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Linear *vs.* bent M-O-R bonds in d^0 metal alkoxides: X-ray crystal structure of $(C_5Me_5)Ta(S^tBu)_3(O^nBu)$ and EHMO analysis

Kazuyuki Tatsumi and Akitoshi Tahara
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560 (Japan)

Akira Nakamura
Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

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Abstract

The tantalum n-butoxide complex of $Cp^*Ta(S^tBu)_3(O^nBu)$ (1) ($Cp^* = C_5Me_5$) has been isolated as a minor product from the reaction of Cp^*TaCl_4 with LiS^tBu in THF. The crystal structure of 1 consists of two crystallographically independent molecules with distinctly different Ta-O-C angles, where a larger angle is associated with a longer Ta-O bond and *vice versa*. EHMO calculations on the model $CpTa(SH)_3(OH)$ showed that the potential energy curve against the Ta-O-H angle is in fact flat while the Ta-O overlap population decreases as the Ta-O-H bond bends. Crystallographic data: 1, space group $P2_1$, $a = 9.134(4)$, $b = 12.078(7)$, $c = 27.74(2)$ Å, $\beta = 92.39(6)°$; $Z = 4$; 4515 reflections with $I > 3.0\sigma(I)$; $R = 0.038$, $R_w = 0.052$.

Key words: Tantalum; Thiolate; Alkoxide; X-ray diffraction; Molecular orbital calculations

1. Introduction

Alkoxides and aryloxides are known to coordinate at electron-deficient early transition metals with varying amounts of M-O multiple bond character, as is manifested by a wide range of M-O-R angles and relatively short M-O distances [1-5]. There is no doubt that the O pπ orbitals of alkoxide and aryloxides can donate electrons to a metal whenever a vacant dπ orbital of the same symmetry is present. But to what extent does it do so? How significant is the effect of pπ-dπ interactions on large M-O-R angles? Early transition metal alkoxides and aryloxides often carry bulky substituents and their steric pressure alone could result in large M-O-R angles, making it difficult to isolate the contribution of pπ-dπ interactions from the steric effect.

In the course of our study of sulfide and thiolate complexes comprising a half-sandwich Cp*Ta fragment [6,7], we have isolated $Cp^*Ta(S^tBu)_3(O^nBu)$ (1) as a minor product of the reaction between Cp^*TaCl_4 and LiS^tBu in THF. An interesting aspect of 1 is that the complex crystallizes with two independent molecules in each asymmetric unit; one with a large Ta-O-C angle and the other with a smaller angle. This finding provided us with a good opportunity to examine electronic properties of the alkoxide ligand at a d^0 metal centre. We report in this paper the crystal structure of 1, focussing on the coordination geometry of the n-butoxy group, with a molecular orbital analysis based on extended Hückel calculations.

2. Experimental section

All manipulations were carried out under an argon atmosphere using dry solvents and conventional Schlenk techniques. ^tBuSH was used as purchased (Aldrich) and its lithium salt was prepared by adding butyllithium to ^tBuSH in THF and isolated in a straightforward manner as a white powder. ^1H NMR spectra were recorded on a JEOL GX-270 spectrome-

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Correspondence to Professor K. Tatsumi.

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ter, and UV-visible spectra were run on a Jasco Ubest-30 spectrometer.

Our investigation of reactions between Cp^*TaCl_4 and varying amounts of LiS^tBu in THF resulted in a successful isolation of $Cp^*Ta(S^tBu)_2Cl_2$ (red), $Cp^*Ta(S^tBu)_3Cl$ (red brown), and $Cp^*TaS(S^tBu)_2$ (yellow) [8]. During this study we noticed formation of red crystals in a (1:6) $Cp^*TaCl_4 : LiS^tBu$ reaction system, subsequently shown to be **1**. The yield of **1** varies from a trace amount to 5% according to the ^1H NMR spectra of the crude product, while the major product isolated is $Cp^*TaS(S^tBu)_2$ (50–60% yield). The n-butoxy group might be contained as a trace amount of impurity in butyllithium used for preparation of LiS^tBu, or might originate from THF via a ring-opening step. While we are continuing our efforts, we have not been able to develop a rational synthesis of **1**. Isolation of **1** from the reaction of $Cp^*Ta(S^tBu)_3Cl$ with LiO^nBu has not been successful.

