Inorg. Chem. **2008**, *47*, 10682−10691

Inorganic Chemistry
Article

Mono(cycloheptatrienyl) Tantalum Chemistry: Synthesis and Characterization of New Tantalum Halide, Hydride, and Alkyl Species

Wontae Noh and Gregory S. Girolami*

School of Chemical Sciences, University of Illinois at Urbana−Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received August 11, 2008

The new tantalum(II) complex (η^6-C_7H_8)$TaCl_2(PMe_3)_2$ (**1**) was synthesized by the reduction of $TaCl_5$ with *n*-butyllithium in the presence of PMe_3 and cycloheptatriene. Compound **1** adopts a four-legged piano stool structure in which the tantalum center is bound to a η^6-cycloheptatriene ring in addition to two chlorides and two phosphine ligands in a transoid arrangement. Treatment of **1** with methyllithium results in a loss of the equivalents of HCl and formation of the η^7-cycloheptatrienyl complex (η^7-C_7H_7)$TaCl(PMe_3)_2$ (**2**), whereas treatment of **1** with sodium or sodium borohydride affords small amounts of the η^5-cycloheptadienyl complex (η^5-C_7H_9)$TaCl_2(PMe_3)_2$ (**3**). Compound **2** adopts a three-legged piano stool structure; the η^7-C_7H_7 ring is fully aromatic and planar. The molecular structure of **3** is similar to that of **1**, except for the η^5 binding mode of the seven-membered ring. Treatment of the previously described sandwich compound $(C_5Me_5)Ta(C_7H_7)$ with allyl bromide affords the tantalum(V) product $(C_5Me_5)Ta(C_7H_7)Br$ (**4**), which reacts with $LiAlH_4$ to give the tantalum(V) hydride $(C_5Me_5)Ta(C_7H_7)H$ (**5**). Compound **4** also reacts with alkylating agents to generate the methyl, allyl, and cyclopropyl complexes $(C_5Me_5)Ta(C_7H_7)Me$ (**6**), $(C_5Me_5)Ta(C_7H_7)(\eta^1$-$CH_2CH{=}CH_2)$ (**7**), and $(C_5Me_5)Ta(C_7H_7)(c$-$C_3H_5)$ (**8**). Compounds **4**−**8** all adopt bent sandwich structures in which the dihedral angle between the two carbocyclic rings is 34.9° for the bromo compound **4**, 26.6° for the hydride **5**, 33.1° for the methyl compound **6**, 34.2° for the allyl compound **7**, and 37.5° for the cyclopropyl compound **8**. ^1H and ^{13}C NMR data are reported for the diamagnetic compounds.

Introduction

Tantalum metal is increasingly being considered as a diffusion barrier material in ultra-large-scale integration circuits.[1,2] Although it is straightforward to generate tantalum thin films by physical vapor deposition, essentially no methods have been described that afford pure tantalum thin films by chemical vapor deposition (CVD). In commercially available metal−organic sources, such as the imide $Ta(NEt_2)_3$(N-*t*-Bu), the tantalum center is in a high oxidation state, usually Ta^V, and attempts to reduce the Ta to the metallic state invariably result in some degree of carbon incorporation. Even in the presence of atomic hydrogen, $Ta(NMe_2)_3$(N-*t*-Bu) affords films of TaN/TaC.[3]

Bis(arene) complexes of certain transition metals, such as bis(benzene)chromium, have long been known to serve as useful precursors for the thermal CVD of pure metal thin films.[4−9] Conceptually, these precursors are attractive because the metal is formally in the zero oxidation state, and conversion to the metal can be envisaged as involving simple dissociation of the arene ligands. For tantalum, the bis(benzene) complex $Ta(C_6H_6)_2$ is known, but it is difficult to prepare without specialized apparatus.[10] A potential alternative to $Ta(C_6H_6)_2$ is the isomeric complex (cyclopentadienyl)

---

* Author to whom correspondence should be addressed. E-mail: girolami@scs.uiuc.edu.

(1) Kim, H. *J. Vac. Sci. Technol., B* **2003**, *21*, 2231–2261.

(2) Rossnagel, S. M.; Sherman, A.; Turner, F. *J. Vac. Sci. Technol., B* **2000**, *18*, 2016–2020.

(3) Park, J. S.; Park, H. S.; Kang, S. W. *J. Electrochem. Soc.* **2002**, *149*, C28−C32.

(4) Knap, J. E.; Pesetsky, B.; Hill, F. N. *Plating (Paris)* **1966**, *53*, 772–782.

(5) Anantha, N. G.; Doo, V. Y.; Seto, D. K. *J. Electrochem. Soc.* **1971**, *118*, 163–165.

(6) Koleshko, V. M.; Reznikov, B. S.; Utkina, E. A. *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **1979**, *15*, 612–615.

(7) Maury, F. *Appl. Organomet. Chem.* **1992**, *6*, 619–626.

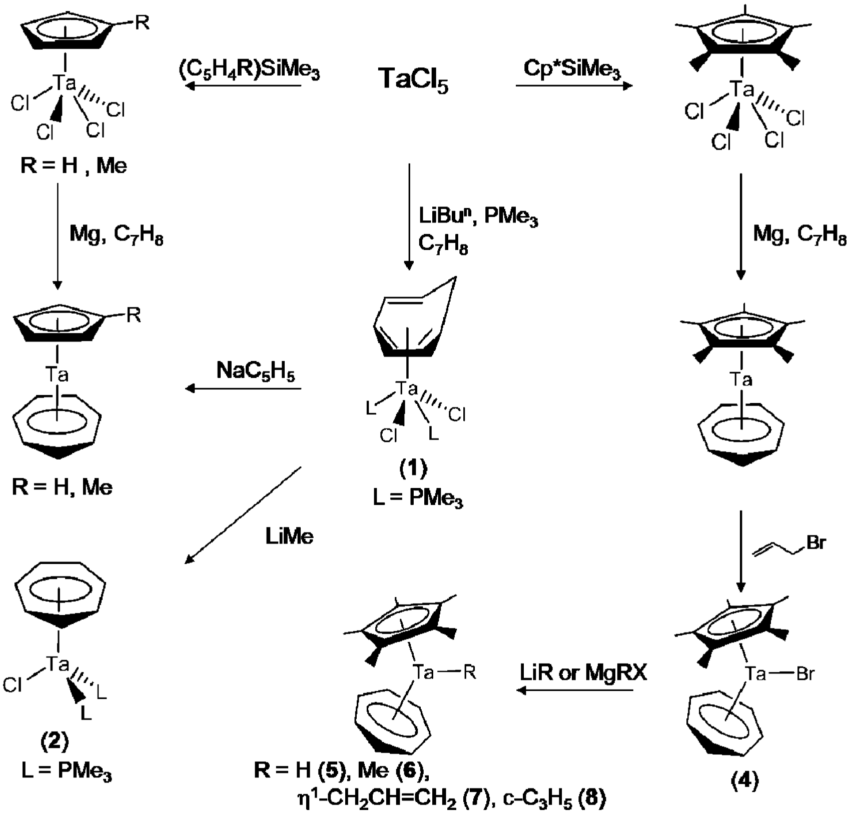
(8) Hanko, K.; Vass, G.; Szepes, L. *J. Organomet. Chem.* **1995**, *492*, 235–239.

(9) Maury, F.; Vahlas, C.; Abisset, S.; Gueroudji, L. *J. Electrochem. Soc.* **1999**, *146*, 3716–3723.

(10) Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938–1943.

10.1021/ic8015035 CCC: $40.75

Scheme 1. Reaction Chemistry of the New Tantalum Compounds



(cycloheptatrienyl)tantalum $Ta(C_5H_5)(C_7H_7)$. The related titanium compound $Ti(C_5H_5)(C_7H_7)$ has been briefly investigated by others as a CVD precursor for titanium-containing films.[11] These authors suggested that $Ti(C_5H_5)(C_7H_7)$ may rearrange to the bis(arene) complex $Ti(C_6H_6)_2$ upon ionization in the gas phase, and that this rearrangement helps prevent carbon incorporation in the deposited films. If so, the deposition of pure metals may be possible by CVD from their mixed cyclopentadienyl/cycloheptatrienyl complexes. Transition metal compounds that contain cycloheptatriene (C_7H_8) and cycloheptatrienyl (C_7H_7) rings are rare relative to compounds with cyclopentadienyl and arene ligands.[12] For tantalum, the chemistry of $(\eta^6\text{-}C_7H_8)Ta$ and $(\eta^7\text{-}C_7H_7)Ta$ complexes is particularly poorly developed; for example, half-sandwich complexes of tantalum bearing one cycloheptatrienyl ring are completely unknown. Recently, we have reported a series of the mixed sandwich compounds, $(C_5R_5)Ta(C_7H_7)$ (R = H, Me), electron paramagnetic resonance spectra and electronic parameters of these complexes and the structural comparison of $(C_5R_5)M(C_7H_7)$ based on the radii of the metal centers.[13]

In an effort to expand the chemistry of $(\eta^6\text{-}C_7H_8)Ta$ and $(\eta^7\text{-}C_7H_7)Ta$ complexes, we describe our efforts to synthesize new tantalum compounds containing $\eta^5\text{-}C_7H_9$, $\eta^6\text{-}C_7H_8$, and $\eta^7\text{-}C_7H_7$ rings. In the course of this work, we have developed a new synthetic entry into such species, $(\eta^6\text{-}C_7H_8)TaCl_2(PMe_3)_2$ (**1**), which can be prepared by the reduction of $TaCl_5$ in the presence of PMe_3 and cycloheptatriene. In the following report, we describe the conversion of this complex to a variety of compounds, including $(\eta^7\text{-}C_7H_7)TaCl(PMe_3)_2$ (**2**), $(\eta^5\text{-}C_7H_9)TaCl_2(PMe_3)_2$ (**3**), and several derivatives of the type $(C_5Me_5)Ta(C_7H_7)R$, where R is a halide, hydride, or alkyl group. All of these compounds have been characterized by X-ray crystallography. The interconversions of these compounds are summarized in Scheme 1.

