mattson Galaxy Series FTIR 3000 spectrometer. Mass spectrometry (MS) analyses were obtained at the UCB mass spectrometry facility on AEI MS-12 and Kratos MS-50 mass spectrometers. Conductivity measurements were obtained using a Fisher Scientific Co. digital conductivity meter. GC analyses were performed on an HP 5890A gas chromatograph equipped with a 95:5 dimethylsilicone/phenylmethylsilicone column. An HP 5970 Series mass selective detector attached to an HP 5890A GC instrument was used in GCMS analyses. Elemental analyses were obtained from the UCB Microanalytical Laboratory.

Benzene, toluene, pentane, Et_2O, and THF were distilled from sodium/benzophenone. Methylene chloride and acetonitrile were distilled from CaH_2. Trimethylphosphine and trimethyl phosphite were dried over sodium. 1,2-Dibromoethane was dried over 4-Å molecular sieves. $NaCH_2CN$ was prepared by allowing acetonitrile to react with $NaN(SiMe_3)_2$ in THF at −78 °C.[35] $Cp_2Ta(CH_2)(CH_3)$,[19] $CpPd(\eta^3\text{-}C_3H_5)$,[20] and $Cp^*Pd(\eta^3\text{-}C_3H_5)$[25] were prepared according to the literature. All other reagents were obtained from commercial suppliers and used without further purification.

Reactions with transferrable liquids involved condensation of a calculated pressure (ideal-gas law) of gas from a bulb of known volume into the reaction vessel at 77 K utilizing an MKS Baratron gauge attached to a high-vacuum line. Sealed NMR tubes were prepared by connecting a NMR tube to a Kontes vacuum adaptor via a Cajon joint, freezing and degassing the sample once (unless otherwise stated), and flame-sealing the tube with an oxygen/propane torch.

$Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ (1). In the drybox $Cp_2Ta(CH_2)(CH_3)$ (289 mg, 0.850 mmol) and $CpPd(\eta^3\text{-}C_3H_5)$ (183 mg, 0.681 mmol) were added as solids to a 19-mL glass bomb; 5 mL of THF was added into a separate glass bomb. The flask containing the solids was evacuated on a vacuum line at −78 °C to prevent loss of the volatile $CpPd(\eta^3\text{-}C_3H_5)$. THF was degassed by three freeze–pump–thaw cycles and then vacuum-transferred into the bomb containing the solids. The flask was transferred immediately to a −78 °C bath (acetone/CO_2) and warmed slowly to 5 °C over 4 h. The volatile materials were then removed from the reaction mixture (dark red solution containing a tan precipitate) under vacuum. The resulting brown powder was washed with Et_2O (3 × 15 mL) in the drybox followed by extraction with 10 mL of methylene chloride. The CH_2Cl_2 extract (dark orange-red solution) was filtered through Celite. Compound 1 was isolated in 70% yield (116 mg) as an orange crystalline solid by cooling this solution to −35 °C. ^1H NMR (CD_2Cl_2): δ 6.40 (s, 4H, CH_2), 6.19 (s, 5H, Cp), 4.60 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 118.1 (s, CH_2), 97.4 (s, Cp), 95.9 (s, Cp). IR (KBr): 3120 (m), 3097 (m), 2941 (m), 2898 (s), 1433 (m), 1332 (m), 1014 (s), 937 (m), 902 (m), 866 (m), 848 (s), 839 (s), 833 (s), 820 (s), 748 (s) cm^{-1}. Anal. Calcd. for $C_{17}H_{19}PdTa$: C, 39.98; H, 3.76. Found: C, 39.70; H, 3.60.

