Synthesis and Characterization of the Cycloheptatrienyl Tantalum “Mixed-Sandwich” Compounds (C₅R₅)Ta(C₇H₇)

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The molecule (cycloheptatrienyl)(cyclopentadienyl)tantalum, (C₅H₅)Ta(C₇H₇) (1), and its methylcyclopentadienyl and pentamethylcyclopentadienyl analogues (C₅H₅Me)Ta(C₇H₇) (2), and (C₅Me₅)Ta(C₇H₇) (3) have been synthesized by magnesium reduction of the corresponding (C₅R₅)TaCl₄ 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 C₇H₇ ring are significantly shorter (by about 0.1 Å) than those to the cyclopentadienyl ring; the difference reflects stronger bonding to the C₇H₇ ring. A comparison with the structures of other (C₅R₅)M(C₇H₇) 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 σ bonding with the ring. For 1–3, the EPR spectra at room temperature consist of octets due to the tantalum nuclear spin. Both Aiso and giso 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 (C₅H₅)M(C₇H₇), or their ring-substituted analogs, are known for Ti,²⁻⁷ Zr,²⁻⁸ Hf,²⁻¹⁰ V,⁷⁻¹¹⁻¹³ Nb,⁹⁻¹⁴ Ta,¹⁵ Cr,⁷⁻¹⁶⁻¹⁸ 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

(18) Fischer, E. O.; Breitschaft, S. Angew. Chem. 1965, 73, 94–95.
Such C₅—C₇ mixed-sandwich complexes, which are iso-electronic with bis(arene)metal compounds, have been the subject of extensive spectroscopic studies and theoretical calculations. The formal charge of the bound cycloheptatrienyl ring, C₇H₇, can be considered to be either 1+ or 3−, both of which satisfy Hückel’s 4n + 2 rule. Photoelectron spectroscopic studies of (C₅H₅)M(C₇H₇) 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. Theoretical calculations on the same systems showed smaller contributions of the metal orbitals to the C₇H₇ ligand.

In contrast to the situation for other group 4 to group 6 transition elements, the chemistry of (cyclopentadienyl)-tantalum complexes is relatively poorly developed: only the methylcycloheptatrienyl mixed-sandwich compound (C₅H₄Me)Ta(C₇H₇) has been described previously. Here, we report the syntheses of the analogous cyclopentadienyl and tetratrienyl ring, C₇H₇, can be considered to be either 1, 3, or 5.

Results and Discussion

Synthesis and Characterization. In 1992, Green showed that the magnesium reduction of (C₅H₄Me)TaCl₄ in the presence of cycloheptatriene afforded the mixed-sandwich compound (C₅H₄Me)Ta(C₅H₅). These workers reported that they were unable to obtain the unsubstituted compound (C₅H₅)Ta(C₇H₇) 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 (C₅R₅)TaCl₄ with magnesium in tetrahydrofuran in the presence of cycloheptatriene affords the mixed-sandwich species (C₅H₅)Ta(C₇H₇) (1), (C₅H₄Me)Ta(C₅H₅) (2), and (C₅Me₃)Ta(C₇H₇) (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, (C₅H₄Me)Ta(C₅H₅) was reported to be blue, but in our hands it was red-brown both in solution and in the solid state.

\[(C₅R₅)TaCl₄ + 2Mg + C₇H₈ \rightarrow (C₅R₅)Ta(C₅H₅) + 2MgCl₂ + “H”\]

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 (C₅H₅)Ta⁺.

![Figure 1. Molecular structure of (C₅H₄Me)Ta(C₅H₅) (2).](image)

![Figure 2. Molecular structure of (C₅Me₃)Ta(C₅H₅) (3).](image)

as has previously been claimed for certain vanadium and titanium analogues.

The IR spectrum of C₅H₅ compound 1 shows two equal-intensity bands at 1170 and 1156 cm⁻¹ that are assigned to in-plane C−H deformations of the C₅H₅ ring and a band at 1013 cm⁻¹ due to in-plane C−H bending of the C₅H₅ ring. The IR spectrum of C₅H₄Me compound 2 shows similar C₅H₅ bands at 1171 and 1151 cm⁻¹ and C₅H₄Me bands at 1036 and 1024 cm⁻¹, whereas C₅Me₃ compound 3 shows C₅H₅ bands at 1167 and 1156 cm⁻¹ and a methyl rocking band at 1033 cm⁻¹ from the C₅Me₃ 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 (C₅Me₅)(C₅H₅)-TaH (below).