Results and Discussion

Synthesis and Characterization of $(\eta^6\text{-}C_7H_8)TaCl_2(PMe_3)_2$ (1). The reaction of $TaCl_5$ in diethyl ether with three equivalents of *n*-butyllithium in the presence of PMe_3, followed by the addition of excess C_7H_8, affords a dark red solution, from which the 17-electron cycloheptatriene tantalum compound $(\eta^6\text{-}C_7H_8)TaCl_2(PMe_3)_2$ (**1**) can be obtained by crystallization at −20 °C. Dark brown crystals of **1** are obtained in ~29% yield.

$$TaCl_5 + 2PMe_3 + 3Li(n\text{-}Bu) + C_7H_8 \rightarrow \underset{\mathbf{1}}{(\eta^6\text{-}C_7H_8)TaCl(PMe_3)_2} + 3LiCl + ...$$

The preparation of **1** depends sensitively on the order and timing of reagent additions: the $TaCl_5$ should be treated with PMe_3 before the addition of *n*-butyllithium, and the cycloheptatriene should be added after the resulting solution turns brown. Analogues of compound **1** cannot be obtained when PMe_3 is replaced with other Lewis bases such as PPh_3 or THF. In addition, *n*-butyllithium is the only successful

---

(11) Charatan, R. M.; Gross, M. E.; Eaglesham, D. J. *J. Appl. Phys.* **1994**, *76*, 4377–4382.

(12) Green, M. L. H.; Ng, D. K. P. *Chem. Rev.* **1995**, *95*, 439–473.

(13) Noh, W.; Girolami, G. S. *Inorg. Chem.* **2008**, *47*, 535–542.

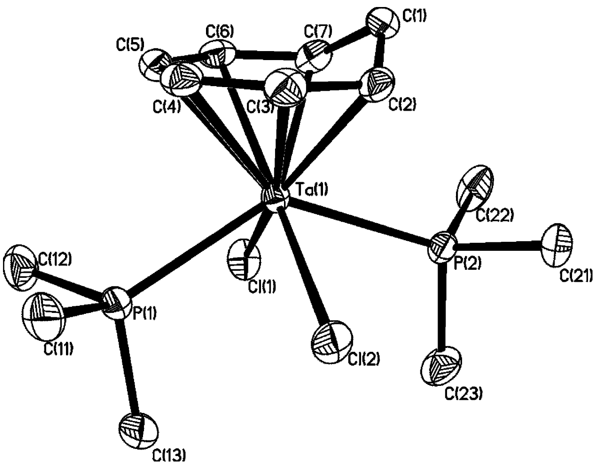


Figure 1. Molecular structure of (η^6-C_7H_8)$TaCl_2(PMe_3)_2$ (**1**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

reducing agent.[14] Other common reductants—such as Na, Na/Hg, and Mg, which are useful in the syntheses of the Nb[15] and the Zr[16] analogs—react with $TaCl_5$ and PMe_3 in the presence of cycloheptatriene to afford the known Ta^{IV} species $TaCl_4(PMe_3)_3$.[17]

The field desorption mass spectrum of **1** shows a group of peaks centered at 496.2 due to the molecular ion. The relative peak intensities within this envelope correspond well with the calculated isotope distribution for **1**. The IR spectrum of **1** shows two bands at 3045 and 3029 cm^{-1} due to sp^2 C−H stretching modes, and two additional bands at 1174 and 1150 cm^{-1} that are assigned to in-plane C−H deformation modes of the C_7H_8 ring.[18,19] Strong bands due to PMe_3 at 1279, 1268, and 959 cm^{-1} are also observed.[20] Chemically related to **1** are compounds of stoichiometry (η^6-C_7H_8)MX_2L_2 where M = Zr[16] or Nb,[15,21] X = Cl or I, and L = PMe_3, THF, or $^1/_2Me_2PCH_2CH_2PMe_2$.

The molecular structure of **1** is shown in Figure 1. Crystallographic data are summarized in Table 1, and important bond distances and angles are given in Table 2. The coordination geometry about the Ta center corresponds to a four-legged piano stool; the tantalum center is capped with a η^6-C_7H_8 ligand and is bound to two chlorides and two phosphine ligands. As is typical of cycloheptatrienyl rings, the six sp^2-hybridized carbon atoms of the C_7H_8 ring are more or less coplanar, whereas the sp^3 carbon (which is not bound to the Ta center) lies out of this plane. The two chlorine atoms are mutually transoid, as are the two phosphine groups. The Ta−C distances range from 2.312(6) to 2.418(6) Å. The C−C distances between the methine carbon atoms of the C_7H_8 ring range from 1.378(8) to 1.431(8) Å, with the shortest distances being seen for C(2)−C(3) and C(6)−C(7), the bonds at the ends of the π system. The C−C distances to the methylene carbon, which are 1.496(9) and 1.521(9) Å, are typical of single C−C bonds. The average Ta−Cl distance is 2.53 Å, and the average Ta−P distance is 2.61 Å.

Compound **1** is isostructural with its Nb[15] and Zr[16] analogues, (η^6-C_7H_8)$MCl_2(PMe_3)_2$, which crystallize in the same space group and exhibit similar unit cell dimensions. For comparison, in the Nb compound, the Nb−C distances to the seven-membered ring range from 2.349(5) to 2.413(5) Å, and the average Nb−Cl and Nb−P distances are 2.53 and 2.64 Å, respectively. In the Zr compound, the Zr−C distances to the seven-membered ring range from 2.395(15) to 2.487(7) Å, and the average Zr−Cl and Zr−P distances are 2.52 and 2.77 Å, respectively. Within this series, the metal−ligand distances vary as Ta < Nb < Zr, and this order agrees with the relative sizes of these metals.

Synthesis and Characterization of (η^7-C_7H_7)$TaCl(PMe_3)_2$ (2). Attempts to alkylate **1** with two equivalents of various organolithium and organomagnesium reagents invariably result in the formation of maroon-colored solutions, but in most cases, we could not isolate pure products. Treatment of **1** with one equivalent of methyllithium in diethyl ether, however, followed by crystallization at −20 °C, gave dark brown crystals of the new 17-electron compound (η^7-C_7H_7)$TaCl(PMe_3)_2$ (**2**) in 11% yield. In this reaction, methyllithium is simply acting as a base to remove the components of HCl. Because *n*-butyllithium can also act as a base as well as a reductant, small amounts of **2** are sometimes observed among the products formed in the synthesis of **1**.

$$(\eta^6\text{-}C_7H_8)TaCl_2(PMe_3)_2 + LiR \rightarrow \underset{\mathbf{2}}{(\eta^7\text{-}C_7H_7)TaCl(PMe_3)_2} + LiCl + RH$$

The IR spectrum of **2** shows bands at 1172 and 1154 cm^{-1} due to in-plane C−H deformations of the seven-membered ring, and bands at 1279, 1268, and 959 cm^{-1} due to PMe_3. A few compounds are known that are chemically similar to **2**: these have the stoichiometry (η^7-C_7H_7)MXL_2 where M = Ti,[22] Zr,[23,24] Nb,[15,21] or W;[25] X = Cl or I; and L = PMe_3, THF or $^1/_2Me_2PCH_2CH_2PMe_2$.

The molecular structure of **2** is shown in Figure 2. Crystallographic data are summarized in Table 1, and important bond distances and angles are given in Table 3. The molecular structure of **2** can be described as a three-legged piano stool; the tantalum center is capped with a η^7-C_7H_7 ligand and is coordinated to one chloride and two phosphine ligands. Unlike the η^6-C_7H_8 ring in **1**, the C_7H_7

---

(14) Eisch, J. J.; Gitua, J. N. *Eur. J. Inorg. Chem.* **2002**, 3091–3096.

(15) Green, M. L. H.; Hughes, A. K.; McGowan, P. C.; Mountford, P.; Scott, P.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1591–1600.

(16) Diamond, G. M.; Green, M. L. H.; Mountford, P.; Walker, N. M.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 417–422.

(17) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 4046–4050.

(18) Satink, R. G.; Meijer, G.; von Helden, G. *J. Am. Chem. Soc.* **2003**, *125*, 15714–15715.

(19) Harvey, P. D.; Butler, I. S.; Gilson, F. R. *Inorg. Chem.* **1987**, *26*, 32–38.

(20) Halmann, M. *Spectrochim. Acta* **1960**, *16*, 407–412.

(21) Green, M. L. H.; Mountford, P.; Scott, P.; Mtetwa, V. S. B. *Polyhedron* **1991**, *10*, 389–392.

(22) Diamond, G. M.; Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Dalton Trans.* **1992**, 2259–2261.

(23) Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 908–909.

(24) Green, J. C.; Green, M. L. H.; Walker, N. M. *J. Chem. Soc., Dalton Trans.* **1991**, 173–180.

(25) Green, M. L. H.; Ng, D. K. P.; Wong, H.-V. *J. Chem. Soc., Dalton Trans.* **1993**, 3213–3217.