$Cp_2Ta(\mu\text{-}CH_2)_2Pd(PMe_3)(Cl)$ (2). In the drybox 10 mL of a CH_2Cl_2 solution of 1 (130 mg, 0.255 mmol) was added to a 50-mL glass bomb. Trimethylphosphine (34.4 torr, 29.7 mL, 0.255 mmol) was added by vacuum transfer at 77 K after degassing the solution. The reaction mixture was heated to 45 °C for 19 h, during the course of which the solution turned yellow. The volatile materials were removed under vacuum. The sticky yellow solid remaining was converted to a yellow powder by triturating once with pentane. The powder was then washed with Et_2O (3 × 3 mL). The off-white powder remaining was dissolved in 12 mL of hot benzene, and this solution was filtered through Celite. White platelike crystals of 2 were obtained in 85% yield (120 mg) by vapor diffusion of pentane into the benzene solution at room temperature. Analysis of the first Et_2O washing by GC confirmed the identity of $Cp_2(CH_2)$ as a reaction coproduct.[36] ^1H NMR (CD_2Cl_2): δ 7.19 (d, J_{HP} = 8.7 Hz, 2H, CH_2), 5.36 (s, 10H, Cp), 5.19 (d, J_{HP} = 5.1 Hz, 2H, CH_2), 1.42 (d, J_{HP} = 8.3 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 159.6 (d, J_{CP} = 45.9 Hz, CH_2), 118.8 (s, CH_2), 98.6 (s, Cp), 16.0 (d, J_{CP} = 22.4 Hz, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −20.7 (s). IR (KBr): 3109 (m), 3072 (s), 2960 (m), 2900 (s), 1432 (s), 1421 (m), 1280 (m), 1014 (m), 955 (s), 843 (s), 818 (s), 731 (m), 681 (m) cm^{-1}. HRMS (FAB): *m/e* calcd for $C_{21}H_{29}ClPPdTa$ 553.9746, found 553.9736.

$Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(Cl)$ (3). Into a 50-mL glass bomb was added an orange solution of 1 (132 mg, 0.259 mmol) dissolved in 10 mL of methylene chloride in the drybox. Trimethyl phosphite (31 μL, 0.263 mmol) was added to the solution by syringe. The reaction mixture was heated to 45 °C for 20 h, by which time the solution had turned cloudy tan. Removal of the volatile materials under vacuum left a sticky tan solid, which was converted to a powder by triturating once with pentane in the drybox. The crude product was washed with Et_2O (3 × 3 mL) and extracted with two 8-mL portions of benzene. The yellow-orange benzene solutions were filtered through Celite and reduced in volume to 4 mL each under vacuum with heating. Long white platelike crystals of 3 were obtained by vapor diffusion of pentane into the benzene solutions at room temperature. A second crop of crystals were obtained by cooling the resulting benzene/pentane (1:3) solutions to −35 °C, resulting in a combined yield of 66% (103 mg). Analysis of the first Et_2O wash by GC

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(36) Attempts to quantify the yield of $Cp_2(CH_2)$ against an internal standard by GC were complicated by its decomposition on the GC column (this was also observed for the authetic sample).

confirmed the identity of $Cp_2(CH_2)$ as a reaction coproduct.[36] ^{1}H NMR (C_6D_6): δ 7.22 (d, J_{HP} = 12.4 Hz, 2H, CH_2), 5.68 (d, J_{HP} = 2.9 Hz, 2H, CH_2), 4.61 (s, 10H, Cp), 3.81 (d, J_{HP} = 11.6 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.0 (d, J_{CP} = 63.5 Hz, CH_2), 121.0 (s, CH_2), 98.2 (s, Cp), 52.0 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.2 (s). IR (KBr): 3124 (m), 2964 (m), 2933 (m), 2925 (m), 1458 (m), 1439 (m), 1178 (m), 1070 (m), 1057 (m), 995 (s), 870 (m), 852 (m), 833 (m), 820 (m), 800 (s), 787 (m), 748 (s), 677 (m), 534 (m) cm^{-1}. A small amount of **3** was recrystallized a second time for elemental analysis by pentane diffusion into a saturated benzene solution at 25 °C. Anal. Calcd for $C_{21}H_{29}ClO_3PPdTa$ ($3{\cdot}C_6H_6$): C, 36.91; H, 4.28. Found: C, 36.51; H, 4.15.

