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Synthesis and Characterization of the Cycloheptatrienyl Tantalum "Mixed-Sandwich" Compounds $(C_5R_5)Ta(C_7H_7)$

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The molecule (cycloheptatrienyl)(cyclopentadienyl)tantalum, $(C_5H_5)Ta(C_7H_7)$ (**1**), and its methylcyclopentadienyl and pentamethylcyclopentadienyl analogues $(C_5H_4Me)Ta(C_7H_7)$ (**2**), and $(C_5Me_5)Ta(C_7H_7)$ (**3**) have been synthesized by magnesium reduction of the corresponding $(C_5R_5)TaCl_4$ species in the presence of cycloheptatriene. The crystal structures of **2** and **3** show that the two rings are planar and essentially parallel to each other. Interestingly, the Ta–C distances to the C_7H_7 ring are significantly shorter (by about 0.1 Å) than those to the cyclopentadienyl ring; the difference reflects stronger bonding to the C_7H_7 ring. A comparison with the structures of other $(C_5R_5)M(C_7H_7)$ shows that the M–C distances to the seven-membered ring are especially sensitive to the d-orbital energies of the metal center and its ability to engage in δ bonding with the ring. For **1**–**3**, the EPR spectra at room temperature consist of octets due to the tantalum nuclear spin. Both A_{iso} and g_{iso} increase as the number of methyl groups on the cyclopentadienyl ring increases. EPR spectra of **1**–**3** as frozen glasses correspond to axial symmetry, and the hyperfine couplings and g factors are deduced from simulations.

Introduction

Transition-metal compounds that bear both a seven-membered cycloheptatrienyl ring and a five-membered cyclopentadienyl ring are interesting examples of mixed-sandwich complexes.[1,2] Electrically neutral sandwich complexes of formula $(C_5H_5)M(C_7H_7)$, or their ring-substituted analogs, are known for Ti,[2−7] Zr,[2,8,9] Hf,[2,10] V,[7,11−13] Nb,[9,14] Ta,[15] Cr,[7,9,16−18] Mo,[9,19] and W[20]; in addition, corresponding cations are known for M = Nb,[21] Cr,[22,23] Mn,[24,25] and Ru,[26,27] and anions for M = Ti,[28] Nb,[21] and Cr.[29] Some of these compounds have been considered as precursors for the deposition of metallic thin films.[30,31]

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Such C_5-C_7 mixed-sandwich complexes, which are isoelectronic with bis(arene)metal compounds, have been the subject of extensive spectroscopic studies[12,32] and theoretical calculations.[33] The formal charge of the bound cycloheptatrienyl ring, C_7H_7, can be considered to be either 1+ or 3−, both of which satisfy Hückel's $4n + 2$ rule. Photoelectron spectroscopic studies of $(C_5H_5)M(C_7H_7)$ compounds (M = Ti, Nb, Ta, Mo) suggested that neither formalism accurately describes the metal-ring bonding, owing to the significant mixing of metal and ligand orbital character in the HOMOs.[34] Theoretical calculations on the same systems showed smaller contributions of the metal orbitals to the HOMOs and were more consistent with assigning a 3− charge to the C_7H_7 ligand.[35]

In contrast to the situation for other group 4 to group 6 transition elements, the chemistry of (cycloheptatrienyl)tantalum complexes is relatively poorly developed: only the methylcycloheptatrienyl mixed-sandwich compound $(C_5H_4Me)Ta(C_7H_7)$ has been described previously.[15] Here, we report the syntheses of the analogous cyclopentadienyl and pentamethylcyclopentadienyl species $(C_5H_5)Ta(C_7H_7)$ and $(C_5Me_5)Ta(C_7H_7)$ and a comparison of the molecular and electronic structures of these compounds across the series.

Results and Discussion

Synthesis and Characterization. In 1992, Green showed that the magnesium reduction of $(C_5H_4Me)TaCl_4$ in the presence of cycloheptatriene afforded the mixed-sandwich compound $(C_5H_4Me)Ta(C_7H_7)$.[15] These workers reported that they were unable to obtain the unsubstituted compound $(C_5H_5)Ta(C_7H_7)$ by this same route. We now find that the method is a general one, although the isolated yield of the unsubstituted compound is low (~6%). Thus, reduction of the mono(cyclopentadienyl)tantalum compounds $(C_5R_5)TaCl_4$ with magnesium in tetrahydrofuran in the presence of cycloheptatriene affords the mixed-sandwich species $(C_5H_5)Ta(C_7H_7)$ (**1**), $(C_5H_4Me)Ta(C_7H_7)$ (**2**), and $(C_5Me_5)Ta(C_7H_7)$ (**3**). Compounds **1** and **2** sublime at 80 °C in vacuum, whereas **3** decomposes under these conditions and is best purified by crystallization from pentane. Previously, $(C_5H_4Me)Ta(C_7H_7)$ was reported to be blue,[15] but in our hands it was red-brown both in solution and in the solid state.

$$(C_5R_5)TaCl_4 + 2Mg + C_7H_8 \rightarrow (C_5R_5)Ta(C_7H_7) + 2MgCl_2 + \text{“H”}$$

Both **1** and **2** give strong molecular ions in their field ionization mass spectra. It is noteworthy that there is no evidence in the mass spectra of the ionization-induced formation of arene tantalum fragments such as $(C_6H_6)Ta^+$, as has previously been claimed for certain vanadium and titanium analogues.[3,6,36]

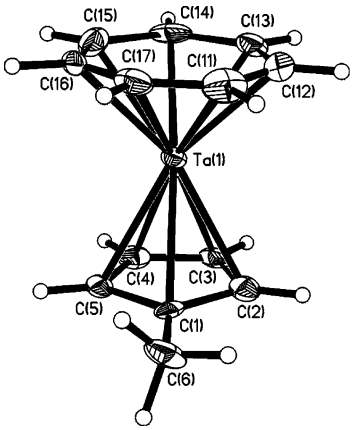

Figure 1. Molecular structure of $(C_5H_4Me)Ta(C_7H_7)$ (**2**).