Table 1. Crystallographic Data for the New Tantalum Compounds at 193 K ($\lambda = 0.71073$ Å)

	1	2	3	4	5	6	7	8
space group	$P2_12_12_1$	Pn	$P2_1/n$	$P\bar{1}$	$Pbca$	$Pnma$	$P2_1/c$	$Pnma$
a/Å	11.5356(15)	6.689(3)	13.038(3)	9.352(3)	9.2628(19)	10.750(3)	15.475(3)	15.463(3)
b/Å	12.1675(16)	12.867(5)	10.2103(19)	11.499(4)	13.519(3)	12.064(4)	15.264(3)	11.574(2)
c/Å	13.2211(17)	9.599(4)	14.903(3)	15.065(5)	23.560(5)	11.646(4)	14.326(3)	9.2783(18)
α/deg	90	90	90	103.903(6)	90	90	90	90
β/deg	90	91.052(6)	115.158(3)	90.182(6)	90	90	92.191(4)	90
γ/deg	90	90	90	91.093(6)	90	90	90	90
V/Å^3	1855.7(4)	826.0(6)	1795.7(6)	1572.3(9)	2950.3(10)	1510.3(8)	3381.6(13)	1660.5(6)
Z	4	2	4	4	8	4	8	4
data/restraints/parameters	4561/0/169	3001/103/160	4417/0/169	5791/0/353	2683/530/264	1959/0/95	6219/0/389	1596/0/118
goodness-of-fit on F^2	1.013	0.974	0.936	0.835	0.954	1.020	0.923	1.161
R_1 [$I > 2\sigma(I)$]^a	0.0324	0.0901	0.0383	0.0349	0.0307	0.0314	0.0347	0.0240
wR_2 (all data)^a	0.0654	0.2267	0.0832	0.0690	0.0633	0.0926	0.0774	0.0649

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances and Angles for (η^6-C_7H_8)$TaCl_2(PMe_3)_2$ (**1**)

Bond Distances (Å)			
Ta(1)−C(2)	2.312(6)	Ta(1)−C(3)	2.414(6)
Ta(1)−C(4)	2.418(6)	Ta(1)−C(5)	2.401(6)
Ta(1)−C(6)	2.398(5)	Ta(1)−C(7)	2.329(6)
Ta(1)−Cl(1)	2.5332(14)	Ta(1)−Cl(2)	2.5235(14)
Ta(1)−P(1)	2.5940(15)	Ta(1)−P(2)	2.6334(14)
C(1)−C(2)	1.521(9)	C(2)−C(3)	1.388(9)
C(3)−C(4)	1.415(8)	C(4)−C(5)	1.431(8)
C(5)−C(6)	1.404(9)	C(6)−C(7)	1.378(8)
C(7)−C(1)	1.496(9)		
Bond Angles (deg)			
C(1)−C(2)−C(3)	123.5(5)	C(2)−C(3)−C(4)	125.7(6)
C(3)−C(4)−C(5)	129.3(6)	C(4)−C(5)−C(6)	128.7(5)
C(5)−C(6)−C(7)	127.3(5)	C(6)−C(7)−C(1)	123.5(6)
C(7)−C(1)−C(2)	113.0(5)	Cl(1)−Ta(1)−Cl(2)	111.07(5)
Cl(1)−Ta(1)−P(1)	75.81(5)	Cl(1)−Ta(1)−P(2)	76.40(5)
Cl(2)−Ta(1)−P(1)	76.12(5)	Cl(2)−Ta(1)−P(2)	76.16(5)
P(1)−Ta(1)−P(2)	129.84(5)		

Table 3. Selected Bond Distances and Angles for (η^7-C_7H_7)$TaCl(PMe_3)_2$ (**2**)

Bond Distances (Å)			
Ta(1)−C(1)	2.29(3)	Ta(1)−C(2)	2.32(3)
Ta(1)−C(3)	2.35(3)	Ta(1)−C(4)	2.34(3)
Ta(1)−C(5)	2.28(3)	Ta(1)−C(6)	2.29(3)
Ta(1)−C(7)	2.33(3)	Ta(1)−Cl(1)	2.523(8)
Ta(1)−P(1)	2.599(7)	Ta(1)−P(2)	2.612(8)
C(1)−C(2)	1.42(4)	C(2)−C(3)	1.44(4)
C(3)−C(4)	1.41(4)	C(4)−C(5)	1.43(4)
C(5)−C(6)	1.36(4)	C(6)−C(7)	1.42(4)
C(7)−C(1)	1.44(4)		
Bond Angles (deg)			
C(1)−C(2)−C(3)	131(3)	C(2)−C(3)−C(4)	129(2)
C(3)−C(4)−C(5)	125(3)	C(4)−C(5)−C(6)	130(3)
C(5)−C(6)−C(7)	132(3)	C(6)−C(7)−C(1)	126(3)
C(7)−C(1)−C(2)	127(3)	Cl(1)−Ta(1)−P(1)	81.1(3)
Cl(1)−Ta(1)−P(2)	80.7(2)	P(1)−Ta(1)−P(2)	97.5(3)

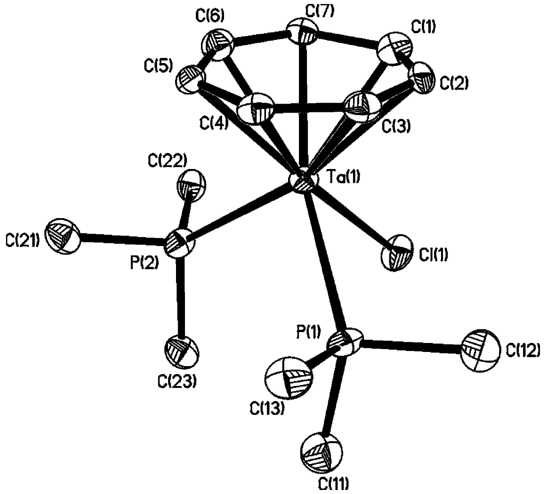


Figure 2. Molecular structure of (η^7-C_7H_7)$TaCl(PMe_3)_2$ (**2**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

ring in **2** is fully aromatic and planar. The Ta−C distances range from 2.29(3) to 2.35(3) Å, and the C−C distances within the C_7H_7 ring range from 1.36(4) to 1.44(4) Å. The Ta−Cl distance is 2.523(8) Å, and the average Ta−P distance is 2.61 Å. Interestingly, the Ta−C, Ta−Cl, and Ta−P distances are almost exactly the same as those in **1**. Although **1** and **2** have the same electron counts (17) and coordination numbers (7), they do have different formal oxidation states (Ta^{II} for **1** and Ta^0 or Ta^{IV} for **2**, depending on the charge assigned to the C_7H_7 ring). Evidently, the bond distances in these complexes are not strongly correlated with the formal oxidation state.

Compound **2** is isostructural with its (η^7-C_7H_7)$NbI(PMe_3)_2$[15,21] and (η^7-C_7H_7)$ZrI(PMe_3)_2$[23] analogues, which crystallize in the same space group and exhibit similar unit cell dimensions. In the Nb compound, the mean Nb−C distance to the seven-membered ring is 2.34 Å, and the average Nb−P distance is 2.66 Å; in the Zr compound, the mean Zr−C distance is 2.36 Å, and the average Zr−P distance is 2.81 Å. These distances again reflect the relative sizes of the metals, Ta < Nb < Zr.

Synthesis and Characterization of (η^5-C_7H_9)$TaCl_2(PMe_3)_2$ (3). Attempts to reduce the Nb analog of **1**, (η^6-C_7H_8)$NbCl_2(PMe_3)_2$, with Na/Hg have been reported to be unsuccessful.[15] We find that the reduction of **1** with Na or $NaBH_4$ produces small amounts of a new compound, (η^5-C_7H_9)$TaCl_2(PMe_3)_2$ (**3**), in which the cycloheptatriene ring is reduced to a cycloheptadienyl group.

$$(\eta^6\text{-}C_7H_8)TaCl_2(PMe_3)_2 + NaBH_4 \rightarrow \underset{\mathbf{3}}{(\eta^5\text{-}C_7H_9)TaCl_2(PMe_3)_2} + ...$$

The molecular structure of **3** is shown in Figure 3. Crystallographic data are summarized in Table 1, and important bond distances and angles are given in Table 4. The molecular structure of **3** resembles that of **1**, except for the binding mode of the seven-membered ring, which is coordinated to the metal center in a η^5 mode. The two

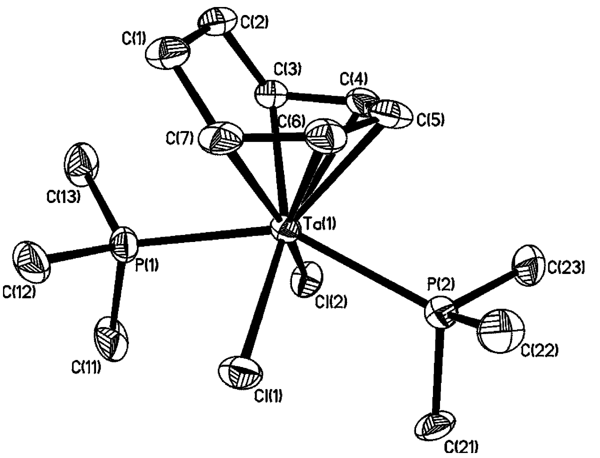


Figure 3. Molecular structure of (η^5-C_7H_9)$TaCl_2(PMe_3)_2$ (**3**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances and Angles for (η^5-C_7H_9)$TaCl_2(PMe_3)_2$ (**3**)

Bond Distances (Å)			
Ta(1)−C(3)	2.269(6)	Ta(1)−C(4)	2.315(6)
Ta(1)−C(5)	2.383(6)	Ta(1)−C(6)	2.297(5)
Ta(1)−C(7)	2.242(5)	Ta(1)−Cl(1)	2.4645(15)
Ta(1)−Cl(2)	2.4618(13)	Ta(1)−P(1)	2.5895(16)
Ta(1)−P(2)	2.6214(17)	C(1)−C(2)	1.530(8)
C(2)−C(3)	1.516(8)	C(3)−C(4)	1.446(8)
C(4)−C(5)	1.410(8)	C(5)−C(6)	1.404(8)
C(6)−C(7)	1.449(8)	C(7)−C(1)	1.532(8)
Bond Angles (deg)			
C(1)−C(2)−C(3)	111.5(5)	C(2)−C(3)−C(4)	116.4(5)
C(3)−C(4)−C(5)	118.8(6)	C(4)−C(5)−C(6)	124.6(6)
C(5)−C(6)−C(7)	124.9(5)	C(6)−C(7)−C(1)	122.0(6)
C(7)−C(1)−C(2)	111.6(5)	Cl(1)−Ta(1)−Cl(2)	102.64(5)
Cl(1)−Ta(1)−P(1)	78.60(6)	Cl(1)−Ta(1)−P(2)	77.37(5)
Cl(2)−Ta(1)−P(1)	81.89(5)	Cl(2)−Ta(1)−P(2)	79.60(5)
P(1)−Ta(1)−P(2)	145.47(5)		

chloride and two phosphine ligands are arranged in a transoid fashion, as seen in **1**.