[Cp$_2$Ta(μ-CH$_2$)$_2$Pd(PMe$_3$)$_2$]Cl (4). An orange solution of **1** (200 mg, 0.391 mmol) in 10 mL of CH_2Cl_2 was added into a 50-mL glass bomb. On a vacuum line trimethylphosphine (115 Torr, 138 mL, 0.856 mmol) was added by vacuum transfer at 77 K after degassing the solution by three freeze–pump–thaw cycles. The solution became pale yellow immediately on thawing. The solution was allowed to stand at room temperature for 18 h as it became more pale. The volatile materials were removed under vacuum, and the pale yellow powder remaining was washed with Et_2O (2 × 3 mL) in the drybox. The crude product was dissolved in 3 mL of acetonitrile and filtered through Celite. Very pale yellow platelike crystals of **4** were obtained by vapor diffusion of Et_2O into the acetonitrile solution at room temperature. A second crop was obtained by cooling the resulting CH_3CN/Et_2O (1:3) solution of −35 °C for a combined yield of 70% (174 mg). Analysis of the first Et_2O wash by GC confirmed the identity of $Cp_2(CH_2)$ as a reaction coproduct.[36] ^{1}H NMR (CD_2Cl_2): δ 6.09 (m, 4H, CH_2), 5.43 (s, 10H, Cp), 1.53 (m, 9H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.0 (m, CH_2), 99.9 (s, Cp) 18.2 (dd, J_{CP} = 14.5, 12.8 Hz, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −24.4 (s). IR (KBr): 3053 (m), 2960 (m), 2898 (m), 1440 (m), 1427 (m), 1286 (m), 1034 (m), 1010 (m), 976 (s), 949 (s), 825 (s), 812 (m), 725 (m), 675 (m), cm^{-1}. A small amount of **4** was recrystallized a second time for elemental analysis by Et_2O diffusion into a saturated acetonitrile solution at room temperature. Anal. Calcd for $C_{20}H_{35}ClNP_2PdTa$ ($4{\cdot}CH_3CN$): C, 35.63; H, 5.23; N, 2.08. Found: C, 35.93; H, 5.44; N, 1.94.

[Cp$_2$Ta(μ-CH$_2$)$_2$Pd(P(OMe)$_3$)$_2$]Cl (5). In the drybox **1** (117 mg, 0.230 mmol) was mixed with 4 mL of methylene chloride. Trimethyl phosphite (58 μL, 0.49 mmol) was added by syringe to the orange mixture (**1** was not completely dissolved) with stirring. The solution turned pale peach and homogeneous within 1 min and pale yellow over the next 1.5 h of standing at 25 °C. The volatile materials were removed under vacuum, and the resulting pale yellow solid was triturated once with Et_2O. The powder remaining was washed with 3 mL of Et_2O and dissolved in 3 mL of acetonitrile. The solution was filtered through Celite. Vapor diffusion of Et_2O into the acetonitrile solution at room temperature led to the isolation of small white platelike crystals of **5**. A second crop was obtained by cooling the 1:3 CH_3CN/Et_2O solution to −35 °C to give a total yield of 63% (106 mg). The production of $Cp_2(CH_2)$ as a reaction coproduct was confirmed by a GC and GCMS analysis of the Et_2O wash.[36] ^{1}H NMR (CD_3CN): δ 6.28 (m, 4H, CH_2), 5.45 (s, 10H, Cp), 3.60 (m, 18H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 137.2 (m, CH_2), 100.4 (s, Cp), 52.3 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.8 (s). IR (KBr): 3072 (m), 3060 (m), 2989 (m), 2945 (m), 2924 (m), 2842 (m), 1446 (m), 1182 (m), 1053 (s), 1018 (s), 995 (s), 877 (m), 856 (m), 841 (m), 822 (s), 802 (s), 777 (s), 766 (s), 742 (s), 542 (m), 528 (m) cm^{-1}. Elemental analysis was performed on a sample of **5** which had been recrystallized a second time by vapor diffusion of Et_2O into a saturated acetonitrile solution at room temperature. Anal. Calcd for $C_{20}H_{35}ClNO_6P_2PdTa$ ($5{\cdot}CH_3CN$): C, 31.19; H, 4.58; N, 1.82. Found: C, 31.09; H, 4.52; N, 1.78.