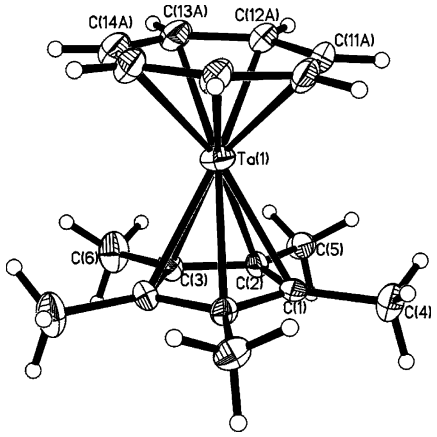

Figure 2. Molecular structure of $(C_5Me_5)Ta(C_7H_7)$ (**3**).

The IR spectrum of C_5H_5 compound **1** shows two equal-intensity bands at 1170 and 1156 cm^{-1} that are assigned to in-plane C−H deformations of the C_7H_7 ring,[9,37,38] and a band at 1013 cm^{-1} due to in-plane C−H bending of the C_5H_5 ring.[39−41] The IR spectrum of C_5H_4Me compound **2** shows similar C_7H_7 bands at 1171 and 1151 cm^{-1} and C_5H_4Me bands at 1036 and 1024 cm^{-1},[6,42] whereas C_5Me_5 compound **3** shows C_7H_7 bands at 1167 and 1156 cm^{-1} and a methyl rocking band at 1033 cm^{-1} from the C_5Me_5 ring. No ^1H NMR resonances could be located for any of these paramagnetic compounds, although the spectrum of **3** showed small amounts of the diamagnetic hydride $(C_5Me_5)(C_7H_7)TaH$ (below).

Crystal Structures of $(C_5H_4Me)Ta(C_7H_7)$ (2) and $(C_5Me_5)Ta(C_7H_7)$ (3). The molecular structures of **2** and **3**

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Table 1. Crystallographic Data for $(C_5H_4Me)Ta(C_7H_7)$ (**2**) and $(C_5Me_5)Ta(C_7H_7)$ (**3**)[a]

	2	**3**
temperature/ K	193(2)	193(2)
wavelength/ Å	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/c$	orthorhombic, *Pnma*
a/ Å	12.420(5)	10.3622(4)
b/ Å	8.047(3)	12.3659(6)
c/ Å	11.436(5)	11.3394(6)
β/ deg	113.118(6)	90
volume/ Å^3	1051.3(8)	1453.01(12)
Z	4	4
calculated density/ g cm^{-1}	2.219	1.862
absorption coefficient/ mm^{-1}	10.410	7.546
F(000)	660	788
cryst size/ mm^3	0.36 × 0.05 × 0.02	0.12 × 0.04 × 0.02
θ range/ deg	1.78−28.30	2.44−28.30
reflns collected/unique	12 673/2591	13 987/1876
R(int)	0.1192	0.1046
absorption correction	face-indexed	face-indexed
Max. and min. transmission	0.821 and 0.227	0.862 and 0.549
data/restraints/params	2591/0/128	1876/134/124
GOF on F^2	0.763	0.785
Final R indices [$I > 2\sigma(I)$]	0.0356	0.0350
wR_2 (all data)	0.0742	0.0632
Largest diff. peak and hole, $\Delta\rho_{elect}$/ eÅ^{-3}	1.982 and −1.798	0.971 and −1.370

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

Table 2. Selected Bond Distances and Angles for $(C_5H_4Me)Ta(C_7H_7)$ (**2**)

	Bond Distances (Angstroms)		
Ta(1)−C(1)	2.419(8)	C(1)−C(2)	1.448(11)
Ta(1)−C(2)	2.375(8)	C(2)−C(3)	1.466(13)
Ta(1)−C(3)	2.369(8)	C(3)−C(4)	1.359(12)
Ta(1)−C(4)	2.355(8)	C(4)−C(5)	1.406(12)
Ta(1)−C(5)	2.388(7)	C(1)−C(5)	1.441(11)
Ta(1)−C(11)	2.274(10)	C(1)−C(6)	1.463(12)
Ta(1)−C(12)	2.257(10)	C(11)−C(12)	1.446(15)
Ta(1)−C(13)	2.261(8)	C(12)−C(13)	1.404(15)
Ta(1)−C(14)	2.307(9)	C(13)−C(14)	1.445(14)
Ta(1)−C(15)	2.284(9)	C(14)−C(15)	1.415(12)
Ta(1)−C(16)	2.272(8)	C(15)−C(16)	1.391(13)
Ta(1)−C(17)	2.262(9)	C(16)−C(17)	1.385(14)
		C(11)−C(17)	1.319(14)
	Bond Angles (Degrees)		
C(1)−C(2)−C(3)	106.9(8)	C(12)−C(13)−C(14)	129.2(9)
C(2)−C(3)−C(4)	107.3(7)	C(13)−C(14)−C(15)	125.5(9)
C(3)−C(4)−C(5)	111.6(9)	C(14)−C(15)−C(16)	129.0(9)
C(4)−C(5)−C(1)	107.4(8)	C(15)−C(16)−C(17)	128.8(8)
C(5)−C(1)−C(2)	106.6(8)	C(16)−C(17)−C(11)	132.4(10)
C(11)−C(12)−C(13)	128.4(10)	C(17)−C(11)−C(12)	126.6(11)

were determined by X-ray crystallography (Figures 1 and 2); crystallographic data and important bond distances and angles are given in Tables 1−3.

