capability of the N4 donor atom, this coordination mode is more favorable, as the Rh(III) center already contains two very strong σ-donating phenyl rings. This work shows that the most favorable coordination mode for the triazole ligands can be changed by the properties of the metal groups. Furthermore, in all cases the pyridyltriazole ligand remains protonated after coordination to the Rh(III) center, which is in contrast to the case of the $Ru(bpy)_2$ analogues. The latter observation is important for determining the reduction potential of the neutral ligand. So far, reliable reduction potentials of the free pyridyltriazole ligand could not be obtained. The correlation of the first reduction potentials between $[Ru(L)_3]^{2+}$ and $[Rh(ppy)_2(L)]^+$ clearly shows that in all cases a L-based reduction is present for the $[Rh(ppy)_2(L)]^+$ complexes, indicating that the LUMO in these complexes is centered on the pyridyltriazole ligand. This correlation is of importance for the assignment of reduction waves of $[Ru(bpy)_2(L)]^{2+}$ complexes, when it is not clear whether the reduction processes are bpy based or L based. Finally, in agreement with the measurements carried out on the $[Ru(bpy)_2(L)]^{2+}$ complexes, the pyridyltriazole ligands appear to have weaker π-acceptor properties compared to 2,2′-bipyridine. A possible exception is the pyridyltriazole ligand with the nitrophenyl substituent (L7), most likely due to the strong electron-withdrawing power of the substituent. The luminescence observed at 77 K for the $[Rh(ppy)_2(L)]^+$ complexes investigated so far appeared to be rather independent of the σ-donor/σ-acceptor properties of the chelating ligand L. Except for the case of L = biq,[22] a ppy-based π → π* emission could be assigned.

Acknowledgment. We wish to thank Mr. S. Gorter for collecting the crystallographic data and C. Erkelens and A. W. M. Lefeber for performing the 300-MHz (COSY) NMR experiments. Finally, we gratefully acknowledge Unilever Research Laboratories for the permission to use their electrochemical equipment.

Registry No. **1**, 136115-72-5; **2**, 136115-74-7; **3**, 136115-76-9; **4**, 136144-67-7; **5**, 136115-78-1; **6**, 136115-80-5; **6**·$(CH_3)_2CO$, 136115-85-0; **7**, 136115-82-7; **8**, 136115-84-9; L8, 136115-94-1; $[Rh(ppy)_2Cl]_2$, 33915-80-9; $[Rh(ppy)_2(L1)]$, 136115-86-1; $[Rh(ppy)_2(L2)]$, 136115-87-2; $[Rh(ppy)_2(L3)]$, 136115-88-3; $[Rh(ppy)_2(L4)]$, 136115-89-4; $[Rh(ppy)_2(L5)]$, 136115-90-7; $[Rh(ppy)_2(L6)]$, 136115-91-8; $[Rh(ppy)_2(L7)]$, 136115-92-9; $[Rh(ppy)_2(L8)]$, 136115-93-0; 2-thiophenecarboxylic acid hydrazide, 2361-27-5; methyl picolinimidate, 19547-38-7.

Supplementary Material Available: Tables of crystallographic data, positional parameters, thermal parameters, and bond distances and angles for $[Rh(ppy)_2(L6)](PF_6)\cdot(CH_3)_2CO$ and an ORTEP diagram of $[Rh(ppy)_2L_6]^+$ (9 pages); a listing of structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055,
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Synthesis and Structure of $(C_5H_4CH_3)Ta(SPh)_4$ and an EHMO Analysis of Its Distorted Four-Legged Piano-Stool Structure

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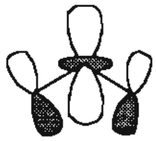
Reaction of $(\eta^5\text{-}C_5H_4Me)TaCl_4$ with 4 equiv of NaSPh at −78 °C gave $(\eta^5\text{-}C_5H_4Me)Ta(SPh)_4$ (**1**). Single-crystal X-ray crystallography showed the molecule to have a distorted four-legged piano-stool structure with two Cp′–Ta–S angles averaging 117.2° and the other two averaging 104.1°. EHMO calculations on $(C_5H_5)Ta(SH)_4$ showed the distortion to be largely electronic in nature as well as showing that cis-ligand interactions in $CpML_4$ complexes cannot be ignored. The Cp–M interaction also has an effect on Cp–M–L angles. Crystal data for **1**: space group $P\bar{1}$; $Z = 2$; $a = 9.817$ (3), $b = 10.458$ (3), $c = 15.612$ (4) Å; $\alpha = 78.78$ (2), $\beta = 71.98$ (2), $\gamma = 67.59$ (2)°; $V = 1404.0$ (6) Å^3; $R = 4.22$, $R_w = 4.30$ based on 4154 reflections with $F_o \geq 5\sigma(F_o)$.