Crystal Structures of (C₅H₄Me)Ta(C₅H₅) (2) and (C₅Me₃)Ta(C₅H₅) (3). The molecular structures of 2 and 3...
Cycloheptatrienyl Tantalum “Mixed-Sandwich” Compounds

Table 1. Crystallographic Data for (C_5H_4Me)Ta(C_7H_7) (2) and (C_6Me_5)Ta(C_7H_7) (3)

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<td>b/Å</td>
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<td>0.971 and -1.370</td>
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* R₁ = Σ||Fo|| - |Fc||/Σ|Fo|, wR² = Σ[w(Fo² - Fc²)²]/Σ[w(Fc²)²]¹/₂.

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

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<td>Ta(1)−C(18)</td>
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<td>107.3(7)</td>
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<td>C(3)−C(4)−C(5)</td>
<td>111.6(9)</td>
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<td>C(4)−C(5)−C(1)</td>
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<td>128.8(8)</td>
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<tr>
<td>C(5)−C(1)−C(2)</td>
<td>106.6(8)</td>
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<tr>
<td>C(11)−C(12)−C(13)</td>
<td>128.4(10)</td>
<td>126.6(11)</td>
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</table>

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 η⁶-C₅H₅Me and η⁷-C₇H₇ rings are essentially parallel to each other (dihedral angle = 1.7⁰). 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 C₇H₇ 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 C₇H₇ group is bound more strongly to the tantalum center.31,21 Interestingly, DFT calculations on (C₅H₅)Ta(C₇H₇) find the same structural feature: the Ta−C(C₅) and Ta−C(C₇) 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 C₇H₇ ring matches the difference seen experimentally. We will return to this point below.

Crystals of 2 are isomorphous with those of its molybdenum analogs19 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 (C₅H₅)MeMo(C₇H₇) 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 pentamethycyclopentadienyl 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 Ti₄, Zr₁₀, and Hf₁₀ 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 (C₆Me₅)(C₇H₇)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 cycloheptatriene⁵³⁻⁵⁴ or of the thf solvent. The synthesis and structure of pure samples of (C₅Me₅)(C₇H₇)TaH will be discussed in detail elsewhere.⁴⁸ Here, we will limit our discussion to the structure of sandwich compound 3.

Each molecule of 3 lies on a mirror plane, which passes through the tantalum atom and a one ring carbon of each of the C₅Me₅ and C₇H₇ rings. In (C₅Me₅)₅Ta(C₇H₇), the η⁵-C₅-Me₅ and η⁷-C₇H₇ rings are planar and essentially parallel to each other, with a dihedral angle of 3.2° (Figure 2). The Ta–C distances to the C₅Me₅ 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 C₇H₇ 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 (C₅R₅)M(C₇H₇) Complexes as a Function of M.** In compounds of the type (C₅R₅)M(C₇H₇), 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(C₇) distance minus the average M–C(C₅) distance in a (C₅R₅)M(C₇H₇) compound. Interestingly, the value of Δ depends strongly on the nature of the metal: +0.03 Å (Cr), +0.06 Å (Mo), +0.07 Å (V), +0.11 Å (Ta), +0.12 Å (Ti), and +0.17 Å (Zr). In other words, for Cr the Cr–C(C₅) and the Cr–C(C₇) distances are essentially equal, whereas for Zr the Zr–C(C₅) bonds are 0.17 Å shorter than the Zr–C(C₇) 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). 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(C₅) 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(C₇) 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?

**Table 3.** Selected Bond Distances and Angles for (C₅Me₅)₅Ta(C₇H₇) (3)*

<table>
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<tr>
<th>Bond Distances (Angstroms)</th>
<th>Bond Angles (Degrees)</th>
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<td>Ta(1)–C(1)</td>
<td>2.360(8)</td>
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<td>Ta(1)–C(2)</td>
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<td>Ta(1)–C(3)</td>
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<td>Ta(1)–C(12A)</td>
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<td>Ta(1)–C(14A)</td>
<td>2.29(2)</td>
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<td>C(1)–C(2)</td>
<td>1.416(7)</td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.410(7)</td>
</tr>
</tbody>
</table>

*Primed atoms generated by the transformation x, −y + 3/2, z.