In **2**, the planar η^5-C_5H_4Me and η^7-C_7H_7 rings are essentially parallel to each other (dihedral angle = 1.7°). For the five-membered ring, the Ta−C distances to the proton-bearing carbons range from 2.355(8) to 2.388(7) Å, whereas the Ta−C distance to the methyl-bearing carbon is slightly longer, 2.419(8) Å. For the C_7H_7 ring, the Ta−C distances range from 2.257(10) to 2.307(9) Å. These latter distances are significantly shorter (by about 0.1 Å) than those to the five-membered ring and suggest that the C_7H_7 group is bound more strongly to the tantalum center.[5,13,21] Interestingly, DFT calculations on $(C_5H_5)Ta(C_7H_7)$ find the same structural feature: the Ta−C(C_5) and Ta−C(C_7) distances are predicted to be 2.465 and 2.372 Å by BLYP, and 2.423 and 2.355 Å by PBE, respectively.[35] All of these distances are longer than those found in the X-ray structure of **2**, but the ∼0.1 Å shorter distance to the C_7H_7 ring matches the difference seen experimentally. We will return to this point below.

Crystals of **2** are isostructural with those of its molybdenum analog:[19] they have the same space group, $P2_1/c$, and very similar unit cell dimensions. The M−C distances to the five-membered ring in the molybdenum compound $(C_5H_4Me)Mo(C_7H_7)$ show the same pattern seen for **2**: the Mo−C distances to the proton-bearing carbons range from 2.304(5) to 2.317(5) Å, and the distance to the methyl-substituted carbon is slightly longer at 2.334(4) Å.[19]

Most of the crystals of pentamethylcyclopentadienyl complex **3** did not diffract well and were unsuited for crystallographic study; in retrospect, these poorly diffracting crystals probably contain pure **3**. A few crystals were found from which data could be collected; these crystals were isomorphous with those of the Ti,[4] Zr,[10] and Hf[10] analogs of **3** (same space group and similar unit cell dimensions). Despite this similarity, the data crystal proved to be a mixture of **3** and the hydride $(C_5Me_5)(C_7H_7)TaH$, small amounts of which were present in samples of **3** as shown by NMR spectroscopy (above). The hydride ligand is probably generated by the activation of cycloheptatriene[43−47] or of the thf solvent. The synthesis and structure of pure samples of $(C_5Me_5)(C_7H_7)TaH$ will be discussed in detail elsewhere.[48] Here, we will limit our discussion to the structure of sandwich compound **3**.

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Each molecule of **3** lies on a mirror plane, which passes through the tantalum atom and a one ring carbon of each of the C_5Me_5 and C_7H_7 rings. In $(C_5Me_5)Ta(C_7H_7)$, the η^5-C_5Me_5 and η^7-C_7H_7 rings are planar and essentially parallel to each other, with a dihedral angle of 3.2° (Figure 2). The Ta−C distances to the C_5Me_5 ring carbons, which range from 2.360(8) to 2.384(5) Å, are very similar to those found in **2**. The Ta−C distances to the C_7H_7 ring carbons, which range from 2.21(2) to 2.28(2) Å, show a little scatter. These ring positions are made somewhat uncertain owing to the presence in the crystal of the admixed tantalum hydride.

Structural Comparisons of $(C_5R_5)M(C_7H_7)$ Complexes as a Function of M. In compounds of the type $(C_5R_5)M(C_7H_7)$, the bond distances to the five- and seven-membered rings vary in an interesting and systematic way as a function of M. Let us define Δ as the average M−C(C_5) distance minus the average M−C(C_7) distance in a $(C_5R_5)M(C_7H_7)$ compound. Interestingly, the value of Δ depends strongly on the nature of the metal: +0.03 Å (Cr),[7] +0.06 Å (Mo),[19] +0.07 Å (V),[7] +0.11 Å (Ta), +0.12 (Ti),[7] and +0.17 Å (Zr).[8] In other words, for Cr the Cr−C(C_7) and the Cr−C(C_5) distances are essentially equal, whereas for Zr the Zr−C(C_7) bonds are 0.17 Å *shorter* than the Zr−C(C_5) bonds.

The above ordering of metals from small to large values of Δ is very similar to the ranking of these same metals according to their covalent radii: the single-bond metallic radii vary as Cr (1.176 Å) < V (1.224 Å) < Mo (1.296 Å) < Ti (1.324 Å) < Ta (1.343 Å) < Zr (1.454 Å).[49] Empirically, the value of Δ becomes larger as the metal radius becomes larger (Figure 3). If we plot the M−C distances themselves as a function of metal radius (Figure 4), we find that the M−C(C_5) distances track the metal radius as expected (i.e, with a slope of near 1). In contrast, in Figure 4 the line for the M−C(C_7) distances as a function of metal radius has a slope of near 0.5.