The Ta−C distances range from 2.242(6) to 2.383(6) Å. These distances range over a larger spread than seen for **1** and **2**: within the π system, the shortest Ta−C distances are to the two terminal carbon atoms, and the longest is to the central carbon atom. The C−C distances within the C_7H_9 π system range from 1.404(8) to 1.449(8) Å; in contrast, the C−C distances involving the two methylene carbons are much longer, ~1.52 Å, and correspond to single bonds. The bonding of the Ta center to the η^5-C_7H_9 ring is similar to that found in other complexes of this ligand, such as K[(η^5-C_7H_9)$M(CO)_3$] (M = Cr, Mo)[26] and [(η^5-C_7H_9)$W(CO)_2(PPh_3)_2$]BF_4.[27] The average Ta−Cl distance is 2.46 Å, and the average Ta−P distance is 2.61 Å. Interestingly, the Ta−Cl distance in **3** is ~0.06 Å shorter than those in **1** and **2**, whereas the Ta−P distance is essentially the same.

Synthesis of the Sandwich Compound (C_5H_5)Ta(C_7H_7). Treatment of **1** with sodium cyclopentadienide in THF at reflux, followed by extraction with pentane, evaporation of the solvent, and sublimation of the residue at 80 °C and 0.05 Torr, affords red-brown crystals of the mixed sandwich complex (C_5H_5)Ta(C_7H_7). We have recently described the preparation of this complex, along with its C_5H_4Me and C_5Me_5 analogs, by a different route: the Mg reduction of the corresponding (C_5R_5)$TaCl_4$ complex in the presence of cycloheptatriene.[13] This latter route proceeds in higher yield and, therefore, is preferable for synthetic purposes.

One question is whether these mixed sandwich complexes are useful starting materials for the preparation of other cycloheptatrienyl derivatives of tantalum. The answer to this question is yes, as shown by the results in the next section.

Synthesis and Characterization of (C_5Me_5)Ta(C_7H_7)-R, where R = Br (4), H (5), Me (6), η^1-$CH_2CH{=}CH_2$ (7), and c-C_3H_5 (8). As mentioned above, we have described elsewhere that the reaction of (C_5Me_5)$TaCl_4$ with Mg in the presence of cycloheptatriene affords the sandwich compound (C_5Me_5)Ta(C_7H_7) along with small amounts of the hydride (C_5Me_5)Ta(C_7H_7)H.[13] We find that treatment of this mixture with allyl bromide gives orange crystals of the bromotantalum(V) product (C_5Me_5)Ta(C_7H_7)Br (**4**). A similar reaction is also known to convert (C_5R_5)Nb(C_7H_7) to (C_5R_5)Nb(C_7H_7)Br.[15] Compound **4** is relatively air-stable. Its ^{1}H NMR spectrum features two singlets, one at δ 1.69 due to the C_5Me_5 ring and one at δ 4.36 due to the C_7H_7 ring. The $^{13}C\{^1H\}$ NMR spectrum shows three singlets, two at δ 12.2 and 109.7 due to the C_5Me_5 ring and one at δ 84.1 due to the C_7H_7 ring.

$$(C_5Me_5)Ta(C_7H_7) + BrCH_2CH{=}CH_2 \rightarrow \underset{\mathbf{4}}{(C_5Me_5)Ta(C_7H_7)Br} + ...$$

The bromo compound **4** is a good starting material for the preparation of other organotantalum species. It reacts with aluminum hydride salts, alkyllithium reagents, Grignard reagents, and dialkyl magnesium reagents in diethyl ether to afford products in which the Ta−Br group is replaced by hydride and alkyl groups. In the following discussions of the ^{1}H and ^{13}C NMR spectra of these compounds, we will omit mention of the chemical shifts for the C_5Me_5 and C_7H_7 rings because they are all similar to those seen for the bromo starting material **4**; details can be found in the Experimental Section.

$$(C_5Me_5)Ta(C_7H_7)Br + LiAlH_4 \rightarrow \underset{\mathbf{5}}{(C_5Me_5)Ta(C_7H_7)H} + LiBr + AlH_3$$

$$(C_5Me_5)Ta(C_7H_7)Br + LiR \rightarrow (C_5Me_5)Ta(C_7H_7)R + LiBr \quad [R = Me\ (\mathbf{6}), \eta^1CH_2CH{=}CH_2\ (\mathbf{7})]$$

$$(C_5Me_5)Ta(C_7H_7)Br + \tfrac{1}{2}Mg(c\text{-}C_3H_5)_2 \rightarrow \underset{\mathbf{8}}{(C_5Me_5)Ta(C_7H_7)(c\text{-}C_3H_5)} + \tfrac{1}{2}MgBr_2$$

Thus, treatment of (C_5Me_5)Ta(C_7H_7)Br (**4**) with $LiAlH_4$ affords pure samples of the hydride (C_5Me_5)Ta(C_7H_7)H (**5**) in ~30% yield. The ^{1}H NMR spectrum of **5** contains a binomial octet due to the hydride group at δ 6.40; the coupling of 2.5 Hz is to the seven hydrogen atoms on the

---

(26) Wang, C.; Sheridan, J. B. *Organometallics* **1994**, *13*, 3639–3643.

(27) Carruthers, K. P.; Helliwell, M.; Hinchliffe, J. R.; de Souza, A.-L. A. B.; Spencer, D. M.; Whiteley, M. W. *J. Organomet. Chem.* **2004**, *689*, 848–859.

C_7H_7 ring. Correspondingly, the resonance due to the C_7H_7 ring appears as a doublet with the same $^3J_{HH}$ coupling constant of 2.5 Hz. The origin of these splittings was confirmed by a decoupling experiment: irradiation at the hydride site causes the doublet for the C_7H_7 ring to collapse into a singlet. The relatively deshielded chemical shift of δ 6.40 for the hydride is not unusual for d^0 transition metal hydrides; for example, other tantalum(V) hydrides such as $TaH(O_2C_{20}H_{10}\{SiMe_3\}_2\text{-}3,3')_2$,[28] $Ta_2H_2(\mu\text{-}CH_2)(\mu\text{-}O)(OSi\text{-}t\text{-}Bu_3)_4$,[29] and $(C_5H_5)_2TaH_3$[30] have chemical shifts between δ 11 and δ 22.

Compound **5** can also be prepared in low yield by the reaction of $(C_5Me_5)Ta(C_7H_7)Br$ (**4**) with *n*-butyllithium, the major product of this reaction being the *n*-butyl compound $(C_5Me_5)Ta(C_7H_7)(n\text{-}Bu)$. The ^1H NMR spectrum of the latter shows a triplet at δ 0.61 (α-CH_2), another triplet at 1.01 (δ-Me), and two multiplets at 1.25 (β-CH_2) and 1.52 (γ-CH_2) for the *n*-butyl ligand.

The reaction of **4** with methyllithium affords the tantalum methyl compound $(C_5Me_5)Ta(C_7H_7)Me$ (**6**) in ~17% yield. The Ta−Me group in **6** appears as a singlet at δ −0.20 in the ^1H NMR spectrum and at δ 11.3 in the $^{13}C\{^1H\}$ NMR spectrum.

The reaction of **4** with allylmagnesium bromide in diethyl ether, followed by extraction with pentane and crystallization at −20 °C, affords the η^1-allyl complex $(C_5Me_5)Ta(C_7H_7)(\eta^1\text{-}CH_2CH{=}CH_2)$ (**7**) in ~5% yield. The ^1H NMR spectrum of **7** features multiplets at δ 1.06 (α-CH_2), 6.27 (β-CH), and 4.53 and 4.58 (γ-CH_2) for the η^1-allyl group. The $^{13}C\{^1H\}$ NMR spectrum shows singlets at δ 34.6, 149.7, and 101.2 for the α, β, and γ carbons of the η^1-allyl group, respectively. Unlike many other early transition metal η^1-allyl complexes, which are dynamic and whose α- and γ-CH_2 groups exchange readily by means of η^1- to η^3-allyl interconversions,[31] **7** is static on the NMR time scale. This behavior undoubtedly reflects the electron count of 18, which strongly disfavors the formation of an η^3-allyl structure.