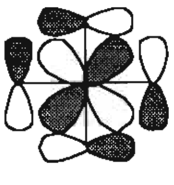
Introduction

Compounds of the formula $CpML_4$ have structures described as "four-legged piano stools". They may also be viewed as square pyramids if the Cp ligand is considered to occupy a single coordination site.

Hoffmann et al. have done an EHMO analysis of the structure of $CpML_4$ compounds to rationalize the preference for the four-legged piano-stool structure over other possible conformers.[1] The major d-orbital interactions are as follows:[1-3] The $d_{x^2-y^2}$ orbital is used up in σ bonding with the four L ligands. The d_{xz} and d_{yz} orbitals are mostly involved with the Cp ligand, although some σ-bonding interactions with the L ligands are also possible. For 18-electron compounds with π-donating ligands, the HOMO is found to be a π* interaction between the metal d_{z^2} orbital and the p_z orbital on each of the L ligands (I*). The SHOMO is also a π* interaction, but between the metal d_{xy} orbital and the p_x or p_y orbital on each of the L ligands (II*). For a 14-electron compound these MOs will be empty; i.e., II* will be the LUMO. The corresponding bonding MOs, I and II, are found much lower in energy.



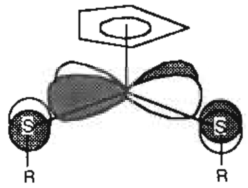
(I*)

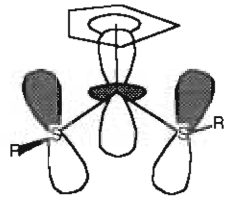


(II*)

Poli has recently described the distortions of individual L ligands in terms of the Cp–M–L angle, θ.[2,3] He found the distortions to be largely dependent on the π-bonding ability of the ligand, the nature of the ligand trans to it, and the metal electron count.

For a thiolate ligand, SR, the orientation of the R substituent will determine with which d orbital the π-donor orbital of the sulfur atom is able to interact. Hence, an orientation with R directed away from the Cp ligand will favor π bonding with the d_{xy} orbital, while R oriented into the plane of the four L ligands will favor π bonding with the d_{z^2} orbital.[1,4]





[†] University of Michigan.
[‡] University of Delaware.

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Table I. Crystallographic Data for Cp′Ta(SPh)$_4$ (**1**)

$C_{30}H_{27}S_4Ta$	fw = 696.5
$a = 9.817\ (3)$ Å	space group = $P\bar{1}$ (No. 2)
$b = 10.458\ (3)$ Å	$T = 298$ K
$c = 15.612\ (4)$ Å	$\lambda = 0.71073$ Å
$\alpha = 78.78\ (2)°$	$\rho_{calcd} = 1.647$ g/cm^3
$\beta = 71.98\ (2)°$	$\mu = 44.24$ cm^{-1}
$\gamma = 67.59\ (2)°$	$T(\max)/T(\min) = 2.367$
$V = 1404.0\ (6)$ Å^3	$R(F) = 4.22\%$
$Z = 2$	$R_w(F) = 4.30\%$

Table II. Atomic Coordinates and Isotropic Thermal Parameters for Cp′Ta(SC$_6$H$_5$)$_4$