This result is intriguing. We have at least two questions to answer: (1) why is the M−C distance to the seven-membered ring always shorter (and sometimes considerably shorter) than to the five-membered ring, and (2) why does the difference Δ appear to be correlated with the size of M, being large for large metals and essentially zero for smaller ones?

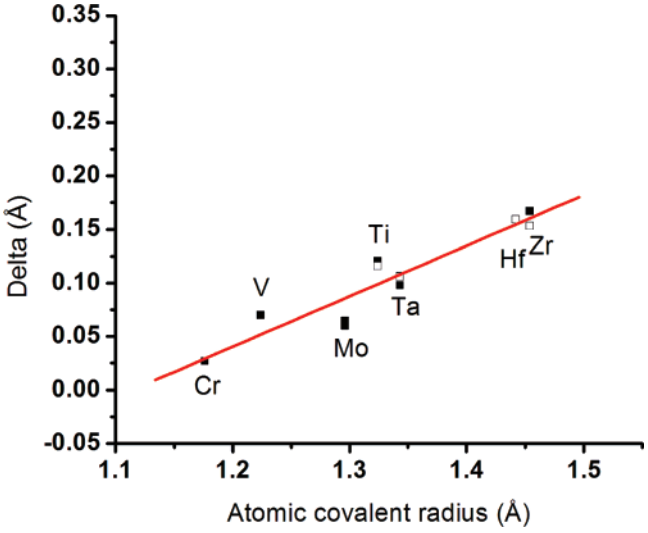

Figure 3. Plot of Δ = M−C(C_5) − M−C(C_7) for known $(C_5R_5)M(C_7H_7)$ compounds. Key: ■ = C_5H_5/C_5H_4Me compounds; □ = C_5Me_5 compounds.

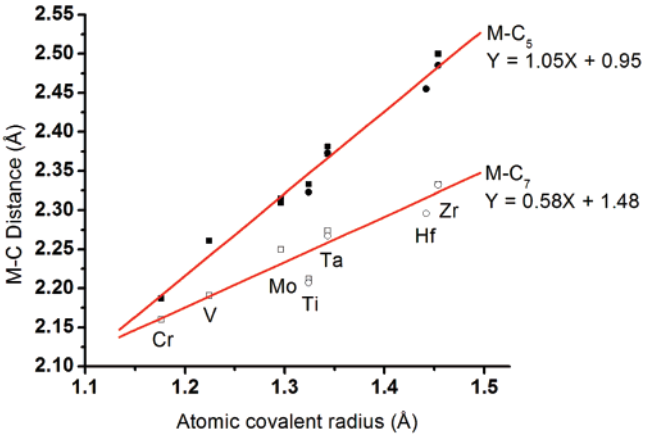

Figure 4. Plot of M−C distances for $(C_5R_5)M(C_7H_7)$ compounds. Key: M−C(C5) distances are shown in black, M−C(C7) distances are shown in white, distances for C_5H_5/C_5H_4Me compounds are shown as squares, and distances for C_5Me_5 rings are shown as circles.

Geometric considerations may play a role in answering these questions. The bonding between a metal center and a cyclic π system is well known to depend on their relative sizes. For example, the peripheral substituents on C_nR_n rings are invariably displaced out of the ring plane toward the metal center for $n > 5$, but are displaced away from the metal

Table 3. Selected Bond Distances and Angles for $(C_5Me_5)Ta(C_7H_7)$ (**3**)[a]

		Bond Distances (Angstroms)	
Ta(1)−C(1)	2.360(8)	C(3)−C(3)′	1.43(1)
Ta(1)−C(2)	2.375(6)	C(1)−C(4)	1.508(10)
Ta(1)−C(3)	2.384(5)	C(2)−C(5)	1.506(7)
Ta(1)−C(11A)	2.21(2)	C(3)−C(6)	1.512(7)
Ta(1)−C(12A)	2.271(16)	C(11A)−C(11A)′	1.410(7)
Ta(1)−C(13A)	2.296(15)	C(11A)−C(12A)	1.410(6)
Ta(1)−C(14A)	2.29(2)	C(12A)−C(13A)	1.397(7)
C(1)−C(2)	1.416(7)	C(13A)−C(14A)	1.410(6)
C(2)−C(3)	1.410(7)		
		Bond Angles (Degrees)	
C(1)−C(2)−C(3)	108.3(5)	C(11A)−C(12A)−C(13A)	129.3(7)
C(2)−C(1)−C(2)′	107.9(7)	C(12A)−C(13A)−C(14A)	129.0(4)
C(2)−C(3)−C(3)′	107.7(3)	C(13A)−C(14A)−C(13A)′	127.3(8)
		C(12A)−C(11A)−C(11A)′	127.9(4)

[a] Primed atoms generated by the transformation $x, -y + {}^3/_2, z$.

center for $n < 5$.[50,51] These displacements increase the overlap between the π system and the d orbitals of the metal atom. This phenomenon is visualized in terms of a rehybridization of the π system so that the constituent p_π atomic orbitals on each carbon atom are no longer perpendicular to the plane of the ring. For a larger ring, the rehybridization causes the lobes of the p_π orbitals proximal to the metal to point inward toward the metal center. In the present case, similar geometric considerations suggest that the relatively large C_7H_7 ring should form the strongest overlap with the d orbitals of large metals such as zirconium, but should overlap more poorly with smaller metals such as chromium, consistent with the experimental trends seen in Figures 3 and 4.