2.1. *Characterization of $(C_5Me_5)Ta(S^tBu)_3(O^nBu)$ (1)*

^1H NMR (270 MHz, C_6D_6, 30°C): δ 0.96 (t, 3H, $OCH_2CH_2CH_2CH_3$), 1.25 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.84 (s, 9H, S^tBu), 1.85 (s, 18H, S^tBu), 1.88 (m, 2H, $OCH_2CH_2CH_2CH_3$), 2.10 (15H, Cp^*), 4.63 (m, 2H, $OCH_2CH_2CH_2CH_3$). UV/Vis ($\lambda_{max}(\epsilon)$, THF): nm 484sh, 381(3000). Anal. Calcd. for $C_{26}H_{51}OS_3Ta$: C, 47.54; H, 7.83; S, 14.64. Found: C, 46.92; H, 7.80; S, 13.72%.

2.2. *X-ray structure analysis of 1*

A single crystal of **1** was mounted in a thin-walled glass capillary and sealed under Ar. Diffraction measurements were made on a Rigaku AFC5R fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The cell dimensions were determined and refined from 20 randomly selected reflections. The intensity data were collected using the ω scan technique up to a maximum 2θ value of 50°. The intensity measurements were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied with use of azimuthal scans. Inspection of the systematic absences indicated possible space groups $P2_1$ and $P2_1/m$. The mean E^2-1 value and packing considerations suggested noncentric $P2_1$, and the successful solution and refinement of the structure support the choice as the correct space group. The structure was solved by a combination of direct methods (MITHRIL) and different Fourier synthesis. All non-hydrogen atoms were assigned anisotropic thermal parameters, and hydrogen atoms were included in the structure factor calculations. The structure was refined to $R = 0.038$ and $R_w = 0.052$ by a full-matrix least-squares refinement using 4515 reflections with $I > 3\sigma(I)$. Crystal data are summarized in Table 1, and the positional and isotropic thermal parameters are given in Table 2. Additional data, including full experimental details, and complete listings of atomic and thermal parameters, tables of observed and calculated structure factors are available on request from the authors.

TABLE 1. Crystal data for $Cp^*Ta(S^tBu)_3(O^nBu)$ (1)

formula	$C_{26}H_{51}OS_3Ta$
fw	656.8
space group	$P2_1$
a, Å	9.134(4)
b, Å	12.078(7)
c, Å	27.74(2)
β, deg	92.39(6)
V, Å^3	3058(3)
Z	4
ρ_{calcd}, g/cm^3	1.43
μ, cm^{-1}	37.6
radiation	Mo K$_\alpha$
no. of observed reflcns	4515 ($I > 3.0\sigma(I)$)
no. of variables	619
GOF	2.35
$R(R_w)$	0.038(0.052)

3. Results and discussion

Figure 1 presents the structure of one of the two independent molecules (molecule A), while selected bond distances and angles for the molecules A and B are listed in Table 3. The four-legged piano-stool geometry is distorted in such a way that the two smaller Cp*(centroid)–Ta–S angles are associated with the two *trans* thiolate ligands: molecule A (molecule B); Cp*–Ta–S1(S4), 102.9(2)° (102.0(3)°); Cp*–Ta–S3(S6), 104.0(2)° (102.7(3)°). The other two basal ligands are bent away from Cp*: Cp*–Ta–S2(S5), 112.7(2)° (117.1(2)°); Cp*–Ta–O1(O2), 115.0(3)° (114.7(3)°). This type of deformation was described as "angular *trans* influence" [9], and its detailed theoretical analysis has recently been reported [10]. Orientation of the ^{t}Bu groups is variegated, where the Cp*–Ta–S–C torsional angles range from 86.7(5)° for Cp*–Ta2–S5–C45 to 178.1(6)° for Cp*–Ta2–S4–C41. The ^{n}Bu group of alkoxide ligand is oriented perpendicular to the Cp*–Ta vector (Cp*–Ta–O–C torsional angles of 96(1)° and 92(2)° for molecule A and molecule B, respectively). The Ta–S distances and the Ta–S–C angles are normal [11].