atom	*x*	*y*	*z*	*U*,[a] Å^2
Ta	0.26056 (3)	0.19988 (3)	0.34675 (2)	0.0433 (1)
S(1)	0.5106 (2)	0.1576 (2)	0.3683 (1)	0.055 (1)
S(2)	0.3874 (2)	0.0675 (2)	0.2180 (1)	0.048 (1)
S(3)	0.1331 (2)	0.3915 (2)	0.2500 (1)	0.056 (1)
S(4)	0.2089 (3)	0.3983 (3)	0.4302 (1)	0.066 (1)
C(1)	0.0907 (10)	0.1609 (10)	0.4893 (5)	0.071 (4)
C(2)	0.2183 (11)	0.0389 (11)	0.4771 (5)	0.075 (5)
C(3)	0.2211 (10)	−0.0189 (9)	0.4023 (5)	0.065 (4)
C(4)	0.0931 (9)	0.0666 (8)	0.3709 (5)	0.057 (3)
C(5)	0.0072 (9)	0.1783 (9)	0.4260 (5)	0.063 (4)
C(6)	−0.1412 (10)	0.2878 (11)	0.4212 (7)	0.090 (5)
C(11)	0.7782 (6)	0.0404 (5)	0.2453 (3)	0.066 (4)
C(12)	0.9053	−0.0689	0.2063	0.079 (5)
C(13)	0.9169	−0.2058	0.2385	0.081 (5)
C(14)	0.8014	−0.2334	0.3095	0.077 (5)
C(15)	0.6743	−0.1241	0.3485	0.068 (4)
C(16)	0.6628	0.0128	0.3163	0.051 (3)
C(21)	0.5254 (6)	0.2670 (5)	0.1330 (3)	0.060 (4)
C(22)	0.6201	0.3179	0.0593	0.078 (5)
C(23)	0.6998	0.2419	−0.0159	0.091 (5)
C(24)	0.6850	0.1150	−0.0176	0.098 (6)
C(25)	0.5904	0.0641	0.0561	0.069 (4)
C(26)	0.5106	0.1401	0.1314	0.049 (3)
C(31)	0.2078 (7)	0.3972 (7)	0.0652 (4)	0.074 (5)
C(32)	0.2003	0.3694	−0.0167	0.109 (7)
C(33)	0.1129	0.2912	−0.0172	0.101 (7)
C(34)	0.0331	0.2408	0.0642	0.101 (7)
C(35)	0.0407	0.2686	0.1462	0.079 (5)
C(36)	0.1280	0.3468	0.1466	0.055 (3)
C(41)	0.4543 (8)	0.4855 (7)	0.3921 (5)	0.106 (7)
C(42)	0.5416	0.5685	0.3464	0.145 (9)
C(43)	0.4962	0.6686	0.2777	0.126 (9)
C(44)	0.3633	0.6857	0.2548	0.182 (15)
C(45)	0.2759	0.6027	0.3006	0.121 (9)
C(46)	0.3214	0.5026	0.3692	0.054 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances, Bond Angles, and Torsion Angles for Cp′Ta(SC$_6$H$_5$)$_4$[a]

	Bond Distances (Å)		
Ta–CNT	2.116 (8)	Ta–S(1)	2.442 (2)
Ta–S(2)	2.394 (2)	Ta–S(3)	2.438 (2)
Ta–S(4)	2.470 (3)	S(1)–C(16)	1.785 (4)
S(2)–C(26)	1.777 (5)	S(3)–C(36)	1.784 (7)
S(94)–C(46)	1.783 (8)		
	Bond Angles (deg)		
CNT–Ta–S(1)	118.5 (3)	CNT–Ta–S(2)	102.8 (3)
CNT–Ta–S(3)	115.9 (3)	CNT–Ta–S(4)	105.3 (3)
S(1)–Ta–S(2)	88.3 (1)	S(1)–Ta–S(3)	124.8 (1)
S(1)–Ta–S(4)	77.9 (1)	S(2)–Ta–S(3)	88.7 (1)
S(2)–Ta–S(4)	151.9 (1)	S(3)–Ta–S(4)	79.7 (1)
Ta–S(1)–C(16)	115.9 (2)	Ta–S(2)–C(26)	113.4 (2)
Ta–S(3)–C(36)	116.0 (2)	Ta–S(4)–C(46)	111.5 (3)
	Torsion Angles (deg)		
CNT–Ta(1)–S(1)–C(16)	83.0 (3)		
CNT–Ta(1)–S(2)–C(26)	179.6 (3)		
CNT–Ta(1)–S(3)–C(36)	−83.9 (4)		
CNT–Ta(1)–S(4)–C(46)	177.0 (4)		

[a] CNT = centroid of atoms C(1)–C(5).

Table IV. Parameters Used in EHMO Calculations

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	C_1[a]	C_2[a]
Ta	5d	−10.30	4.76	1.94	0.6597	0.5589
	6s	−8.60	2.28			
	6p	−5.83	2.24			
S	3s	−20.00	1.82			
	3p	−11.10	1.82			
C	3s	−21.40	1.625			
	3p	−11.40	1.625			
H	1a	−13.60	1.30			

[a] Coefficients in double-ζ expansion.

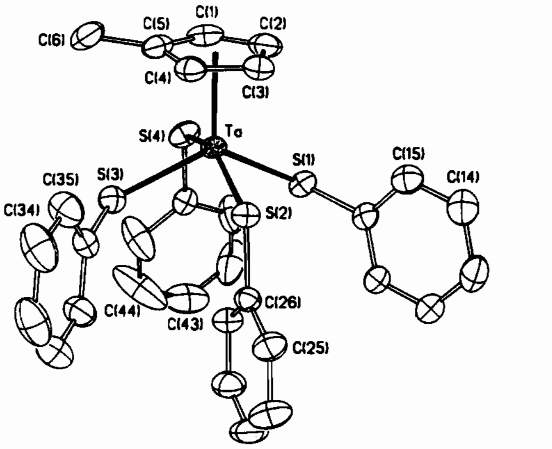

Figure 1. ORTEP diagram of Cp′Ta(SPh)$_4$, showing the atom-labeling scheme.