This geometric argument can be complemented by an electronic argument based on the MO diagram of $(C_5H_5)M(C_7H_7)$ complexes, which is well understood.[35,8,52] The lowest lying d orbital is d_{z^2}, which is essentially nonbonding because the carbon atoms of both rings lie very close to the nodal surface of this orbital. As a result, changing the d electron configuration of the metal center from d^0 to d^1 to d^2 (e.g., from Ti to V to Cr) has no direct effect on the bonding with the ligands.[53] Instead, the trends in Figures 3 and 4 can be understood in terms of changes in the metal−ligand bonding orbitals. From highest energy to lowest, the filled metal−ligand bonding orbitals are (1) the δ bond between the e_2 orbitals of the C_7H_7 ring and the d_{xy} and $d_{x^2-y^2}$ orbitals on the metal, (2) the π bond between the e_1 orbitals of the C_5H_5 ring and the d_{xz}/p_x and d_{yz}/p_y hybrids on the metal, and (3) the π bond between the e_1 orbitals of the C_7H_7 ring and the d_{xz}/p_x and d_{yz}/p_y hybrids. For both rings, the totally symmetric a_1 orbitals on the rings are core-like and in the $(C_5H_5)M(C_7H_7)$ sandwich compounds are essentially unmixed with metal orbitals.

The first (and highest-energy) of these metal−ligand bonding orbitals, the δ bond, is especially sensitive to the nature of the metal. For an early transition metal such as zirconium, the d orbitals are large and high in energy owing to the small value of the effective nuclear charge. As a result, the bonding to the C_7H_7 ring consists of strong π and δ components, and this bonding is stronger than the bonding to the C_5H_5 ring, which has only a π component. As the metal becomes smaller and the d orbitals become lower in energy and more contracted, the δ bonding to the C_7H_7 weakens significantly. These effects completely account for the trends seen in Figures 3 and 4.

DFT calculations on a series of $(C_5R_5)M(C_7H_7)$ compounds match the experimental data almost exactly: Δ is predicted to be ~0.02 Å for chromium and ~0.15 Å for zirconium and hafnium, with the calculated Δ values for the other group 4 to group 6 metals falling between these limits.[35,8] Although these papers did not comment on the reasons for this trend, an earlier ab initio SCF-LCAO-MO study[52] reached essentially the same conclusions we have articulated above.

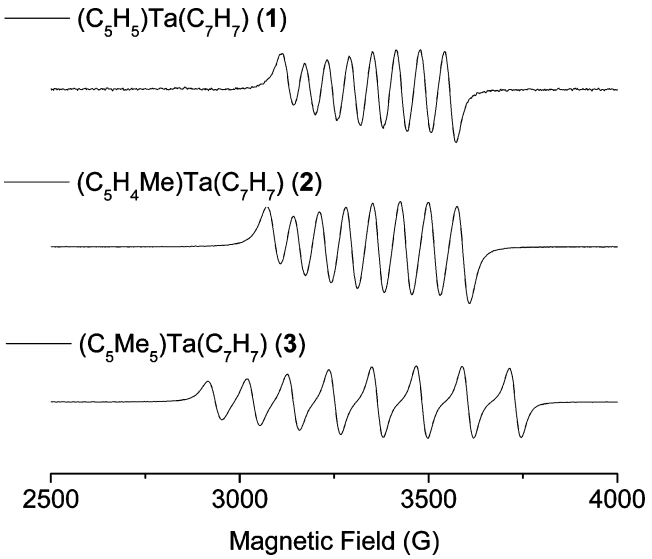

Figure 5. EPR spectra of $(C_5H_5)Ta(C_7H_7)$ (**1**), $(C_5H_4Me)Ta(C_7H_7)$ (**2**), and $(C_5Me_5)Ta(C_7H_7)$ (**3**) in toluene at 25 °C.

No crystal structure has been carried out on a niobium compound of the type $(C_5R_5)M(C_7H_7)$, but a gas-phase electron diffraction study of $(C_5H_5)Nb(C_7H_7)$ has been reported.[54] Interestingly, this investigation concluded that the M−C(C_5) distances are *shorter* than the M−C(C_7) distances: 2.315(14) versus 2.390(9) Å, respectively, giving $\Delta = -0.1$ Å (vs the +0.1 Å value expected from Figure 3 and predicted from DFT calculations[35]). We believe that the distances deduced from the electron diffraction study are almost certainly in error. In general, it will be difficult to distinguish M−C distances to one ring versus the other in such a compound from electron diffraction data, owing to the intrinsically poor resolution of the radial distribution curve. As further evidence that the electron diffraction study is in error, Δ is +0.08 and +0.12 Å, respectively, in the X-ray crystal structures of the cation $(C_5H_4Me)Nb(C_7H_7)(thf)^+$ and the anion $(C_5H_5)Nb(C_7H_7)^-$.[21]

EPR Studies. Paramagnetic transition-metal sandwich complexes such as $(C_5H_5)_2M$ (M = V, Cr^+, Fe^+, Co, Ni^+),[55] $(C_5R_5)_2Mn$ (R = H,[56] Me[57]), $(C_6H_6)_2M$ (M = V[58], Nb,[58] Ta,[58,59] Co[60]), $(C_5H_5)V(C_7H_7)$,[36] $(C_5H_5)M(C_6H_6)$ (M = Co^+,[61] Fe[62]), $(C_5H_5)V(C_8H_9)$,[45] and $(C_5H_5)Ti(C_8H_8)$,[63,64] have been extensively characterized by EPR spectroscopy. The EPR spectra of **2** both in solution and as a frozen glass have been reported previously;[15] our results are essentially identical,