By comparing the structural parameters between the two crystallographically independent molecules, we see that the angles at O1 and O2 are quite different: Ta1–O1–C23 angle of 133.2(7)° *vs.* Ta2–O2–C53 angle of 159.6(7)°. Interestingly the large Ta2–O2–C53 angle

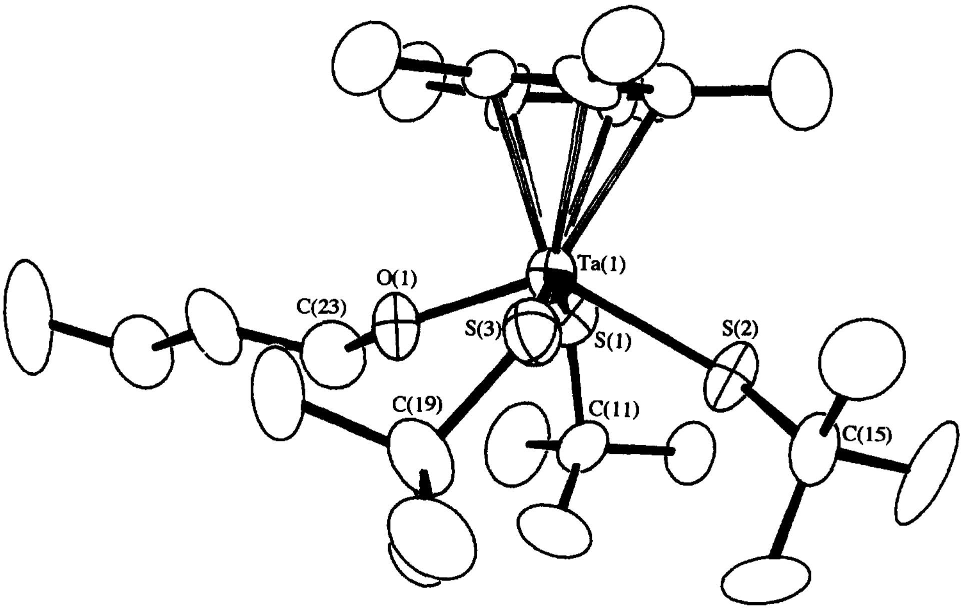
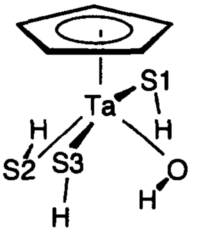


Fig. 1. Structure of molecule A in **1** shown with 50% probability ellipsoids.

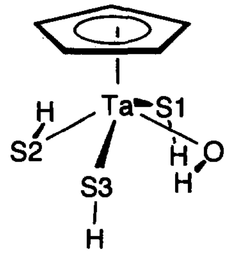
of molecule B accompanies the short Ta–O2 bond, which is shorter than the Ta1–O1 bond of molecule A by 0.063(7) Å. This observation provides direct evidence that widening of the Ta-O-C angle in fact strengthens the Ta-O bond. The presence of the two distinctive alkoxide coordination geometries in the same crystals indicates that their energy difference must be small and that shortening of the Ta–O bond does not contribute much to further stabilization of the complex.

In order to gain a deeper insight into the Ta–O bonding, we carried out extended Hückel calculations on the model complex, $CpTa(SH)_3(OH)$ [12*]. All the alkyl substituents in complex **1** were replaced by hydrogen atoms to avoid complication arising from steric influence. Orientations of the thiolate H and hydroxy H atoms were idealized in such a way that the Cp–Ta–O-H and Cp-Ta-S2-H torsional angles are 90° (latitudinal orientation) and the Cp–Ta–S1–H and Cp–Ta–S3–H angles are 180° (longitudinal orientation). This conformation resembles roughly the observed structure of **1**, and is analogous to the geometry identified by Curtis *et al.* in calculations on $CpTa(SH)_4$ [13].