The preparation and X-ray crystal structure of Cp′Ta(SPh)$_4$ (**1**) revealed an unprecedented CpML$_4$ structure, which is best described as being between that of a four-legged piano stool and a trigonal bipyramid. In order to explain this, EHMO calculations were done on CpTa(SH)$_4$.

Experimental Section

General Methods. All reactions and manipulations were carried out under a nitrogen atmosphere by use of standard Schlenk line techniques or in an inert-atmosphere glovebox. All solvents were dried and distilled by standard procedures before use. Proton NMR spectra were recorded on a Bruker AM-300 spectrometer. Elemental analyses were carried out by the Microanalysis Laboratory, University of Michigan.

Preparation of Cp′Ta(SPh)$_4$ (1). Cp′TaCl$_4$[5] (5.00 g, 12.4 mmol) was dissolved in 50 mL of THF, and the mixture was slowly added to a stirred solution of NaSPh[6] (6.58 g, 49.8 mmol) in 50 mL of THF at −78 °C. The resulting dark red solution was allowed to warm to room temperature before being filtered through Celite. The solvent was then removed in vacuo, and dark red crystals (4.50 g, 52% yield) of Cp′Ta(SPh)$_4$ were obtained by recrystallization from a CH$_2$Cl$_2$/hexane solution at −20 °C. Fine powder of a light red paramagnetic compound (1.37 g) was easily separated from the much larger crystals of **1** but could not be identified. ^{1}H NMR (C$_6$D$_6$): δ 7.45 (m, 8 H, Ph *H*), 6.97 (m, 8 H, Ph *H*), 6.82 (m, 4 H, Ph *H*), 5.90 (t, *J* = 2.6 Hz, 2 H, Cp *H*), 5.78 (t, *J* = 2.6 Hz, 2 H, Cp *H*), 2.29 (s, 3 H, CpC*H*$_3$). Anal. Calcd for C$_{30}$H$_{27}$S$_4$Ta: C, 51.68; H, 3.90. Found: C, 51.62; H, 3.96.

Crystallographic Analysis of Cp′Ta(SC$_6$H$_5$)$_4$ (1). Crystallographic data are collected in Table I. A red crystal was mounted on a fine glass fiber with epoxy cement. The unit cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic evidence showed $\bar{1}$ Laue symmetry. *E* statistics suggested the centrosymmetric alternative $P\bar{1}$, which was confirmed by the chemically sensible results of refinement. A laminar absorption correction was applied to the data set (216 ψ-scan reflections; face (100); 3° glancing angle). The structure was solved by means of a Patterson map, which located the Ta atom. The remaining non-hydrogen atoms were located through subsequent least-squares and difference Fourier synthesis. All hydrogen atoms were included as idealized isotropic contributions (*d*-

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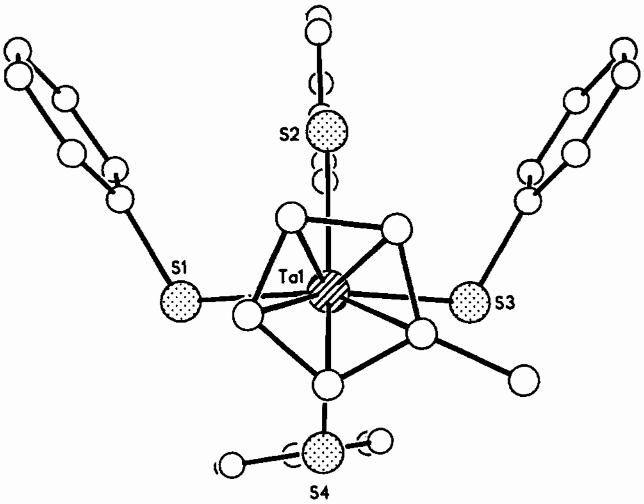

Figure 2. PLUTO plot of $Cp'Ta(SPh)_4$, displaying the orientation of the phenyl rings.

Table V. Fixed Bond Distances (Å) and Angles (deg) for $CpTa(SH)_4$[a]

C–H	1.00	Ta–S	2.44
CNT–C	1.22	S–H	1.25
Ta–CNT	2.12		
C–CNT–Ta	90.0	Ta–S–H	114.0

[a] CNT = center of Cp ligand.

(CH) = 0.960 Å, $U = 1.2U$ for attached C). Phenyl rings were constrained to rigid planar hexagons (d(CC) = 1.395 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters. Table II contains positional parameters, and Table III, selected bond distances, bond angles, and torsion angles. Figure 1 shows the atom-labeling scheme, while Figure 2 displays the orientation of the phenyl rings.