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(53) Actually, the d_{z^2} orbital is very slightly metal-C_7H_7 antibonding, but this effect is not sufficient to account for the magnitude of the trends seen in Figures 3 and 4.
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except that we find a somewhat different value for $A_\perp$. In toluene at room temperature, the EPR spectra of all three compounds consist of isotropic octets due to the $I = {}^7/_2$ tantalum nuclear spin (Figure 5). No superhyperfine structure attributed to hydrogen atoms was resolved in any of the room-temperature spectra. The tantalum isotropic hyperfine coupling constant A_{iso} scales linearly with the number of methyl groups on the C_5R_5 ring: from 61 G for C_5H_5 compound **1**, to 71 G for C_5H_4Me compound **2**, to 113 G for C_5Me_5 compound **3**. This trend indicates that the electron donating methyl substituents on the C_5R_5 ring shift the unpaired electron density more completely onto the tantalum nucleus. A similar but more subtle linear trend is also seen for the isotropic g factor g_{iso}: 1.944 for **1**, 1.945 for **2**, and 1.949 for **3**.

The EPR spectra of **1**−**3** as frozen glasses at 110 K all correspond to axial symmetry. Simulations afford line shapes that agree very closely with those observed (Figure 6). The hyperfine coupling with the tantalum center is highly anisotropic, with $A_{||}$ being considerably larger than $A_\perp$. The values of the isotropic and anisotropic hyperfine splittings clearly show that, in all three compounds, all of these parameters have the same sign. Like A_{iso}, both $A_{||}$ and $A_\perp$ increase linearly with the number of methyl groups on the C_5R_5 ring: $A_{||}$ increases from 153 G for **1** to 208 G for **3**, whereas $A_\perp$ increases from 8 to 60 G. Superhyperfine structure due to hydrogen atoms was seen in the spectrum of only C_5Me_5 compound **3**, and the 6.3 G splitting was attributed to the protons on the C_7H_7 ring. Superhyperfine splittings of 4.6 and 6.1 G have been seen for $CpV(C_7H_7)$[36] and 6.1 G in $(C_6H_6)_2Ta$,[58] respectively. To our knowledge, the splitting due to the ring protons in **3** is larger than in any other transition-metal sandwich complex, which suggests that there is significant delocalization of the unpaired electron onto the C_7H_7 ring.

The values of the tantalum hyperfine splittings afford insights into the electronic structure of these complexes. A previous photoelectron spectroscopic study of $(C_5H_4Me)Ta(C_7H_7)$ suggested that one unpaired electron resides in the a_1 HOMO, which has mainly d_{z^2} character.[65] This conclusion is consistent with several other findings: the results of DFT calculations,[35] the closeness of the g values to 2, and the fact that the EPR spectra are readily observable at room temperature. McGarvey has shown that, for a d^1 system with the unpaired electron in an orbital of d_{z^2} character, the hyperfine splittings are given by the following expressions:[66]

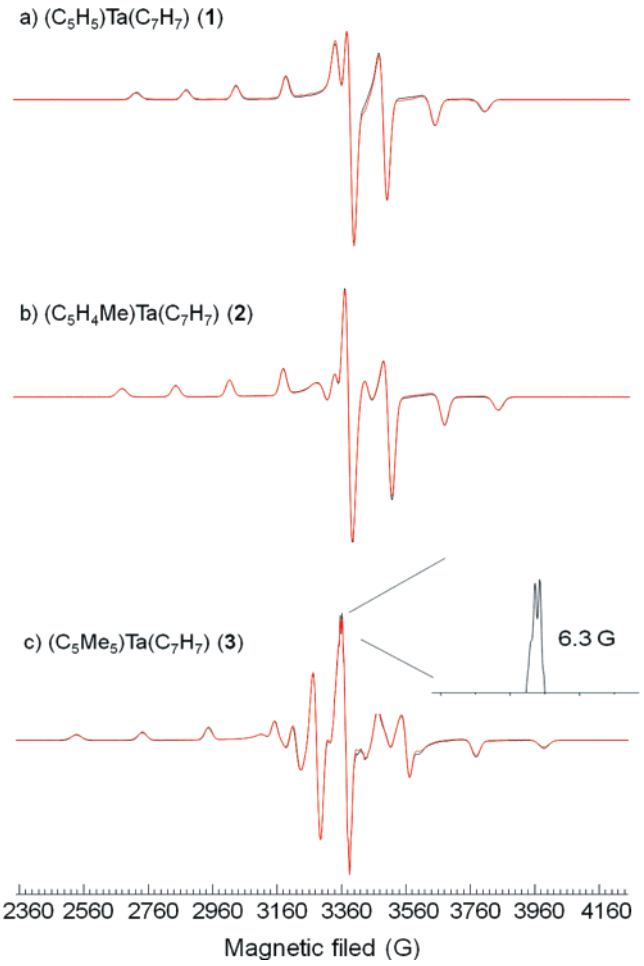

Figure 6. EPR spectra of (a) $(C_5H_5)Ta(C_7H_7)$ (**1**), (b) $(C_5H_4Me)Ta(C_7H_7)$ (**2**), and (c) $(C_5Me_5)Ta(C_7H_7)$ (**3**) at 110 K (black line = experiment; red line = simulation).