**Figure 3.** Plot of Δ = M–C(C₅) − M–C(C₇) for known (C₅R₅)M(C₇H₇) compounds. Key: ■ = C₅H₅/C₅H₄Me compounds; □ = C₅Me₅ compounds.

**Figure 4.** Plot of M–C distances for (C₅R₅)M(C₇H₇) compounds. Key: M–C(C₅) distances are shown in black, M–C(C₇) distances are shown in white, distances for C₅H₅/C₅H₄Me compounds are shown as squares, and distances for C₅Me₅ 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 C₅R₅ rings are invariably displaced out of the ring plane toward the metal center for n > 5, but are displaced away from the metal.
Cycloheptatrienyl Tantalum “Mixed-Sandwich” Compounds

center for \( n < 5.05^{51} \) These displacements increase the overlap between the \( \pi \) system and the \( d \) orbitals of the metal atom. This phenomenon is visualized in terms of a rehybridization of the \( \pi \) system so that the constituent \( p_x \) 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 \( p_x \) orbitals proximal to the metal to point inward toward the metal center. In the present case, similar geometric considerations suggest that the relatively large \( \text{C}_7\text{H}_7 \) 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 (\( \text{C}_5\text{H}_5 \))\( M \)-(\( \text{C}_7\text{H}_7 \)) complexes, which is well understood.\(^{53,58,52} \) 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 \( \delta \) bond between the \( e_2 \) orbitals of the \( \text{C}_7\text{H}_7 \) ring and the \( d_{xy} \) and \( d_{x^2-y^2} \) orbitals on the metal, (2) the \( \pi \) bond between the \( e_1 \) orbitals of the \( \text{C}_7\text{H}_7 \) ring and the \( d_{x^2}/d_p \) and \( d_{y^2}/d_p \) hybrids on the metal, and (3) the \( \pi \) bond between the \( e_1 \) orbitals of the \( \text{C}_7\text{H}_7 \) ring and the \( d_{x^2} \) and \( d_{y^2} \) hybrids. For both rings, the totally symmetric \( a_1 \) orbitals on the rings are core-like and in the (\( \text{C}_5\text{H}_5 \))\( M \)-(\( \text{C}_7\text{H}_7 \)) sandwich compounds are essentially unmixed with metal orbitals.

The first (and highest-energy) of these metal—ligand bonding orbitals, the \( \delta \) 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 \( \text{C}_7\text{H}_7 \) ring consists of strong \( \pi \) and \( \delta \) components, and this bonding is stronger than the bonding to the \( \text{C}_7\text{H}_7 \) ring, which has only a \( \pi \) component. As the metal becomes smaller and the \( d \) orbitals become lower in energy and more contracted, the \( \delta \) bonding to the \( \text{C}_7\text{H}_7 \) weakens significantly. These effects completely account for the trends seen in Figures 3 and 4.

DFT calculations on a series of (\( \text{C}_5\text{R}_5 \))\( M \)-(\( \text{C}_7\text{H}_7 \)) compounds match the experimental data almost exactly: \( \Delta \) is predicted to be \( \sim 0.02 \) \( \text{Å} \) for chromium and \( \sim 0.15 \) \( \text{Å} \) for zirconium and hafnium, with the calculated \( \Delta \) values for the other group

Figure 5. EPR spectra of (\( \text{C}_5\text{H}_4 \text{Me} \))\( \text{Ta} \)-(\( \text{C}_7\text{H}_7 \)) (1), (\( \text{C}_5\text{H}_4 \text{Me} \))\( \text{Ta} \)-(\( \text{C}_7\text{H}_7 \)) (2), and (\( \text{C}_5\text{Me}_5 \))\( \text{Ta} \)-(\( \text{C}_7\text{H}_7 \)) (3) in toluene at 25 °C.

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.