All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (version 5.1) (G. Sheldrick, Nicolet Corp., Madison, WI).

EHMO Calculations. These were done on an idealized $(C_5H_5)Ta(SH)_4$ molecule, using the parameters given in Tables IV and V. Programs by Hoffmann were used to perform the calculations: CDNT-2 (atom Cartesian coordinate calculations) and ICON-8 (extended Hückel calculations).

"Cricket Graph" (version 1.2), by Cricket Software, was used to fit the graphic data.

Discussion

Synthesis. Interest in heterobimetallic sulfur compounds for the study of hydrodesulfurization catalysis[7] has led to the use of thiolates as potential bridging ligands.[8,9] $Cp'Ta(SPh)_4$ was prepared as a potential precursor to such compounds.

The synthesis of 1 was done by reaction of $Cp'TaCl_4$ with NaSPh in THF at −78 °C. The low temperature for this reaction is critical, as an unidentified white powder is obtained at higher temperatures. Nakamura et al. prepared the first monocyclopentadienyl group V tetrathiolates, $Cp^*Ta(SCH_2CH_2S)_2$ and $(C_5Me_4R)Ta(SCH{=}CHS)_2$ (R = CH_3, C_2H_5), by a similar route at −10 °C.[10] Crystal structures of these have not been done, however.

Structure. The structure of 1 is that of a distorted four-legged piano stool, whereby two of the thiolate ligands, S(1) and S(3), have been bent away from the Cp′ ligand (Cp′–Ta–S angles of 118.5 (3) and 115.9 (3)°, respectively). The other two, S(2) and S(4), have been bent toward the Cp′ ligand (Cp′–Ta–S angles of 102.8 (3) and 105.3 (3)°, respectively).

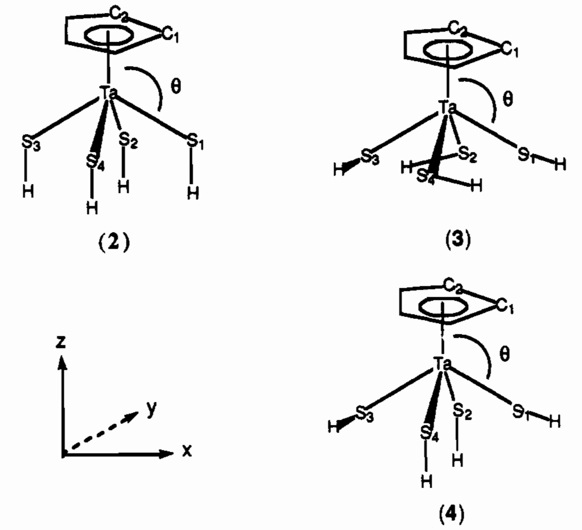

Figure 3. Conformers of the $CpTa(SH)_4$ molecule.

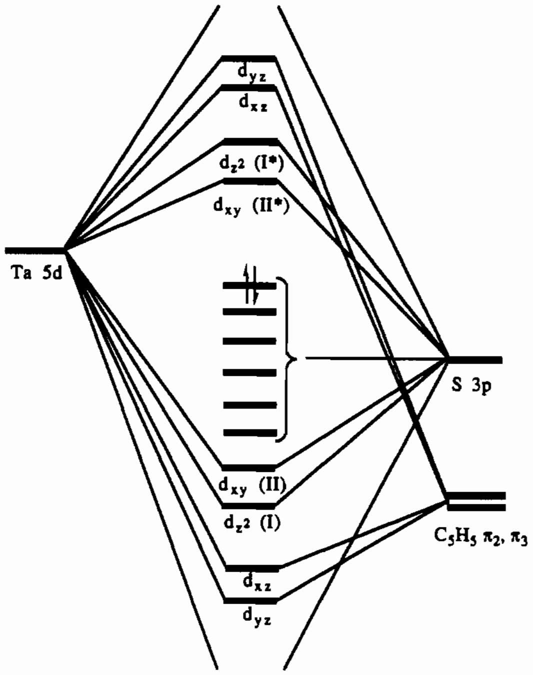

Figure 4. Partial MO diagram for $CpTa(SH)_4$.

The phenyl groups on S(2) and S(4) are oriented away from the Cp′ ligand (Cp′–Ta–S–C torsion angles of 179.6 (3) and 177.0 (4)°, respectively) so as to avoid a steric interaction with the Cp′ ring. The phenyl rings are perpendicular to each other so as to minimize steric interactions. The phenyl groups on S(1) and S(3) are directed into the plane of the S atoms (Cp′–Ta–S–C torsion angles of 83.0 (3) and −83.9 (4)°, respectively) and toward S(2), so as to avoid the phenyl ring on S(4).