$$A_{||} = P[-\kappa + 4c^2/7 - (g_\perp - g_e)/7] \quad (1)$$

$$A_\perp = P[-\kappa - 2c^2/7 + 15(g_\perp - g_e)/14] \quad (2)$$

where P is the dipolar interaction constant, κ is Fermi isotropic contact term, c^2 is the fraction of d_{z^2} character in the orbital carrying the unpaired electron, and $g_e = 2.0023$. These equations assume that the spin−orbit parameter λ is small compared to the energy difference between d_{z^2} and the other orbitals with metal character; for **1**−**3**, this is very likely to be a good assumption. With two observables and three variables (P, κ, and c^2), there is no unique fit to these equations. A PES study[34] and a DFT calculation[35] suggest that c^2 is close to 1 for $(C_5H_4R)Ta(C_7H_7)$, and a MO study of the analogous vanadium compound gave a value for c^2 of 0.90.[36] By using a similar value of 0.90 for c^2 for all three compounds **1**−**3**, we can deduce values for P and κ (Table 5) from the following rearranged forms of eqs 1 and 2:

$$P = 14(A_{||} - A_\perp)/[12c^2 - 17(g_\perp - g_e)] \quad (3)$$

$$\kappa = \{A_{||}[4c^2 - 15(g_\perp - g_e)] + A_\perp[8c^2 - 2(g_\perp - g_e)]\}/14(A_\perp - A_{||}) \quad (4)$$

Physically meaningful values for P and κ are obtained only

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Table 4. EPR Data for $(C_5H_5)Ta(C_7H_7)$ (**1**), $(C_5H_4Me)Ta(C_7H_7)$ (**2**), and $(C_5Me_5)Ta(C_7H_7)$ (**3**)[a]

	A_{iso} (G)	g_{iso}	$A_{\|}$ (G)	$g_{\|}$	$A_{\perp}$ (G)	$g_{\perp}$	a_H (G)	κ	P (G)
$(C_5H_5)Ta(C_7H_7)$ (**1**)	61	1.944	153	1.989	8	1.921	[b]	−0.4	166.6
$(C_5H_4Me)Ta(C_7H_7)$ (**2**)	71	1.945	166	1.987	20	1.921	[b]	−0.5	167.8
$(C_5Me_5)Ta(C_7H_7)$ (**3**)	113	1.949	208	1.989	60	1.927	6.3	−0.7	171.5

[a] The deduced values for κ and P assume that $c^2 = 0.9$ in eqs 3 and 4 (see text). [b] Not observed.

if the signs of all of the hyperfine couplings are assumed to be positive; positive signs for the hyperfine couplings were also observed for $(C_6H_6)_2Ta$.[58] The fits show that the dipolar interaction constant P is very similar for **1**−**3**. The magnitude of the Fermi isotropic contact term $|\kappa|$ increases from **1** to **2** to **3**, a trend that is consistent with the increased donor properties of the C_5R_5 ring and the consequent higher energy of the d_{z^2} orbital.

Experimental Section

All of the syntheses were performed under an argon atmosphere with glove box and Schlenk techniques. Solvents were dried over sodium/benzophenone and distilled under nitrogen immediately before use. The starting materials cycloheptatriene (90%, Lancaster), and magnesium turnings (99.9+ %, Alfa Aesar) were used as received. The compounds $(C_5H_5)TaCl_4$, $(C_5H_4Me)TaCl_4$, and $(C_5Me_5)TaCl_4$ were prepared by following literature procedures.[67] IR spectra were recorded on a Nicolet Impact 410 as Nujol mulls between KBr plates. The ^{1}H 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, X-ray diffraction data were collected on a Siemens Smart CCD instrument. EPR spectra were recorded in toluene either as solutions or as frozen glasses on a Varian E-122 X band spectrometer in the Illinois EPR Research Center at the University of Illinois. The magnetic fields were calibrated with a Varian NMR Gaussmeter. The EPR simulations were performed on the *SIMPIPM* program, which is a modified version of *QPOW*.[68]

(Cycloheptatrienyl)(cyclopentadienyl)tantalum(IV), (1). To a suspension of $(C_5H_5)TaCl_4$ (2.0 g, 5.2 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 magnesium 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 magnesium, 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, and taken to dryness. The residue was sublimed at 80 °C and 0.05 Torr to afford a red-brown solid. Yield: 0.1 g (5.8%). Anal. Calcd C, 42.7; H, 3.59; Ta, 53.7. Found. C, 42.7; H, 4.14; Ta, 52.7. FI−MS (*m/z*; relative intensity; assignment): 91.0 (8, $C_7H_7^+$), 337.1 (100, M^+). IR (cm^{-1}): 1305 m, 1170 w, 1156 w, 1013 m, 949 m, 853 w, 793 s, 680 m.

(Cycloheptatrienyl)(monomethylcyclopentadienyl)tantalum-(IV), (2).[15] This compound was prepared as described above for **1** except that $(C_5H_4Me)TaCl_4$ (2 g, 5.0 mmol) was the starting material, and the product was obtained as red-brown crystals from the filtered pentane extracts by concentration to ca. 60 mL and cooling to −20 °C. Yield: 0.35 g (20%). FI−MS (*m/z*, relative intensity, assignment): 351.1 (100, M^+). IR (cm^{-1}): 1309 s, 1171 m, 1151 m, 1036 m, 1024 m, 949 m, 897 w, 847 w, 787 vs, 680 w.