Treatment of **4** with di(cyclopropyl)magnesium in diethyl ether gives the cyclopropyl complex $(C_5Me_5)Ta(C_7H_7)(c\text{-}C_3H_5)$ (**8**) in 8% yield. In the ^1H NMR spectrum, the cyclopropyl group of **8** gives resonances that correspond to an ABB′CC′ spin system (Figure 4). The α-CH group gives an apparent triplet of triplets, whereas the two chemically inequivalent sets of methylene protons exhibit second-order splitting patterns that resemble (but are not) doublets of triplets of doublets. A simulation of the line shapes affords the true H−H coupling constants (see the Experimental Section). The $^{13}C\{^1H\}$ NMR spectrum shows singlets at δ 12.9 and δ 18.7 due to the α-CH and β-CH_2 groups of the cyclopropyl ring, respectively. Few other transition metal cyclopropyl complexes have been described; among these are $Tp^{Me2}NbPh(c\text{-}C_3H_5)(MeCCMe)$ (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate),[32] $Pt(c\text{-}C_3H_5)_2(PMe_2Ph)_2$,[33] and $IrCl_2(c\text{-}C_3H_5)(CO)(PMePh_2)_2$.[34,35]

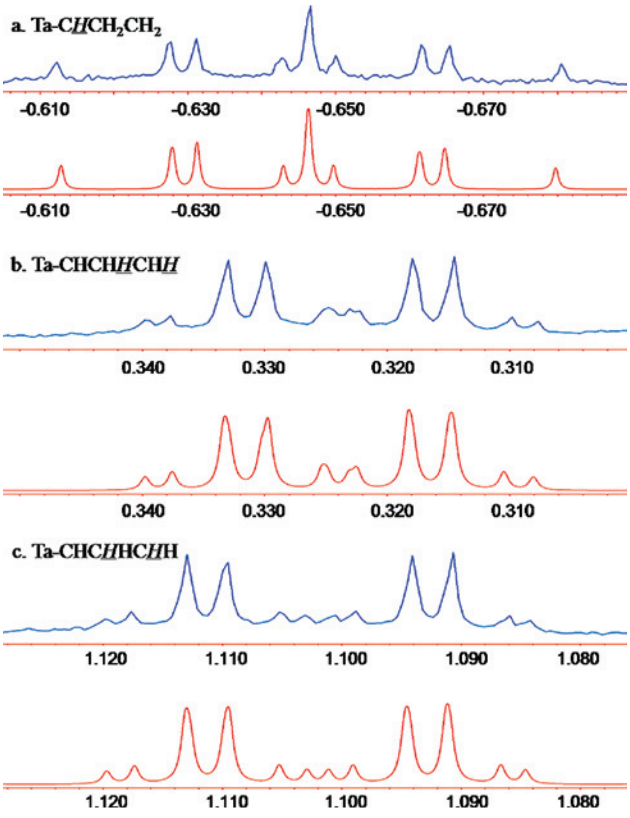


Figure 4. 500 MHz ^1H NMR resonances of the cyclopropyl group in $(C_5Me_5)Ta(C_7H_7)(c\text{-}C_3H_5)$ (**8**) dissolved in d_6-benzene (experimental spectra in blue, simulations in red).

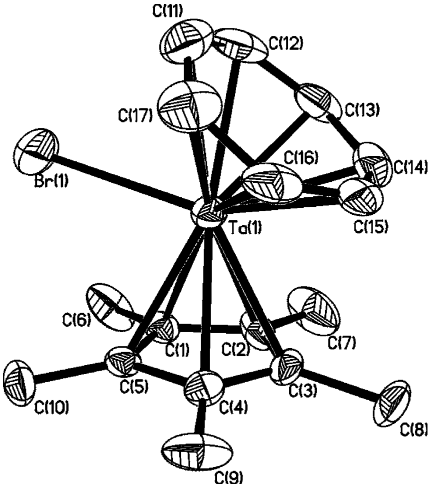


Figure 5. Molecular structure of $(C_5Me_5)Ta(C_7H_7)Br$ (**4**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

X-Ray Crystal Structures of $(C_5Me_5)Ta(C_7H_7)R$, where R = Br (4), H (5), Me (6), η^1-$CH_2CH{=}CH_2$ (7), or c-C_3H_5 (8). The molecular structures of **4**−**8** are shown in Figures 5−9. Crystallographic data are summarized in Table 1, and important bond distances and angles are given in Tables 5

---

(28) Weinert, C. S.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2005**, *24*, 5759–5766.

(29) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570–5588.

(30) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 4854–4859.

(31) Abrams, M. B.; Yoder, J. C.; Loeber, C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1389–1401.

(32) Oulié, P.; Boulho, C.; Vendier, L.; Coppel, Y.; Etienne, M. *J. Am. Chem. Soc.* **2006**, *128*, 15962–15963.

(33) Jones, N. L.; Ibers, J. A. *Organometallics* **1982**, *1*, 326–330.

(34) Jones, N. L.; Ibers, J. A. *Organometallics* **1983**, *2*, 490–494.

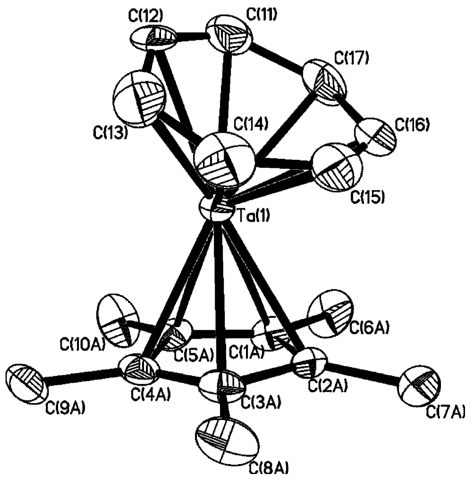


Figure 6. Molecular structure of $(C_5Me_5)Ta(C_7H_7)H$ (**5**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

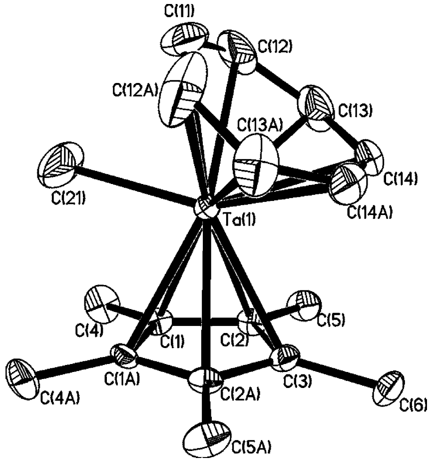


Figure 7. Molecular structure of $(C_5Me_5)Ta(C_7H_7)Me$ (**6**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

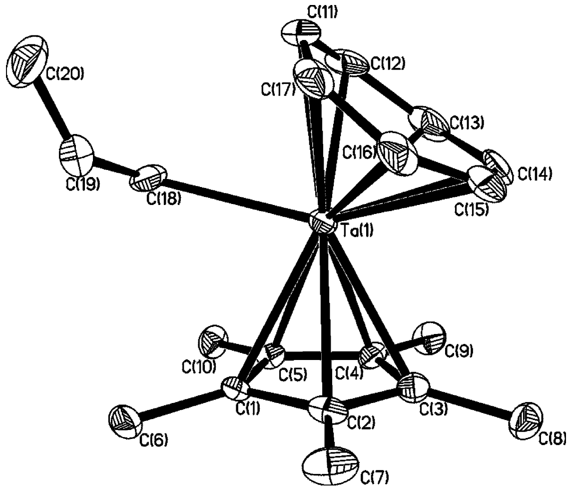


Figure 8. Molecular structure of $(C_5Me_5)Ta(C_7H_7)(\eta^1\text{-}CH_2CH{=}CH_2)$ (**7**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

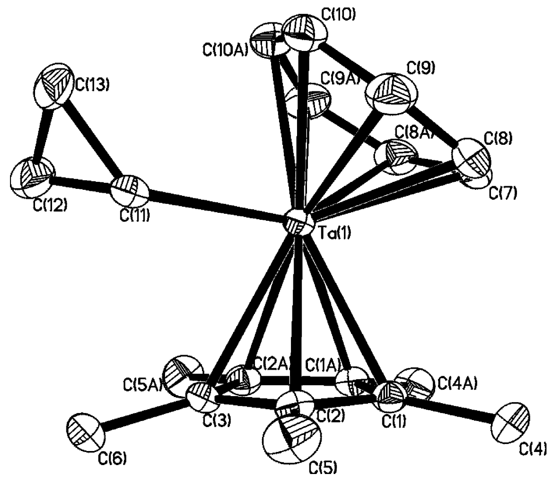


Figure 9. Molecular structure of $(C_5Me_5)Ta(C_7H_7)(c\text{-}C_3H_5)$ (**8**), showing the 30% probability density surfaces. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances and Angles for $(C_5Me_5)Ta(C_7H_7)Br$ (**4**)