The Ta–S(2) distance, at 2.394 (2) Å, is slightly shorter than the other three Ta–S distances (2.44–2.47 Å); this may be due to increased π bonding, as this is the only thiolate where the phenyl π ring is aligned with the S π-donor orbital. All of the Ta–S distances are in the range of typical tantalum(V)–thiolate distances, 2.35–2.47 Å.[4,11]

EHMO Studies. In order to determine the cause of the distortion in 1, EHMO calculations were performed on $CpTa(SH)_4$; SH ligands were used to simplify the calculations and to remove

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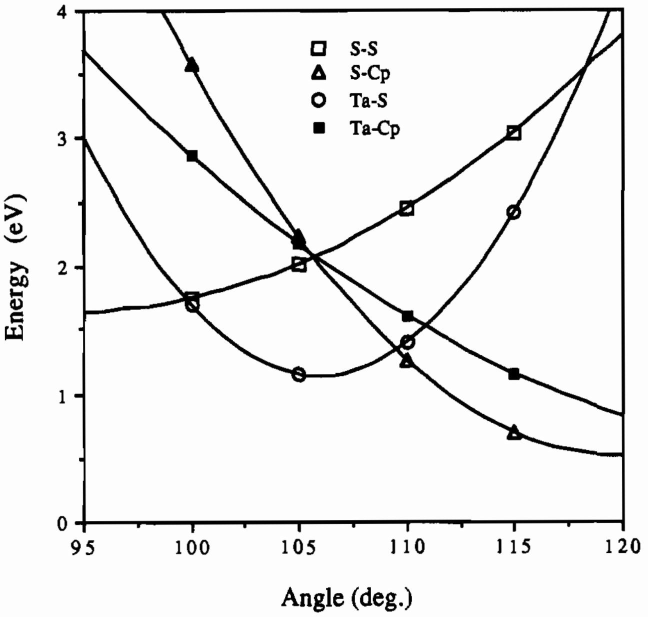


Figure 5. Graph of energy versus angle θ for the major interactions in conformer **4**.

any steric effects caused by the phenyl groups.

Three conformers (**2**–**4**), with different orientations of the thiolate H atoms, were studied (Figure 3). Conformer **2** has the H atoms directed away from the Cp ring (Cp–Ta–S–H torsion angle of 180°), **3** has them parallel to the plane of the S atoms (Cp–Ta–S–H torsion angle of 90°), and **4** is essentially a mixture of **2** and **3** and resembles the observed structure of Cp′Ta(SPh)$_4$. The orientation with the H atoms toward the Cp ring was not considered because of the strong steric interaction.

A general MO energy level diagram is shown in Figure 4. Of the twelve sulfur p orbitals, four are involved in σ bonding to the H atoms. The six highest occupied MOs are largely made up of sulfur p orbitals, with some σ and π interactions with the d orbitals. The d_{xy} and d_{z^2} orbitals form two filled π and two empty π^* (the LUMO and second LUMO) MOs with the sulfur p orbitals. The d_{xz} and d_{yz} orbitals are mostly involved with the π_2 and π_3 orbitals of the Cp ring but also take part in forming the Ta–S σ bonds. The $d_{x^2-y^2}$ orbital is not localized into any one MO but is involved in several σ-type MOs.

When all Cp–Ta–S angles are constrained to be equal, the conformers **2**–**4** all have minimum energy when the Cp–Ta–S angle, θ, is approximately 110°. Conformer **4** has the lowest energy (−930.8 eV compared to −930.3 and −930.6 eV for conformers **2** and **3**, respectively) because S$_1$ and S$_3$ are not competing for the same d orbital as S$_2$ and S$_4$.

The calculated minimum angle of 110° is approximately the average of the ideal angles for overlap with the d_{xy} and d_{z^2} orbitals of 90 and 135°, respectively. However, almost all π neutral ligands have Cp–M–L angles around 110°,[2] regardless of the other ligands and the metal electron count (the only exceptions are Cp*Re(SiMe$_3$)$_2$H$_2$[12] and CpIrH$_3$(PMe$_3$)$^+$,[13] and these structures may lie on the reaction coordinate for the elimination of Me$_3$SiH and H$_2$, respectively[2,13]). This suggests that 110° is the optimum angle for σ bonding with the metal and that any deviation is probably an effect of π bonding or steric interactions.