The angular *trans* influence in $CpTa(SH)_3(OH)$ could give rise to two different deformed geometries depending on whether the OH group and its *trans*-SH partner move to the position with a large Cp–Ta–L angle (deformation X), that corresponds to the structure of **1**, or to the position with a small Cp–Ta–L angle (deformation Y). The geometrical choice may be affected by the orientation of the OH group. For the latitudinal orientation, the O pπ orbital overlaps with the metal z^2 orbital, and larger Cp–Ta–OH angles would result in stronger pπ–z^2 interactions. Conversely the longitudinal orientation is suited for the O pπ–xy interaction, and smaller Cp–Ta–OH angles would be preferred. These pπ-dπ interactions are schematically shown below.



deformation X



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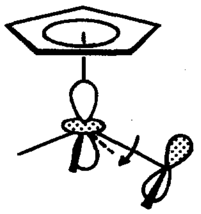
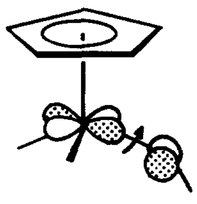


latitudinal-OH



longitudinal-OH

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* Reference number with asterisk indicates a note in the list of references.

TABLE 2. Fractional atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms in $Cp^*Ta(S^tBu)_3(O^nBu)$ (**1**) with esd's in parentheses

	x	y	z	B_{eq}
Ta1	0.13331(5)	0	0.12272(1)	3.15(2)
Ta2	0.13405(5)	0.02297(3)	0.62284(1)	3.13(2)
S1	0.1456(3)	−0.1980(2)	0.1403(1)	4.5(1)
S2	0.2861(3)	−0.0699(3)	0.0592(1)	4.2(1)
S3	0.2455(3)	0.1850(2)	0.1122(1)	4.3(1)
S4	0.1413(3)	0.2284(2)	0.6350(1)	3.9(1)
S5	0.2941(4)	0.0911(2)	0.5609(1)	4.1(1)
S6	0.2402(3)	−0.1603(2)	0.61497(9)	3.7(1)
O1	0.174(1)	0.0298(6)	0.1899(3)	4.2(4)
O2	0.1748(8)	0.0212(5)	0.6889(2)	3.4(3)
C1	−0.059(1)	0.1144(8)	0.0802(4)	3.6(5)
C2	−0.106(1)	0.0982(8)	0.1264(3)	3.4(4)
C3	−0.124(1)	0.0230(8)	0.1346(4)	3.1(5)
C4	−0.111(1)	−0.0743(9)	0.0896(3)	4.2(4)
C5	−0.078(1)	0.0010(8)	0.0595(4)	3.1(4)