	Bond Distances (Å)		
Ta(1)−C(1)	2.431(7)	Ta(1)−C(2)	2.440(8)
Ta(1)−C(3)	2.430(8)	Ta(1)−C(4)	2.431(8)
Ta(1)−C(5)	2.422(7)	Ta(1)−C(11)	2.415(8)
Ta(1)−C(12)	2.360(8)	Ta(1)−C(13)	2.280(8)
Ta(1)−C(14)	2.303(8)	Ta(1)−C(15)	2.341(8)
Ta(1)−C(16)	2.291(8)	Ta(1)−C(17)	2.348(8)
Ta(1)−Br(1)	2.710(1)	C(1)−C(2)	1.400(10)
C(2)−C(3)	1.404(11)	C(3)−C(4)	1.361(11)
C(4)−C(5)	1.413(10)	C(1)−C(5)	1.423(10)
C(1)−C(6)	1.510(9)	C(2)−C(7)	1.511(11)
C(3)−C(8)	1.544(10)	C(4)−C(9)	1.545(10)
C(5)−C(10)	1.483(10)	C(11)−C(12)	1.408(13)
C(12)−C(13)	1.394(12)	C(13)−C(14)	1.415(10)
C(14)−C(15)	1.346(12)	C(15)−C(16)	1.414(12)
C(16)−C(17)	1.421(11)	C(11)−C(17)	1.402(12)
	Bond Angles (deg)		
C(1)−C(2)−C(3)	107.1(7)	C(2)−C(3)−C(4)	108.9(7)
C(3)−C(4)−C(5)	109.8(7)	C(4)−C(5)−C(1)	105.5(7)
C(5)−C(1)−C(2)	108.7(7)	C(11)−C(12)−C(13)	127.8(9)
C(12)−C(13)−C(14)	125.9(10)	C(13)−C(14)−C(15)	129.8(10)
C(14)−C(15)−C(16)	130.8(9)	C(15)−C(16)−C(17)	126.4(9)
C(16)−C(17)−C(11)	125.2(10)	C(17)−C(11)−C(12)	131.4(9)

−9. These compounds all adopt very similar bent metallocene structures with one substituent in the open "wedge". Each ring is essentially planar, and the dihedral angle between them varies slightly, being slightly larger for larger Ta−R groups: 34.9° for the bromo compound **4**, 26.6° for the hydride **5**, 33.1° for the methyl compound **6**, 34.2° for the allyl compound **7**, and 37.5° for the cyclopropyl compound **8**. The Ta−C distances to the C_5Me_5 ring carbons and the Ta−C distances to the C_7H_7 ring carbons are summarized in Table 10.

In the structure of **5**, the hydride was not found in the final difference map. In **7**, the allyl group adopts a η^1 binding mode rather than η^3, as expected from the ^1H NMR data.

Other Reactions. Attempts to prepare the unknown molecule bis(cycloheptatriene)tantalum, $(C_7H_8)_2Ta$, by the treatment of $TaCl_5$ with six equivalents of *n*-BuLi or EtMgCl, followed by the addition of excess C_7H_8, afforded red-purple solutions, but no pure material could be obtained from them. The reduction of $TaCl_5$ with six equivalents of sodium naphthalenide, followed by the addition of excess C_7H_8, was similarly unavailing.

Table 6. Selected Bond Distances and Angles for $(C_5Me_5)Ta(C_7H_7)H$ (**5**)

	Bond Distances (Å)		
Ta(1)−C(1)	2.44(4)	Ta(1)−C(2)	2.43(3)
Ta(1)−C(3)	2.41(5)	Ta(1)−C(4)	2.42(3)
Ta(1)−C(5)	2.40(3)	Ta(1)−C(11)	2.368(7)
Ta(1)−C(12)	2.402(7)	Ta(1)−C(13)	2.321(8)
Ta(1)−C(14)	2.309(7)	Ta(1)−C(15)	2.367(7)
Ta(1)−C(16)	2.322(7)	Ta(1)−C(17)	2.259(7)
C(1A)−C(2A)	1.40(4)	C(2A)−C(3A)	1.44(5)
C(3A)−C(4A)	1.36(4)	C(4A)−C(5A)	1.42(4)
C(1A)−C(5A)	1.39(4)	C(1A)−C(6A)	1.58(4)
C(2A)−C(7A)	1.51(4)	C(3A)−C(8A)	1.50(5)
C(4A)−C(9A)	1.52(4)	C(5A)−C(10A)	1.52(4)
C(11)−C(12)	1.357(11)	C(12)−C(13)	1.389(11)
C(13)−C(14)	1.426(12)	C(14)−C(15)	1.425(10)
C(15)−C(16)	1.365(10)	C(16)−C(17)	1.434(10)
C(11)−C(17)	1.438(11)		
	Bond Angles (deg)		
C(1A)−C(2A)−C(3A)	106(4)	C(2A)−C(3A)−C(4A)	108(4)
C(3A)−C(4A)−C(5A)	108(4)	C(4A)−C(5A)−C(1A)	108(3)
C(5A)−C(1A)−C(2A)	109(3)	C(11)−C(12)−C(13)	132.4(8)
C(12)−C(13)−C(14)	125.7(8)	C(13)−C(14)−C(15)	126.8(8)
C(14)−C(15)−C(16)	130.5(7)	C(15)−C(16)−C(17)	127.7(7)
C(16)−C(17)−C(11)	126.6(8)	C(17)−C(11)−C(12)	127.4(8)

Table 7. Selected Bond Distances and Angles for $(C_5Me_5)Ta(C_7H_7)Me$ (**6**)[a]

	Bond Distances (Å)		
Ta(1)−C(1)	2.442(4)	Ta(1)−C(2)	2.443(4)
Ta(1)−C(3)	2.432(7)	Ta(1)−C(11)	2.400(8)
Ta(1)−C(12)	2.338(5)	Ta(1)−C(13)	2.274(5)
Ta(1)−C(14)	2.347(5)	Ta(1)−C(21)	2.256(10)
C(1)−C(2)	1.428(5)	C(2)−C(3)	1.417(5)
C(2A)−C(3)	1.417(5)	C(1)−C(1A)	1.423(7)
C(11)−C(12)	1.407(9)	C(12)−C(13)	1.398(9)
C(13)−C(14)	1.402(7)	C(14)−C(14A)	1.373(9)
	Bond Angles (deg)		
C(1)−C(2)−C(3)	106.8(4)	C(2)−C(3)−C(2A)	109.9(6)
C(1A)−C(1)−C(2)	108.3(2)	C(11)−C(12)−C(13)	127.3(7)
C(12)−C(13)−C(14)	124.6(6)	C(13)−C(14)−C(14A)	130.7(3)
C(12A)-C(11)−C(12)	131.0(9)		

[a] Symmetry transformations to generate equivalent atoms: $x, -y + 1/2, z$.

Table 8. Selected Bond Distances and Angles for $(C_5Me_5)Ta(C_7H_7)(\eta^1\text{-}CH_2CH{=}CH_2)$ (**7**)

	Bond Distances (Å)		
Ta(1)−C(1)	2.442(5)	Ta(1)−C(2)	2.459(6)
Ta(1)−C(3)	2.457(5)	Ta(1)−C(4)	2.423(5)
Ta(1)−C(5)	2.423(5)	Ta(1)−C(11)	2.439(6)
Ta(1)−C(12)	2.350(6)	Ta(1)−C(13)	2.269(6)
Ta(1)−C(14)	2.384(5)	Ta(1)−C(15)	2.349(6)
Ta(1)−C(16)	2.289(5)	Ta(1)−C(17)	2.337(5)
Ta(1)−C(18)	2.370(5)	C(1)−C(2)	1.437(8)
C(2)−C(3)	1.426(7)	C(3)−C(4)	1.408(7)
C(4)−C(5)	1.396(7)	C(1)−C(5)	1.434(7)
C(1)−C(6)	1.504(7)	C(2)−C(7)	1.488(7)
C(3)−C(8)	1.508(7)	C(4)−C(9)	1.528(6)
C(5)−C(10)	1.493(7)	C(11)−C(12)	1.426(8)
C(12)−C(13)	1.396(8)	C(13)−C(14)	1.414(10)
C(14)−C(15)	1.394(9)	C(15)−C(16)	1.408(8)
C(16)−C(17)	1.386(8)	C(11)−C(17)	1.435(9)
C(18)−C(19)	1.470(6)	C(19)−C(20)	1.312(8)
	Bond Angles (deg)		
C(1)−C(2)−C(3)	107.1(4)	C(2)−C(3)−C(4)	108.2(5)
C(3)−C(4)−C(5)	109.3(4)	C(4)−C(5)−C(1)	107.9(5)
C(5)−C(1)−C(2)	107.5(4)	C(11)−C(12)−C(13)	125.8(6)
C(12)−C(13)−C(14)	127.8(6)	C(13)−C(14)−C(15)	128.1(6)
C(14)−C(15)−C(16)	131.3(7)	C(15)−C(16)−C(17)	124.6(6)
C(16)−C(17)−C(11)	128.9(5)	C(17)−C(11)−C(12)	129.3(6)
Ta(1)−C(18)−C(19)	116.2(4)	C(18)−C(19)−C(20)	128.2(6)

Table 9. Selected Bond Distances and Angles for $(C_5Me_5)Ta(C_7H_7)(c\text{-}C_3H_5)$ (**8**)

	Bond Distances (Å)		
Ta(1)−C(1)	2.432(4)	Ta(1)−C(2)	2.448(4)
Ta(1)−C(3)	2.475(5)	Ta(1)−C(7)	2.409(6)
Ta(1)−C(8)	2.314(4)	Ta(1)−C(9)	2.318(5)
Ta(1)−C(10)	2.408(4)	Ta(1)−C(11)	2.344(8)
C(1)−C(2)	1.419(5)	C(2)−C(3)	1.413(5)
C(1)-C(1A)	1.419(7)	C(7)−C(8)	1.401(5)
C(8)−C(9)	1.398(6)	C(9)−C(10)	1.403(7)
C(10)-C(10A)	1.400(9)	C(11)−C(12)	1.47(1)
C(12)−C(13)	1.49(1)	C(11)−C(13)	1.50(1)
	Bond Angles (deg)		
C(1)−C(2)−C(3)	107.5(3)	C(2)−C(3)−C(2A)	108.8(5)
C(1A)-C(1)−C(2)	108.1(2)	C(7)−C(8)−C(9)	128.3(5)
C(8)−C(9)−C(10)	124.7(5)	C(9)−C(10)−C(10A)	130.2(3)
C(8)−C(7)−C(8A)	129.4(6)	C(11)−C(12)−C(13)	61.1(5)
C(11)−C(13)−C(12)	58.7(5)	C(12)−C(11)−C(13)	60.2(5)