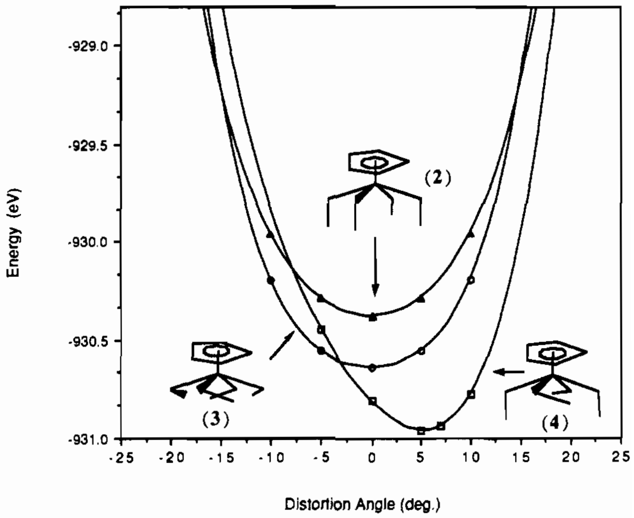


Figure 6. Plot of total energy of the CpTa(SH)$_4$ conformers versus the distortion angle, Δ.

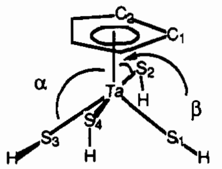
To determine the contributing factors toward the adoption of a θ angle of 110° by the three conformers, the reduced energy matrix for the four major interactions (the Ta–S and Ta–Cp bonds and the S–Cp and *cis*-S–S steric interactions) in conformer **4** were compared. Figure 5 shows the relative energy of these interactions.

The Ta–Cp bond shows a strong preference for θ angles greater than 110°. A σ interaction between the d_{xz} and d_{yz} orbitals and the S atoms would be most favorable at $\theta = 135°$. As θ increases and the σ interaction increases, a second-order interaction with the filled Cp(π_2/π_3)–Ta(d_{xz}/d_{yz}) MOs then lowers the energy of the Ta–Cp bond. The Ta–S bonds have a minimum at 105° because S$_1$ and S$_3$ prefer a larger θ angle while S$_2$ and S$_4$ prefer a smaller θ angle, 105° being the compromise. It follows then that with randomly oriented thiolates, or symmetrical ligands such as halides, an angle of 105° would also be prefered by the Ta–L bonds.

The two steric interactions work in opposite directions, the *cis*-S–S interaction preferring small θ (ideally 90°) and the S–Cp interaction preferring large θ. These two steric interactions combine to give a minima at 112°. Coincidentally, the Ta–S and Ta–Cp bonding interactions combine to give a minima at almost the same value of θ, 109°. It is probably for this reason that steric effects have not been closely looked at in the literature.

The only structurally characterized 14- or 15-electron CpML$_4$ compounds, with four symmetrical π-donor L ligands, are Cp*TaBr$_4$[18] and (C$_5$H$_4$Pr^i)WCl$_4$.[19] These have average θ angles of 110 and 110.6°, respectively. Presumably, the cis steric interaction between the L atoms prevents a larger angle and better donation into the stronger π-accepting d_{z^2} orbital. The two chlorine ligands trans to each other in CpTaCl$_3$SiMe$_3$[14] have Cp–Ta–Cl angles of 110.4 and 110.0°; again, a steric interaction with the other Cl ligand may be preventing a larger angle.

In order to examine the effect of distorting the molecule toward a trigonal-bipyramidal structure, a distortion angle was defined as $\Delta = (\alpha - \beta)/2$, where α is the Cp–Ta–S angle for S$_1$ and S$_3$ and β is the Cp–Ta–S angle for S$_2$ and S$_4$. Hence, for $\Delta = 20°$, the Cp–Ta–S$_{1,3}$ angles would be 130° and the Cp–Ta–S$_{2,4}$ angles would be 90°; this would then correspond to a trigonal-bipyramidal structure.[1]



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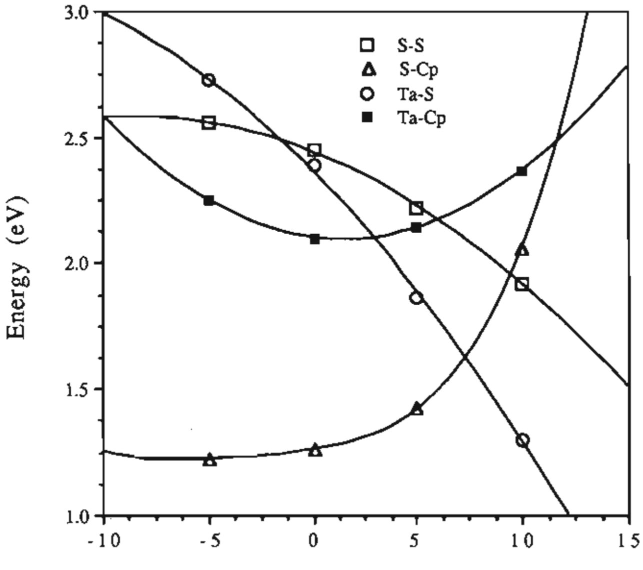


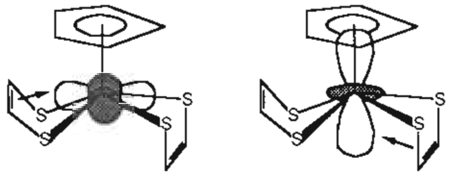
Figure 7. Graph of energy versus distortion angle for the major interactions in conformer **4**.