[Cp$_2$Ta(μ-CH$_2$)$_2$Pd(DMPE)]Cl (6). In the drybox **1** (272 mg, 0.532 mmol) was mixed with 10 mL of methylene chloride. By syringe DMPE (90 μL, 0.54 mmol) was added with stirring. The solution went from orange to yellow-brown over approximately 10 s. The solution was allowed to stand at room temperature for 12 h, after which time the volatile materials were removed under vacuum. The remaining yellow-tan powder was washed with 3 mL of Et_2O and extracted with acetonitrile (2 × 7 mL). The yellow CH_3CN solutions were filtered through Celite. Very pale yellow crystals of **6** (274 mg, 81%) were isolated by vapor diffusion of Et_2O into each of the acetonitrile solutions at 25 °C. GC analysis of the Et_2O wash indicated that $Cp_2(CH_2)$ was a reaction coproduct.[36] ^{1}H NMR (CD_2Cl_2): δ 5.91 (m, 4H, Ta–CH_2–Pd), 5.34 (s, 10H, Cp), 2.00 (d, J_{HP} = 17.0 Hz, 4H, DMPE CH_2), 1.59 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 130.4 (m, Ta–CH_2–Pd), 99.2 (s, Cp), 29.0 (m, DMPE CH_2), 14.6 (m, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 52.2 (s). IR (KBr): 3518 (m), 3323 (m), 3273 (m), 3203 (m), 3105 (m), 3057 (m), 2951 (m), 2908 (m), 2897 (s), 1423 (m), 1286 (m), 968 (m), 945 (s), 920 (m), 902 (s), 845 (s), 825 (s), 717 (m), 654 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{33}ClNP_2PdTa$ ($6{\cdot}CH_3CN$): C, 35.73; H, 4.95; N, 2.08. Found: C, 35.39; H, 4.91; N, 1.79.

Cp$_2$Ta(μ-CH$_2$)$_2$Pd(P(OMe)$_3$)(CH$_2$CN) (7). Method a. In the drybox 6 mL of acetonitrile was added to **1** (126 mg, 0.246 mmol), and the resulting slurry (**1** is only sparingly soluble) was transferred to a 50-mL glass bomb. Trimethyl phosphite (29 μL, 0.25 mmol) was added to the mixture by syringe. The reaction mixture was heated to 45 °C for 2 days (1 day is sufficient) as the orange mixture was slowly converted to an orange-red homogeneous solution. The volatile materials were removed under vacuum in the drybox, leaving a sticky orange-red residue which can be converted to a powder by repeated Et_2O triturations. ^{1}H NMR analysis of the crude reaction mixture indicated that **7** was formed in approximately 90% yield. The solid was washed once with pentane (3 mL) and extracted with 3 mL of benzene; the orange-red solution was filtered through Celite. The crude product was recrystallized by vapor diffusion of pentane into the 3-mL benzene solution at 25 °C. The solid was collected, dissolved in 2 mL of benzene, and recrystallized again by the same method. A third recrystallization was performed on the solid collected from the second by vapor diffusion of pentane into a 1-mL THF solution. A 2% (3 mg) yield of pale orange crystals, >97% pure by NMR spectroscopy, was isolated from the third recrystallization.

Method b. An acetonitrile (1.5 mL) solution of $NaCH_2CN$ (8.6 mg, 0.14 mmol) was added to 1.5 mL of an acetonitrile solution of $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(Cl)$ (**3**; 78.9 mg, 0.130 mmol) in the drybox with stirring. The light tan solution turned pale yellow as it was stirred at 25 °C for 5 h. The volatile materials were then removed under vacuum, and the sticky pale yellow solid remaining was converted to a tan powder by triturating with pentane three times. The crude product was recrystallized four times in a manner similar to that described in method a: once by pentane vapor diffusion into a benzene solution and then three times by pentane vapor diffusion into a THF solution, each at room temperature. From the fourth recrystallization was isolated 33 mg of solid, determined to be approximately 70% **7** by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 6.47 (d, J_{HP} = 11.3 Hz, 2H, Ta–CH_2–Pd), 5.68 (d, J_{HP} = 3.6 Hz, 2H, Ta–CH_2–Pd), 4.69 (s, 10H, Cp), 3.40 (d, J_{HP} = 12.0 Hz, 9H, CH_3), 2.04 (d, J_{HP} = 9.5 Hz, 2H, CH_2CN). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 141.8 (d, J_{CP} = 6.8 Hz, Ta–CH_2–Pd), 130.2 (s, CN), 125.6 (s, Ta–CH_2–Pd), 98.1 (s, Cp), 50.8 (d, J_{CP} = 1.3 Hz, CH_3), −9.9 (d, J_{CP} = 14.0 Hz, CH_2CN). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 52.0 (s). IR (KBr): 2993 (m), 2951 (s), 2166 (m), 1730 (s), 1479 (m), 1446 (s), 1442 (s), 1386 (m), 1271 (s), 1242 (s), 1192 (s), 1149 (s), 1061 (m), 1010 (s), 841 (m), 820 (m), 791 (m), 748 (m), 686 (m) cm^{-1}. Sufficient quantities of pure **7** for elemental analysis could not be obtained. Attempts at obtaining mass spectral data (EI, FAB) were unsuccessful due to excessive fragmentation.