C6	−0.058(1)	0.217(1)	0.0557(5)	4.0(7)
C7	−0.123(1)	0.186(1)	0.1634(5)	4.5(6)
C8	−0.178(2)	−0.074(1)	0.1790(5)	7.5(8)
C9	−0.158(1)	−0.189(1)	0.0863(4)	4.8(6)
C10	−0.056(2)	−0.019(1)	0.0069(5)	6.4(7)
C11	0.323(1)	−0.274(1)	0.1505(4)	3.8(5)
C12	0.337(1)	−0.350(1)	0.1074(4)	4.7(6)
C13	0.293(2)	−0.354(1)	0.1911(5)	8.8(9)
C14	0.444(1)	−0.195(1)	0.1614(5)	6.6(7)
C15	0.405(1)	0.018(1)	0.0250(3)	4.3(5)
C16	0.317(2)	0.097(1)	−0.0049(5)	5.9(7)
C17	0.551(1)	0.063(1)	0.0479(5)	5.1(6)
C18	0.443(2)	−0.070(1)	−0.0161(5)	7.5(8)
C19	0.377(1)	0.223(1)	0.1575(4)	3.1(6)
C20	0.486(1)	0.142(1)	0.1774(4)	4.7(5)
C21	0.291(1)	0.281(1)	0.2025(4)	6.4(6)
C22	0.481(1)	0.318(1)	0.1440(4)	5.3(6)
C23	0.184(2)	−0.043(1)	0.2339(5)	5.0(7)
C24	0.139(2)	0.0200(9)	0.2750(4)	4.7(5)
C25	0.143(2)	−0.039(1)	0.3256(4)	4.6(6)
C26	0.102(3)	0.019(1)	0.3636(6)	8(1)
C31	−0.065(1)	−0.084(1)	0.5759(4)	3.8(5)
C32	−0.092(1)	−0.074(1)	0.6354(3)	3.8(4)
C33	−0.132(1)	0.0329(9)	0.6423(4)	3.0(4)
C34	−0.113(1)	0.0940(8)	0.5992(4)	4.3(4)
C35	−0.063(1)	0.0101(8)	0.5555(4)	3.2(5)
C36	−0.044(2)	−0.193(1)	0.5525(5)	4.4(7)
C37	−0.101(1)	−0.172(1)	0.6673(5)	5.5(6)
C38	−0.167(1)	0.085(1)	0.6829(4)	4.7(5)
C39	−0.165(2)	0.211(1)	0.5775(5)	6.1(8)
C40	−0.064(1)	0.038(1)	0.5057(4)	5.3(6)
C41	0.318(2)	0.297(1)	0.6522(5)	4.9(7)
C42	0.454(1)	0.217(1)	0.6660(5)	5.6(6)
C43	0.296(1)	0.367(1)	0.6954(5)	6.5(6)
C44	0.368(2)	0.358(1)	0.6134(6)	7.5(8)
C45	0.401(1)	0.0074(9)	0.5145(3)	3.8(5)
C46	0.311(1)	−0.090(1)	0.4925(4)	4.5(6)
C47	0.466(2)	0.091(1)	0.4787(4)	6.0(7)
C48	0.510(1)	−0.043(1)	0.5435(4)	4.0(6)
C49	0.383(1)	−0.202(1)	0.6636(5)	4.1(7)
C50	0.454(2)	−0.296(1)	0.6345(5)	7.8(9)
C51	0.314(1)	−0.236(1)	0.7042(4)	8.2(7)
C52	0.487(1)	−0.090(1)	0.6761(5)	6.2(7)
C53	0.197(2)	0.061(1)	0.7376(4)	4.5(6)
C54	0.127(2)	−0.003(1)	0.7741(6)	7(1)
C55	0.161(2)	0.068(1)	0.8231(5)	9(1)
C56	0.126(3)	0.008(1)	0.8647(5)	8(1)