From Figure 6 it can be seen that molecules **2** and **3** have energy minima corresponding to zero distortion, while **4** has lowest energy with a distortion of ~6° (this is approximately 30% toward the trigonal-bipyramidal structure). This would then give Cp–Ta–$S_{1,3}$ angles of 116° and Cp–Ta–$S_{2,4}$ angles of 104°, which compare very favorably to the observed average angles of 117.2 and 104.1°, respectively. The small energy differences between the three conformers indicate that they would be in rapid equilibrium in solution; thus, NMR spectroscopy is not able to distinguish between the inequivalent phenyl groups of $Cp'Ta(SPh)_4$.

The obvious explanation for the observed distortion is that S(1) and S(3) are bent down to maximize overlap with the d_{z^2} orbital, while S(2) and S(4) bend toward the Cp ligand to maximize overlap with the d_{xy} orbital. It is not that simple, however, as the MOs containing the d_{z^2} and d_{xy} orbitals change very little in energy (maximum of 0.04 eV for a 5° distortion). To discern the causes of the distortion, the reduced energy matrices for the two major bonding interactions and the two steric interactions were compared (Figure 7).

The strength of the Ta–S bonds and the *cis*-S–S steric repulsions are the major factors responsible for the distortion. The Ta–Cp bond favors zero distortion, but the shallow potential well tells us that it is not a major factor. The S–Cp steric interaction, on the other hand, appears to be the most significant factor in limiting the distortion to only 6°, since the energy for this repulsive interaction rises rapidly beyond Δ = 5°.

The structure of $Cp^*Ta(SCH{=}CHS)_2$[10] would also expected to be distorted but in a different way and for slightly different reasons. Low-temperature NMR spectroscopy suggests the presence of two identical conformers in equilibrium, whereby one SCH=CHS ligand is folded toward the empty d_{z^2} orbital, to maximize overlap with the filled C=C π orbital, and the other is folded toward the empty d_{xy} orbital ($d_{x^2-y^2}$ in the original paper).[10]



The structure of $CpMo(SC_6F_5)_4^-$, a 16-electron analogue of **1**, has recently been published.[17] As would be expected, it has structure **3**; the HOMO would correspond to MO II*, i.e. a filled d_{xy} orbital; hence, the C_6F_5 groups orient so that the π-donor orbital on the S atoms donates into the empty d_{z^2} orbital rather than the filled d_{xy} orbital. The Cp–Mo–S average angle is only 111.9°, hardly optimum for overlap with the $d_z{}^2$ orbital. Calculations on $CpTa(SH)_4^{2-}$ predict an angle of 111°. The reason for this small effect is probably a steric interaction between the cis atoms. In $CpW(CO)(SC_6F_5)_3$, steric effects are not a problem; the two thiolates trans to each other are able to bend down, and away from the other thiolate ligand (which has a θ angle of 110.2°), to an average θ angle of 119.9°.

Conclusions

It is apparent that the observed distortion in $Cp'Ta(SPh)_4$ is not a steric effect of the Ph rings; however, the explanation for the distortion is not as simple as it first appears. While π bonding between the S π-donor orbitals and the d_{z^2} and d_{xy} orbitals can be used to explain most of the observed θ angles, steric repulsions between the cis S atoms are quite important; they need to be invoked to explain the small θ angles for **3**, $CpTa(SH)_4^{2-}$, $CpMo(SC_6F_5)_4^-$, Cp^*TaBr_4, and $(C_5H_4Pr^i)WCl_4$.

The d_{xz} and d_{yz} orbitals, i.e. Ta–Cp bonding, cannot be ignored and appear to contribute significantly in the M–L σ bonds of $CpML_4$ compounds. The contributions of the metal $d_{x^2-y^2}$, p_x, and p_y orbitals are difficult to quantify but are certainly important in setting the θ angle at 110° when π effects are unimportant.

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Supplementary Material Available: Listings of complete crystallographic data, bond lengths, bond angles, thermal paramters, and H atom coordinates (4 pages); a table of F_o and F_c values (25 pages). Ordering information is given on any current masthead page.