[Cp$_2$Ta(μ-CH$_2$)$_2$Pd(DMPE)]Cp (8). In the drybox 5 mL of CH_3CN was mixed with the sparingly soluble **1** (191 mg, 0.373 mmol). An orange solution quickly formed as DMPE (65 μL, 0.39 mmol) was added slowly by syringe with stirring. After 9 h of stirring at 25 °C a yellow solution containing a tan precipitate remained, and this was filtered through Celite. Vapor diffusion of Et_2O into the CH_3CN solution at room temperature led to the isolation of tan platelike crystals of **8**. A second crop was obtained by cooling the 3:1 Et_2O/CH_3CN solution to −35 °C for a total yield of 210 mg (85%). ^1H NMR (CD_3CN): δ 5.91 (m, 4H, Ta–CH_2–Pd), 5.48 (s, 5H, free Cp), 5.31 (s, 10H, Ta–Cp), 1.94 (d, J_{HP} = 16.9 Hz, 4H, DMPE CH_2), 1.53 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 130.1 (m, Ta–CH_2–Pd), 104.2 (s, free Cp), 99.7 (s, Ta–Cp), 14.2 (m, DMPE CH_2), 28.9 (dd, J_{CP} = 23.8, 22.6 Hz, CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 28.3 (s). IR (KBr): 3103 (m), 3037 (m), 2952 (m), 2895 (m), 1433 (s), 1419 (s), 1377 (m), 1365 (m), 1284 (m), 1007 (s), 939 (s), 922 (m), 904 (s), 843 (s), 839 (s), 825 (s), 748 (m), 715 (m), 686 (s), 665 (s), 654 (s), 449 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{35}P_2PdTa$: C, 41.80; H, 5.34. Found: C, 41.50; H, 5.32 (performed on the combined crops of **8**).

$Cp_2Ta(\mu\text{-}CH_2)_2PdCp^*$ (9). In the drybox a THF (6 mL) solution of $Cp^*Pd(\eta^3\text{-}C_3H_5)$ (283 mg, 1.62 mmol) was added to a 50-mL glass bomb. To this was added $Cp_2Ta(CH_2)(CH_3)$ (555 mg, 1.63 mmol) dissolved in 4 mL of THF. The reaction mixture was then heated to 45 °C for 21.5 h, during which time the dark brown-purple solution turned dark orange. The volatile materials were removed under vacuum. Inside the drybox the orange-brown residue was washed with pentane (4 × 4 mL) and extracted with benzene (2 × 5 mL). The separate dark orange benzene solutions were filtered through Celite. Dark red crystalline **9** was isolated by vapor diffusion of pentane into each of the two benzene solutions at room temperature. A second crop was obtained by cooling the two benzene/pentane (1:3) solutions to −35 °C for a total yield of 470 mg (50%). ^1H NMR (C_6D_6): δ 5.52 (s, 4H, CH_2), 4.66 (s, 10H, Cp), 2.23 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 124.7 (s, CH_2), 104.2 (s, C_5Me_5), 96.4 (s, Cp), 11.1 (s, $C_5\mathit{Me}_5$). IR (KBr): 3107 (m), 2954 (m), 2922 (s), 2881 (s), 2848 (s), 1435 (m), 1375 (m), 1157 (m), 1012 (m), 922 (m), 897 (m), 831 (s), 810 (s), 598 (m). Anal. Calcd for $C_{22}H_{29}PdTa$: C, 45.49; H, 5.04. Found: C, 45.65; H, 5.05 (performed on the combined crops of **9**).