However, Lin and Hall [10] predicted that smaller Cp–M–L angles should be associated with strong σ-bonding ligands, and deformation Y could be more stable as the OH group is a better σ-donor than SH. Thus the latitudinal orientation of OH stabilizes deformation X, while the strong σ-donor nature of OH opts for deformation Y. A consequence of these two opposing effects may be a small energy difference between the two deformed geometries. In fact, our calculations on the model $CpTa(SH)_3(OH)$ show that the two deformations are energetically balanced, with deformation X (Cp–Ta–O = Cp–Ta–S2 = 115°, Cp–Ta–S1 = Cp–Ta–S3 = 103°) being very slightly less stable (by 0.03 eV) than deformation Y (Cp–Ta–O = Cp–Ta–S2 = 103°, Cp–Ta–S1 = Cp–Ta–S3 = 115°). We think that the observed structure of **1** is determined mainly by the

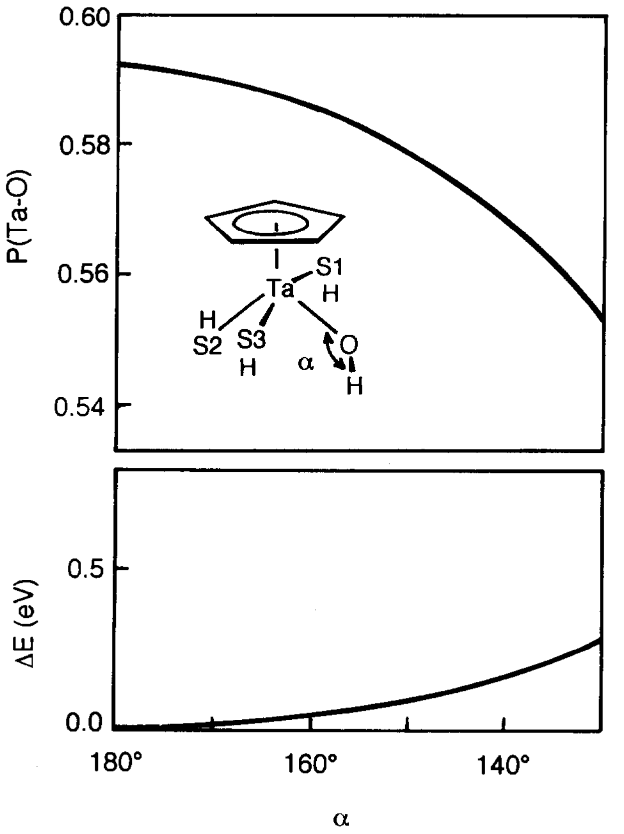

Fig. 2. Potential energy curve and change in the Ta–O overlap population P(Ta–O) for $CpTa(SH)_3(OH)$, varying the Ta–O–H angle α.

TABLE 3. Selected bond distances (Å) and bond angles (deg) for $Cp^*Ta(S^tBu)_3(O^nBu)$ (1) with esd's in parentheses

molecule A			
Ta1–S1	2.442(3)	S1–Ta1–S2	77.4(1)
Ta1–S2	2.445(3)	S1–Ta1–S3	152.8(1)
Ta1–S3	2.480(3)	S2–Ta1–S3	88.6(1)
Ta1–O1	1.919(7)	S1–Ta1–O1	89.1(2)
S1–C11	1.87(1)	S2–Ta1–O1	132.3(3)
S2–C15	1.81(1)	S3–Ta1–O1	83.2(2)
S3–C19	1.76(1)	Ta1–S1–C11	122.9(4)
O1–C23	1.50(2)	Ta1–S2–C15	123.1(4)
		Ta1–S3–C19	115.0(4)
		Ta1–O1–C23	133.2(7)
molecule B			
Ta2–S4	2.504(3)	S4–Ta2–S5	75.4(1)
Ta2–S5	2.444(3)	S4–Ta2–S6	155.0(1)
Ta2–S6	2.430(3)	S5–Ta2–S6	89.5(1)
Ta2–O2	1.856(6)	S4–Ta2–O2	82.8(2)
S4–C41	1.85(1)	S5–Ta2–O2	126.6(2)
S5–C45	1.94(1)	S6–Ta2–O2	90.8(2)
S6–C49	1.91(1)	Ta2–S4–C41	119.6(4)
O2–C53	1.44(1)	Ta2–S5–C45	128.8(3)
		Ta2–S6–C49	116.2(4)
		Ta2–O2–C53	159.6(7)

steric bulk of the ^{t}Bu group. The two bulky ^{t}Bu substituents of the thiolates trans to each other tend to bend down (*i.e.*, a longitudinal orientation for S2–^{t}Bu and S4–^{t}Bu), minimizing their steric repulsion with the S3–^{t}Bu group and also with Cp*. This in turn leads to the latitudinal orientation of O^n–Bu and S3–^{t}Bu.

To examine how the total energy and the Ta–O interaction change with bending of the Ta–O–H bond, we plot in Fig. 2 the potential energy curve and the Ta–O overlap population, P(Ta–O), as a function of the Ta–O–H angle α. It is evident that P(Ta–O) decreases as the OH group bends. Weakening of the Ta–O bond for smaller α is indeed what we found in the structures of the two crystallographically independent molecules A and B for 1. The calculated potential energy curve is flat, where a shallow minimum comes at the linear Ta–O–H geometry. Bending from $\alpha = 180°$ to $\alpha = 133°$ costs an energy of moderate 0.23 eV, and the energy difference between $\alpha = 160°$ and $\alpha = 133°$ is 0.19 eV. This feature means that a variety of Ta–O–H angles is likely to occur in crystals through packing effects and/or steric interactions within molecules, and this argument can apply to other M–O–R bonds with a d^0 electronic configuration.

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