Table 10. Selected Bond Distances in $(C_5Me_5)Ta(C_7H_7)R$, where R = Br (**4**), H (**5**), Me (**6**), $\eta^1\text{-}CH_2CH{=}CH_2$ (**7**), or $c\text{-}C_3H_5$ (**8**)

R	Ta−C_5 (Å)	Ta−C_7 (Å)	Ta−R (Å)
Br (**4**)	2.422(7)−2.440(8)	2.280(8)−2.415(8)	2.710(1)
H (**5**)	2.40(3)−2.44(4)	2.259(7)−2.402(7)	
Me (**6**)	2.432(7)−2.443(4)	2.256(10)−2.400(8)	2.256(10)
$\eta^1\text{-}CH_2CH{=}CH_2$ (**7**)	2.423(5)−2.459(6)	2.269(6)−2.439(6)	2.370(5)
$c\text{-}C_3H_5$ (**8**)	2.432(4)−2.475(5)	2.314(4)−2.409(6)	2.344(8)

Concluding Remarks

The compound $(\eta^6\text{-}C_7H_8)TaCl_2(PMe_3)_2$ (**1**) provides the first useful synthetic entry into half-sandwich cycloheptatrienyl tantalum chemistry. This compound and the others reported above should enable the synthesis of a wide variety of new organotantalum compounds.

Experimental Section

All syntheses were performed under an Ar atmosphere with glovebox and Schlenk techniques. Solvents were dried over Na/benzophenone and distilled under nitrogen immediately before use. The starting materials $TaCl_5$ (99.99%, Cerac), cycloheptatriene (90%, Lancaster), Mg turnings (99.9+ %, Alfa Aesar), *n*-butyllithium (2.5 M in hexane, Aldrich), methyllithium (1.6 M in ether, Aldrich), allyl bromide (99%, Aldrich), and allylmagnesium bromide (1.0 M in diethyl ether, Aldrich) were used as received. The compound $Mg(c\text{-}C_3H_5)_2$ was prepared by following a literature procedure.[36] IR spectra were recorded on a Nicolet Impact 410 FT-IR instrument as Nujol mulls between KBr plates. The ^1H NMR data were collected on a Varian Unity U500 instrument at 500 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS. Microanalyses were performed by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois; the errors in the tantalum analyses were occasionally larger than expected but are reported for completeness. X-ray diffraction data were collected on a Bruker Smart CCD instrument.

(η^6-Cycloheptatriene)dichlorobis(trimethylphosphine)tantalum (1). To a slurry of $TaCl_5$ (1.00 g, 2.79 mmol) suspended in diethyl ether (40 mL) was added PMe_3 (0.8 mL, 7.7 mmol) at −78 °C, and the resulting mixture was treated with *n*-butyllithium (3.4 mL of a 2.5 M solution in hexane, 9.5 mmol). After 15 min, the stirred mixture was warmed to room temperature. When the color of the mixture changed from yellow to brown, cycloheptatriene (1.5 mL, 15.4 mmol) was added. After one day, the dark brown

---

(35) Swepston, P. N.; Jones, N. L.; Ibers, J. A. *Acta Crystallogr.* **1984**, *C40*, 39–41.

(36) Watkins, E. K.; Richey, H. G. *Organometallics* **1992**, *11*, 3785–3794.

solution was filtered from a white precipitate, and the filtrate was concentrated to *ca.* 20 mL and cooled to −20 °C. After 12 h, the dark brown crystals were collected, washed with pentane (10 mL), and dried in a vacuum. Yield: 0.4 g (29%). Anal. calcd: C, 31.5; H, 5.28; Cl, 14.3; Ta, 36.5. Found: C, 32.0; H, 5.33; Cl, 12.9; Ta, 39.1. FD-MS (*m*/*z*, relative intensity): 496.2 (100, M^+). IR (cm^{-1}): 3045 w, 3029 w, 1502 m, 1419 m, 1279 s, 1268 s, 1250 m, 1174 w, 1150 w, 959 vs, 903 m, 872 m, 832 s, 795 s, 730 s, 671 m.

(η^7-Cycloheptatrienyl)chlorobis(trimethylphosphine)tantalum (2). To a solution of **1** (0.40 g, 0.81 mmol) in diethyl ether (30 mL) was added methyllithium (0.5 mL of a 1.6 M in diethyl ether, 0.80 mmol) at −78 °C. The solution was slowly warmed to 25 °C and stirred for 7 h, over which time the solution color changed from brown to dark green-brown and a white precipitate formed. The solution was filtered, and the filtrate was concentrated to *ca.* 10 mL and cooled to −20 °C. After one day, the dark brown crystals were collected. Yield: 0.04 g (11%). Anal. calcd: C, 34.0; H, 5.48; Cl, 7.71; Ta, 39.4. Found: C, 32.8; H, 5.26; Cl, 8.11; Ta, 37.9. IR (cm^{-1}): 1416 m, 1302 w, 1282 m, 1276 m, 1172 w, 1154 w, 945 s, 895 w, 843 w, 802 m, 790 m, 780 s, 668 m.

(η^5-Cycloheptadienyl)dichlorobis(trimethylphosphine)tantalum (3). Method A. To a mixture of **1** (0.3 g, 0.61 mmol) and $NaBH_4$ (0.05 g, 1.32 mmol) was added cooled THF (40 mL) at −78 °C. The mixture was warmed slowly to room temperature. After 18 h, the color of the solution changed from dark brown to dark red. The solvent was removed under vacuum to give a dark brown solid, which was extracted with pentane (40 mL). The extracts were filtered, and the filtrate was concentrated to *ca.* 20 mL and cooled to −20 °C. The brown crystals were collected.

Method B. To sodium (0.4 g, 0.17 mol) suspended in toluene (30 mL) was added a pentane solution of **1** (0.20 g, 0.41 mmol) at 25 °C. After one day, the red brown solution was separated by filtration from the remaining Na. The filtrate was concentrated to *ca.* 10 mL and cooled to −20 °C. After 12 days, the brown crystals were collected. Neither method afforded sufficient material to characterize other than by X-ray crystallography.

(Cycloheptatrienyl)(cyclopentadienyl)tantalum. To a solution of **1**(0.30 g, 0.61 mmol) in THF (40 mL) was added sodium cyclopentadienide (6.0 mL of a 0.7 M solution in THF, 4.2 mmol) at 25 °C. The mixture was heated to reflux for 24 h, during which time the color of the mixture changed from dark brown to a purple brown. The solvent was removed under vacuum to give a red brown oil, which was extracted with pentane (2 × 30 mL). The extracts were combined, filtered, and taken to dryness. The residue was sublimed at 80 °C and 0.05 Torr to afford a red-brown solid. Yield: 0.03 g (15%). Physical data agree with those reported previously.[13]

(Cycloheptatrienyl)(pentamethylcyclopentadienyl)bromotantalum (4). To a suspension of $(C_5Me_5)TaCl_4$ (2.0 g, 4.4 mmol) in tetrahydrofuran (70 mL) was added cycloheptatriene (8 mL, 77 mmol). The mixture was cooled to −78 °C and added to a mixture of Mg turnings (2.0 g, 82 mmol) in THF (10 mL) at −78 °C. After 15 min, the reaction mixture was slowly warmed to 25 °C and was stirred for 3 h. The color of the mixture changed from bright yellow to dark brown. The solution was decanted from the excess Mg, and the solvent was removed under vacuum to give a dark brown solid. The solid was extracted with pentane (2 × 40 mL), and the extracts were combined, filtered, cooled to −78 °C, and treated with allyl bromide (6 mL, 69 mmol). The mixture was warmed to 25 °C and stirred for 3 h to afford a brown solution and a yellow precipitate. The mixture was concentrated to *ca.* 20 mL and cooled to −20 °C. After 12 h, the orange crystals were isolated. Yield: 0.95 g (45%). Anal. calcd: C, 41.9; H, 4.55; Br, 16.4; Ta, 37.1. Found: C, 42.2; H, 4.47; Br 16.1; Ta, 38.7. ^1H NMR (d_6-benzene): δ 1.69 (s, C_5Me_5), 4.36 (s, C_7H_7). $^{13}C\{^1H\}$ NMR (d_6-benzene): δ 12.2 ($C_5\mathit{Me}_5$), 84.1 (C_7H_7), 109.8 (C_5Me_5).

(Cycloheptatrienyl)(pentamethylcyclopentadienyl)hydridotantalum (5). To a suspension of $LiAlH_4$ (0.02 g, 0.53 mmol) in diethyl ether (10 mL) at −78 °C was added a solution of $(C_5Me_5)Ta(C_7H_7)Br$ (**4**) (0.20 g, 0.41 mmol) in diethyl ether (40 mL). The mixture was slowly warmed to 25 °C and stirred for 24 h. The solvent was removed under vacuum, and the residue was extracted with pentane (*ca.* 40 mL). The extract was filtered, concentrated to *ca.* 20 mL, and cooled to −20 °C. The orange crystals were collected. Yield: 0.05 g (30%). FD-MS (*m*/*z*): 408.2 (M^+). ^1H NMR (d_6-benzene, 25 °C): δ 1.85 (s, C_5Me_5), 4.37 (d, C_7H_7, $J_{HH} = 2.5$ Hz), 6.40 (octet, $J_{HH} = 2.5$ Hz, TaH). $^{13}C\{^1H\}$ NMR (d_6-benzene): δ 12.9 ($C_5\mathit{Me}_5$), 82.93 (C_7H_7), 106.9 (C_5Me_5).