Conductivity Measurements of 6 and 8. In the drybox 5 mL of acetonitrile was added by gastight syringe to a weighed amount of either **6** or **8**. The specific conductivity (κ) of the solution was then determined by successive measurements obtained on diluted aliquots from these solutions in order to ensure that the observed conductivity was valid over a range of concentrations. The molar conductivities (Λ_m) for **6** and **8**, calculated from the measured specific conductivity using the standard equation ($\Lambda_m = \kappa/c$, where c = concentration), were found to be consistent with the expected values for a 1:1 electrolyte over a 10-fold concentration range.[37] For example, Λ_m for **6** ranged from 161 Ω^{-1} cm^2 mol^{-1} (1.58 mM) to 190 Ω^{-1} cm^2 mol^{-1} (0.16 mM) and from 167 Ω^{-1} cm^2 mol-1 (1.72 mM) to 192 Ω^{-1} cm^2 mol^{-1} (0.17 mM) for **8**. These values are at the upper limit of what is typically considered a 1:1 electrolyte, indicating the existence of little to no ion pairing. Ion pairing would be expected to result in lower conductivity values, the exact level depending on the extent of pairing.

Reaction of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (8) with $FeCl_2$. A solution of **8** (25.4 mg, 3.84×10^{-5} mol) in 1 mL of acetonitrile was added to $FeCl_2$ (98%, 6.4 mg, 4.95×10^{-5} mol) in the drybox. The pale peach solution quickly became dark yellow. After 15 min of standing at 25 °C the solution was transferred to a sublimation apparatus and the volatiles were removed under vacuum. Ferrocene (5.7 mg, 80%) was isolated by sublimation and identified by ^1H NMR spectroscopy and GC as compared to an authentic sample.[23]

Reaction of $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)]Cp$ (8) with 1,2-Dibromomethane. In the drybox 0.45 mL of a CD_3CN solution of 1,2-dibromoethane (99.9%, 1.2 μL, 1.39×10^{-5} mol) was added to **8** (7.6 mg, 1.15×10^{-5} mol) together with an internal standard (1.8 mg of 1,3,5-trimethoxybenzene). The colorless solution was transferred to an NMR tube, which was sealed under vacuum. Monitoring by ^1H NMR spectroscopy demonstrated that spiro[2.4]hepta-4,6-diene was produced in 50% yield. After 19.5 h at room temperature the reaction mixture was poured into a 19-mL glass bomb and the volatiles, containing unreacted 1,2-dibromoethane and spiro[2.4]hepta-4,6-diene, were transferred to a 3-mL glass bomb by vacuum transfer. The identity of the organic product was confirmed by GC and GCMS analysis of the volatiles as compared to an authentic sample.[24]

X-ray Crystal Structure Determinations. The X-ray crystal structures of **6** and **8** were determined by Dr. F. J. Hollander. Crystals of the compounds, grown as described above, were mounted on glass fibers using poly(cyanoacrylate) cement and coated with the cement to protect them from the atmosphere. The crystal used for data collection was then transferred to a Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded the primitive cell. The final cell parameters and specific data collection parameters for these data sets are given in Table 1 for **6** and Table 4 for **8**. For compound **8** the maximum value of h was expected to be $h = 11$. Data were only collected, however, from $h = 0$ to $h = 7$ due to accidental interruption of the data collection and loss of crystal orientation.

The raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. For complex **6**, the maximum correction for crystal decay was 3.1% on F. No correction for crystal decomposition was necessary for **8**. An empirical correction based on the observed variation in the azimuthal scan data was applied for both compounds. Removal of systematically absent data left the unique data in the final data set. The structures were solved by Patterson methods and refined via standard least-squares and Fourier techniques.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

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Supplementary Material Available: Complete tables of intramolecular bond distances and bond angles and anisotropic thermal parameters for **6** and **8** (5 pages). This material is provided with the archival edition of this journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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