(Cycloheptatrienyl)(pentamethylcyclopentadienyl)tantalum-(IV), (3). This compound was prepared as described above for **1** except that $(C_5Me_5)TaCl_4$ (2 g, 4.4 mmol) was the starting material, and the product was obtained as red brown crystals from the filtered pentane extracts by concentration to ca. 60 mL and cooling to −20 °C. Yield: 0.62 g (35%). Anal. Calcd C, 50.1; H, 5.44. Found. C, 50.8; H, 5.83. IR (cm^{-1}): 1682 w, 1306 s, 1167 m, 1156 m, 1033 m, 947 m, 853 w, 789 s, 767 m. The compound is accompanied by small amounts of (cycloheptatrienyl)(pentamethylcyclopentadienyl)-hydridotantalum(V), $(C_5Me_5)(C_7H_7)TaH$, as judged by ^{1}H NMR spectroscopy and X-ray crystallography.

Crystallographic Data.[69] Single crystals of $(C_5H_4Me)Ta(C_7H_7)$ (**2**), crystallized from pentane, 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 $(C_5Me_5)Ta(C_7H_7)$ (**3**) were obtained and treated similarly. Standard peak search and indexing procedures, followed by least-squares refinement using 863 reflections for **2**, and 1444 reflections for **3**, yielded the cell dimensions given in Table 1. Data were collected with an area detector using the measurement parameters listed in Table 1.

2: The systematic absences $0k0$ ($k \neq 2n$) and $h0l$ ($l \neq 2n$) were consistent only with the space group $P2_1/c$. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, a face-indexed absorption correction was applied. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All of the 2591 unique data were used in the least-squares refinement.

The structure was solved by direct methods (*SHELXTL*). The correct positions for all of the non-hydrogen atoms were deduced from an E-map. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)$,[2] where $w = \{[\sigma(F_o^2)]^2 + (0.02P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all of the structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least-squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. The hydrogen atoms were placed in idealized positions; methine and methyl hydrogen atoms were given displacement parameters equal to 1.2 or 1.5 times U_{eq} for the attached carbon atom, respectively. Successful convergence was indicated by the maximum shift/error of 0.002 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (1.98 e $Å^{-3}$) was located 1.02 Å from the tantalum atom. A final analysis of the variance between observed and calculated structure factors showed no apparent errors.

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(69) Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139−2144.

3: The diffraction record was strongly suggestive of a C-centered orthorhombic cell, but closer inspection showed that the cell was in fact primitive. Systematic absences $0kl$ ($k + l \neq 2n$) and $hk0$ ($h \neq 2n$) suggested the space groups $Pna2_1$ and $Pnma$; the average values of the normalized structure factors suggested the centrosymmetric choice $Pnma$, which was confirmed by the successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. No correction for crystal decay was necessary, but the data were corrected for absorption by the face-indexed method, the maximum and minimum transmission factors being 0.862 and 0.549, respectively. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All of the 1876 unique data were used in the least-squares refinement.

The structure was solved by direct methods (*SHELXTL*); correct positions for the tantalum atom and the carbon atoms of the C_5Me_5 ring were evident in the E-map. Subsequent difference Fourier calculations revealed the locations of the remaining carbon atoms. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)$,[2] where $w = \{[\sigma(F_o^2)]^2 + (0.02P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all of the structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least-squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms.

The displacement parameters of the carbon atoms of the C_7H_7 ring were unexpectedly large and elongated, and so a disorder model was constructed in which each of the carbon atoms of the C_7H_7 ring was split among two positions. Within each disordered component, the C−C distances and C−C−C angles were restrained to be equal, and the displacement parameters for these atoms were restrained to be similar. A common site occupancy factor was refined for each disordered component subject to the restraint that the sum of the factors was equal to one; the site occupancy factor for the major component refined to 0.56(2). The minor C_7H_7 ring was essentially parallel to the C_5Me_5 ring plane (dihedral angle of $3 \pm 1°$), as expected for the molecule $(C_5Me_5)Ta(C_7H_7)$. The major C_7H_7 ring, however, formed a dihedral angle of $16.4 \pm 0.8°$ with respect to the C_5Me_5 ring. This result suggests that the data crystal is a mixture of two molecules: $(C_5Me_5)Ta(C_7H_7)$ and the hydride $(C_5Me_5)(C_7H_7)TaH$. The final refinement model consisted of a superposition of these two molecules, in which the atomic positions of the tantalum atom and the C_5Me_5 ring in the two constituents coincide. The C_7H_7 rings, however, appear disordered over two positions that describe different dihedral angles with respect to the 5-membered ring: nearly parallel for **3** and distinctly tilted for the tantalum hydride impurity.

The partial occupancy hydrogen atom attached to tantalum could not be reliably located in the difference maps. Carbon-bound hydrogen atoms were included in idealized positions (methyl groups except for that on C6 were allowed to rotate about the C−C axes), with C−H distances of 0.98 (methyl) and 0.95 Å (methine). Displacement parameters for the hydrogen atoms were set equal to 1.5 times U_{eq} (methyl) or 1.2 times U_{eq} (methine) of the attached carbon atom. No correction for isotropic extinction was necessary. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (0.97 eÅ^{-3}) was located 1.48 Å from Ta1 and 1.37 Å from C3. A final analysis of variance between observed and calculated structure factors no systematic errors. The z coordinate for the tantalum atom of −0.007 accounts for the observed C-centered pseudosymmetry. Inspection of the original diffraction record showed no signs of a supercell.

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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.

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