Reaction of (η^7-C_7H_7)(η^5-C_5Me_5)TaBr with *n*-Butyllithium. To a solution of $(C_5Me_5)Ta(C_7H_7)Br$ (**4**) (0.20 g, 0.41 mmol) in diethyl ether (40 mL) at −78 °C was added *n*-butyllithium (0.3 mL of a 2.5 M solution in hexane, 7.5 mmol). The mixture was slowly warmed to 25 °C and stirred for 7 h. The color of the solution became dark brown. The solvent was removed under vacuum to give a brown solid, which was extracted with pentane (*ca.* 40 mL). The extract was filtered, and the filtrate was taken into dryness to give a brown oil. The product was shown by NMR spectroscopy to be a 1:4 mixture of the hydride **5** (see above) and the butyl complex (η^7-C_7H_7)(η^5-C_5Me_5)Ta(*n*-Bu), which had the following NMR resonances. ^1H NMR (d_6-benzene, 25 °C): δ 0.61 (t, $J_{HH} = 8.0$ Hz, Ta−$\mathit{CH}_2CH_2CH_2CH_3$), 1.01 (t, $J_{HH} = 7.0$ Hz, Ta-$CH_2CH_2CH_2\mathit{CH}_3$), 1.25 (m, Ta-$CH_2\mathit{CH}_2CH_2CH_3$), 1.52 (m, Ta-$CH_2CH_2\mathit{CH}_2CH_3$), 1.61 (s, C_5Me_5), 4.19 (s, C_7H_7). IR (neat, cm^{-1}): 2962 m, 2903 m, 1684 w, 1481 m, 1452 m, 1415 m, 1375 m, 968 w, 949 w, 936 w, 703 m, 663 w.

(Cycloheptatrienyl)(pentamethylcyclopentadienyl)methyltantalum (6). To a solution of $(C_5Me_5)Ta(C_7H_7)Br$ (**4**) (0.20 g, 0.41 mmol) in diethyl ether (40 mL) at −78 °C was added methyllithium (0.3 mL of a 1.6 M solution in diethyl ether, 4.8 mmol). The mixture was slowly warmed to 25 °C and stirred for 7 h. The solvent was removed under vacuum to give a brown solid, which was extracted with pentane (50 mL). The extract was filtered, and the filtrate was concentrated to *ca.* 20 mL and cooled to −20 °C. After 12 h, the orange crystals were collected. Yield: 0.03 g (17%). Anal. calcd: C, 51.2; H, 5.97; Ta, 42.8. Found: C, 51.1; H, 6.06; Ta, 39.8. ^1H NMR (d_6-benzene): δ −0.20 (s, TaMe), 1.60 (s, C_5Me_5), 4.22 (s, C_7H_7). $^{13}C\{^1H\}$ NMR (d_6-benzene): δ 11.3 (TaMe), 14.3 ($C_5\mathit{Me}_5$), 82.8 (C_7H_7), 107.2 (C_5Me_5).

(Cycloheptatrienyl)(pentamethylcyclopentadienyl)(allyl)tantalum (7). To a solution of **4** (0.20 g, 0.41 mmol) in diethyl ether (40 mL) at −78 °C was added allylmagnesium chloride (0.5 mL of a 1.0 M solution in diethyl ether, 0.5 mmol). The mixture was slowly warmed to 25 °C and stirred for 8 h. The solvent was removed under a vacuum to give a brown solid, which was extracted with pentane (*ca.* 50 mL). The extract was filtered, and the filtrate was concentrated to *ca.* 20 mL and cooled to −20 °C. After 12 h, the reddish-orange crystals were collected. Yield: 0.01 g (5%). FI-MS (*m*/*z*): 407.2 (100, $M^+ - C_3H_5$). ^1H NMR (d_6-benzene): δ 1.06 (ddd, $J_{AD} = 9.0$ Hz, $J_{AC} = 1.5$ Hz, $J_{AB} = 1.05$ Hz, $Ta\mathit{CH}_2$-$CH{=}CH_2$), 1.55 (s, C_5Me_5), 4.16 (s, C_7H_7), 4.53 (ddt, $J_{BD} = 10$ Hz, $J_{BC} = 3.0$ Hz, $J_{AB} = 1.05$ Hz, $TaCH_2CH{=}\mathit{CH}_2$), 4.58 (ddt, $J_{CD} = 17$ Hz, $J_{BC} = 3.0$ Hz, $J_{AC} = 1.5$ Hz, $TaCH_2CH{=}\mathit{CH}_2$), 6.27 (ddt, $J_{CD} = 17$ Hz, $J_{BD} = 10$ Hz, $J_{AD} = 9$ Hz, $TaCH_2\mathit{CH}{=}CH_2$). $^{13}C\{^1H\}$ NMR (d_6-benzene): δ 11.1 ($C_5\mathit{Me}_5$), 34.6 ($Ta\mathit{C}H_2CH{=}CH_2$), 82.8 (C_7H_7), 101.2 ($TaCH_2CH{=}\mathit{C}H_2$), 107.4 (C_5Me_5), 149.7 ($TaCH_2\mathit{C}H{=}CH_2$).

(Cycloheptatrienyl)(pentamethylcyclopentadienyl)cyclopropyltantalum (8). To a solution of **4** (0.13 g, 0.27 mmol) in diethyl ether (40 mL) at −78 °C was added di(cyclopropyl)magnesium (1.0 mL of a 0.21 M solution in THF, 0.21 mmol). The mixture was slowly warmed to 25 °C and stirred for 8 h. The solvent was removed under vacuum to give a brown solid, which was extracted with pentane (*ca.* 50 mL). The extract was filtered, and the filtrate was concentrated to *ca.* 20 mL and cooled to −20 °C. After 12 h, the orange crystals were collected. Yield: 0.01 g (8%). ^{1}H NMR (d_6-benzene): δ −0.55 (tt, $J_{AB} = 9.6$ Hz, $J_{AC} = 8.8$ Hz, α-CH), 0.32 (dm, $J_{AB} = 9.6$ Hz, $J_{BB'} = -2.4$ Hz, $J_{BC} = 9.2$ Hz, $J_{BC'} = 5.1$ Hz, $J_{CC'} = -3.0$ Hz, β-CH$_2$), 1.10 (dm, $J_{AC} = 8.8$ Hz, $J_{BB'} = -2.4$ Hz, $J_{BC} = 9.2$ Hz, $J_{BC'} = 5.1$ Hz, $J_{CC'} = -3.0$ Hz, β-CH$_2$), 1.64 (s, C_5Me_5), 4.12 (s, C_7H_7). ^{13}C{^{1}H} NMR (d_6-benzene): δ 11.9 (C$_5$*Me*$_5$), 12.9 (α-CH), 18.7 (β-CH$_2$), 81.8 (C_7H_7), 108.1 (*C*$_5$Me$_5$).

Crystallographic Data.[37] Single crystals of (η^6-C_7H_8)TaCl$_2$(PMe$_3$)$_2$ (**1**), crystallized from diethyl ether, were mounted on glass fibers with Paratone oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. Crystals of (η^7-C_7H_7)TaCl(PMe$_3$)$_2$ (**2**) and (η^5-C_7H_9)TaCl$_2$(PMe$_3$)$_2$ (**3**) were obtained similarly. Single crystals of (C_5Me_5)Ta(C_7H_7)Br (**4**), (C_5Me_5)Ta(C_7H_7)H (**5**), (C_5Me_5)Ta(C_7H_7)Me (**6**), (C_5Me_5)Ta(C_7H_7)(η^1-CH$_2$CH=CH$_2$) (**7**), and (C_5Me_5)Ta(C_7H_7)(c-C_3H_5) (**8**) were crystallized from pentane and treated similarly. Standard peak search and indexing procedures, followed by least-squares refinement, yielded the cell dimensions given in Table 1. Data were collected with an area detector by using the measurement parameters listed in Table 1. For all crystals, the measured intensities were reduced to structure factor amplitudes, and their estimated standard deviations by correction for background and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, face-indexed absorption corrections were applied. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. Unless specified otherwise, all unique data were used in the least-squares refinement. The structures were solved using direct methods (SHELXTL). The correct positions for all of the non-hydrogen atoms were deduced from an E-map and subsequent difference Fourier calculations. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. Unless otherwise stated, the refinement models had the following features: (1) Independent anisotropic displacement factors were refined for the non-hydrogen atoms. (2) Hydrogen atoms were placed in idealized positions with C−H = 0.95, 0.99, and 0.98 Å for aromatic, methylene, and methyl hydrogens, respectively. (3) The methyl groups were allowed to rotate about the C−X bonds to find the best least-squares positions for the hydrogen atoms. (4) Methyl hydrogen atoms were given displacement parameters equal to 1.5 times U_{eq} for the attached carbon atom, whereas for all other hydrogen atoms the multiplier was 1.2. For all of the data sets, successful convergence was indicated by the maximum shift/error of <0.001 for the last cycle. Unless otherwise stated, a final analysis of variance between observed and calculated structure factors showed no apparent errors. Final refinement parameters are given in Table 1. Specific information about each crystal structure can be found in the Supporting Information.

Acknowledgment. We thank the National Science Foundation for support of this research under grant numbers DMR03-54060 and DMR04-20768. We also thank Scott R. Wilson and Teresa Prussak-Wieckowska for collecting the X-ray crystallographic data.

Supporting Information Available: X-ray crystallographic files in CIF format for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8015035

---

[37] Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139–2144.