No crystal structure has been carried out on a niobium compound of the type (\( \text{C}_5\text{R}_5 \))\( M \)-(\( \text{C}_7\text{H}_7 \)), but a gas-phase electron diffraction study of (\( \text{C}_5\text{H}_5 \))\( \text{Nb} \)-(\( \text{C}_7\text{H}_7 \)) has been reported.\(^{54} \) Interestingly, this investigation concluded that the \( M-(\text{C}_5) \) distances are shorter than the \( M-(\text{C}_7) \) distances: 2.315(14) versus 2.390(9) \( \text{Å} \), respectively, giving \( \Delta \) = \( -0.1 \) \( \text{Å} \) (vs the +0.1 \( \text{Å} \) value expected from Figure 3 and predicted from DFT calculations\(^{55} \)). We believe that the distances deduced from the electron diffraction study are almost certainly in error. In general, it will be difficult to distinguish \( M-(\text{C}_5) \) 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, \( \Delta \) is +0.08 and +0.12 \( \text{Å} \), respectively, in the X-ray crystal structures of the cation (\( \text{C}_5\text{H}_4 \text{Me} \))\( \text{Nb} \)-(\( \text{C}_7\text{H}_7 \)-(thf))\(^+ \) and the anion (\( \text{C}_5\text{H}_4 \text{Me} \))\( \text{Nb} \)-(\( \text{C}_7\text{H}_7 \))\(^- \).\(^{21} \)

EPR Studies. Paramagnetic transition-metal sandwich complexes such as (\( \text{C}_5\text{H}_5 \))\( M \)-(\( \text{V} = \text{V}, \text{Cr}^+ \), \( \text{Fe}^+ \), \( \text{Co}, \text{Ni}^+ \)\),\(^{55} \) (\( \text{C}_5\text{R}_5 \))\( \text{Mn} \)-(\( \text{R} = \text{H}, \text{Me}^5 \)\), \( \text{C}_5\text{H}_5 \))\( M \)-(\( \text{V} = \text{V}^+ \), \( \text{Nb}^+ \), \( \text{Ta}^{58,59} \), \( \text{Co}^{60} \)\), \( \text{C}_5\text{H}_5 \))\( \text{V} \)-(\( \text{C}_7\text{H}_7 \))\(^{26} \) (\( \text{C}_5\text{H}_5 \))\( \text{M} \)-(\( \text{C}_6\text{H}_6 \)) (\( \text{M} = \text{Co}^{7+} \), \( \text{Fe}^{65} \), \( \text{C}_5\text{H}_5 \))\( \text{V} \)-(\( \text{C}_8\text{H}_9 \))\(^{45} \) and (\( \text{C}_5\text{H}_5 \))\( \text{Ti} \)-(\( \text{C}_6\text{H}_6 \))\(^{63,64} \) 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.

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 \( I = \frac{7}{2} \) 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 \( \text{C}_3\text{R}_3 \) ring: from 61 G for \( \text{C}_5\text{H}_5 \) compound 1, to 71 G for \( \text{C}_6\text{HMe} \) compound 2, to 113 G for \( \text{C}_6\text{Me}_5 \) compound 3. This trend indicates that the electron donating methyl substituents on the \( \text{C}_3\text{R}_3 \) 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 \( A_\parallel \) 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 \( A_\parallel \) and \( A_\perp \) increase linearly with the number of methyl groups on the \( \text{C}_3\text{R}_3 \) ring: \( A_\parallel \) 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 \( \text{C}_6\text{Me}_5 \) compound 3, and the 6.3 G splitting was attributed to the protons on the \( \text{C}_7\text{H}_7 \) ring. Superhyperfine splittings of 4.6 and 6.1 G have been seen for \( \text{CpV}(\text{C}_7\text{H}_7)_3 \) and \( \text{CpV}(\text{C}_7\text{H}_7)_3 \) 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 \( \text{C}_7\text{H}_7 \) ring.

The values of the tantalum hyperfine splittings afford insights into the electronic structure of these complexes. A previous photoelectron spectroscopic study of \( \text{CpC}_5\text{H}_4\text{Me} \text{Ta(C}_7\text{H}_7)_3 \) suggested that one unpaired electron resides in the \( \text{a}_1 \) HOMO, which has mainly \( d_z^2 \) character. 65 This conclusion is consistent with several other findings: the results of DFT calculations, 38 the close agreement 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

\[
A_{\parallel} = P[\kappa + 4c^2/7 - (g_\parallel - g_\perp)/7] \\
A_{\perp} = P[\kappa - 2c^2/7 + 15(g_\perp - g_\parallel)/14]
\]

where \( P \) is the dipolar interaction constant, \( \kappa \) is Fermi isotropic contact term, \( c^2 \) is the fraction of \( d_z^2 \) character in the orbital carrying the unpaired electron, and \( g_\perp = 2.0023 \). These equations assume that the spin–orbit parameter \( \lambda \) is small compared to the electron 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 (\( P, \kappa \), and \( c^2 \)), there is no unique fit to these equations. A PES study 64 and a DFT calculation 35 suggest that \( c^2 \) is close to 1 for \( \text{CpC}_5\text{H}_4\text{R} \text{Ta(C}_7\text{H}_7)_3 \), 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 \( \kappa \) (Table 5) from the following rearranged forms of eqs 1 and 2:

\[
P = 14[A_{\parallel} - A_{\perp}]/[12c^2 - 17(g_\perp - g_\parallel)] \\
\kappa = \{A_{\parallel} [4c^2 - 15(g_\perp - g_\parallel)] + A_{\perp}[8c^2 - 2(g_\perp - g_\parallel)]/14(A_{\parallel} - A_{\perp})
\]
if the signs of all of the hyperfine couplings are assumed to be positive; positive signs for the hyperfine couplings were also observed for (C₅H₅)Ta. 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 C₅R₅ ring and the consequent higher energy of the \( \text{d}_z^2 \) orbital.

### Experimental Section

All of the syntheses were performed under an argon atmosphere with glove box and Schlenk techniques. Solvents were dried over sodium/benzophene and distilled under nitrogen immediately before use. The starting materials cycloheptatriene (90%, Lancaster), sodium/benzophenone and distilled under nitrogen immediately with glove box and Schlenk techniques. Solvents were dried over potassium and magnesium turnings (99.9%, Alfa Aesar) were used as received. The compounds (C₅H₅)TaCl₄, (C₅H₄Me)TaCl₄, and (C₅Me₅)TaCl₄ were prepared by following literature procedures. IR spectra were recorded on a Nicolet Impact 410 as Nujol mulls.

**Cycloheptatrienyl Tantalum “Mixed-Sandwich” Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( A_{\text{pp}} ) (G)</th>
<th>( g_{\text{pp}} )</th>
<th>( A_\theta ) (G)</th>
<th>( g_\theta )</th>
<th>( A_L ) (G)</th>
<th>( g_L )</th>
<th>( a_0 ) (G)</th>
<th>( \kappa )</th>
<th>( P ) (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₅H₅)Ta(C₇H₇) (1)</td>
<td>61</td>
<td>1.944</td>
<td>153</td>
<td>1.989</td>
<td>8</td>
<td>1.921</td>
<td>8</td>
<td>0.4</td>
<td>166.6</td>
</tr>
<tr>
<td>(C₅H₅Me)Ta(C₇H₇) (2)</td>
<td>71</td>
<td>1.945</td>
<td>166</td>
<td>1.987</td>
<td>20</td>
<td>1.921</td>
<td>8</td>
<td>0.5</td>
<td>167.8</td>
</tr>
<tr>
<td>(C₅Me₅)Ta(C₇H₇) (3)</td>
<td>113</td>
<td>1.949</td>
<td>208</td>
<td>1.989</td>
<td>60</td>
<td>1.927</td>
<td>6.3</td>
<td>0.7</td>
<td>171.5</td>
</tr>
</tbody>
</table>

* The deduced values for \( \kappa \) and \( P \) assume that \( c^2 = 0.9 \) in eqs 3 and 4 (see text). \(^{b}\) Not observed.


(68) Nilges, M. J. *SIMPIM*; The Illinois EPR Research Center (IERC): University of Illinois at Urbana–Champaign, IL, 1979.

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 $Pnna$; 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$_5$Me$_5$ 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 $\sum w(F_o^2 - F_c^2)^2$ where $w = \{(\sigma F_o)^2 + (0.02P)^2\}^{-1}$ 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$_7$H$_7$ ring were unexpectedly large and elongated, and so a disorder model was constructed in which each of the carbon atoms of the C$_7$H$_7$ 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$_7$H$_7$ ring was essentially parallel to the C$_5$Me$_5$ ring plane (dihedral angle of $3 \pm 1^\circ$), as expected for the molecule (C$_5$Me$_5$)Ta(C$_7$H$_7$). The major C$_7$H$_7$ ring, however, formed a dihedral angle of $16.4 \pm 0.8^\circ$ with respect to the C$_5$Me$_5$ ring. This result suggests that the data crystal is a mixture of two molecules: (C$_5$Me$_5$)Ta(C$_7$H$_7$) and the hydride (C$_5$Me$_5$)(C$_7$H$_7$)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$_5$Me$_5$ ring in the two constituents coincide. The C$_7$H$_7$ 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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