J. Chem. Research (S),
1999, 14–15
J. Chem. Research (M),
1999, 0180–0192

The Classical Structure of $TaCp_2(H)(SiMe_2H)_2$

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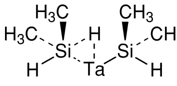
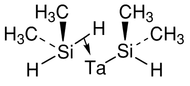
Neutron diffraction analysis of $TaCp_2(H)(SiMe_2H)_2$ (**1**) has revealed a symmetric structure with a classical, rather than agostic, hydride ligand: the Ta–H distance is 1.785(15) Å, the non-bonding H···Si distances are 2.189(18) and 2.190(17) Å, and the H–Ta–Si angles are 55.2(5) and 55.5(5)°; final *R* factor = 8.9% for 1295 reflections.

After the agostic[1] C–H–M interaction was first demonstrated to exist, by neutron diffraction, in the compound $\{Fe(\eta^3\text{–}C_8H_{13})[P(OMe)_3]_3\}^+$,[2] there were numerous attempts to search for analogous Si–H–M systems. Such species are of interest because of their suspected role in hydrosilations and other catalytic reactions involving metallo-silicon compounds.[3] In 1982, Schubert and co-workers published the first (and to date the only) neutron diffraction study of a *bona fide* Si–H–M agostic (or non-classical) interaction, in $Mn(H)(SiPh_2F)(C_5H_4Me)(CO)_2$.[4] Since then, other investigators have succeeded in characterizing Si–H–M interactions with X-ray diffraction methods, for example the Si–H–Ti system in $TiCp_2(SiH_2Ph_2)(PMe_3)$.[5]

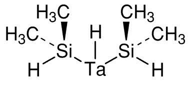
The title compound, $TaCp_2(H)(SiMe_2H)_2$ (**1**), was reported by some of us several years ago from the reaction of $TaCp_2(C_2H_4)(CH_3)$ with SiH_3CH_3.[6] X-Ray analysis of its structure revealed the presence of a weak peak in the electron-density map, which was assigned as the position of the hydride ligand. Because of the apparently asymmetrical location of the hydride peak (it was found 1.83 Å from one Si atom and 2.48 Å from the other Si), it was suggested that the hydride ligand in **1** may be part of a non-classical structure (*i.e.* either **I** or **II** below). In this paper, we report the single-crystal neutron structure determination of compound (**1**), and show that it has the classical structure **III**.



I



II



III

A large single crystal of $TaCp_2(H)(SiMe_2H)_2$ (0.8 × 0.8 × 4.0 mm) was grown *via* recrystallization from toluene/hexane[6] and sealed in a quartz cap under a nitrogen atmosphere. Neutron diffraction data were collected at room temperature at the JRR-3 M reactor of the Japan Atomic Energy Research Institute (JAERI) using the BIX1 single-crystal diffractometer,[7] equipped with an Ordela Model 2250N area detector. A neutron difference-Fourier map, phased by the positions of the non-hydrogen atoms (and the calculated C–H hydrogen atoms) derived from the X-ray analysis,[6] yielded only one large peak, corresponding to the unique hydride ligand. Exhaustive least-squares refinement yielded final agreement factors of $R = 8.9$ and $R_w = 9.5\%$ for all 1295 reflections in the data set.†

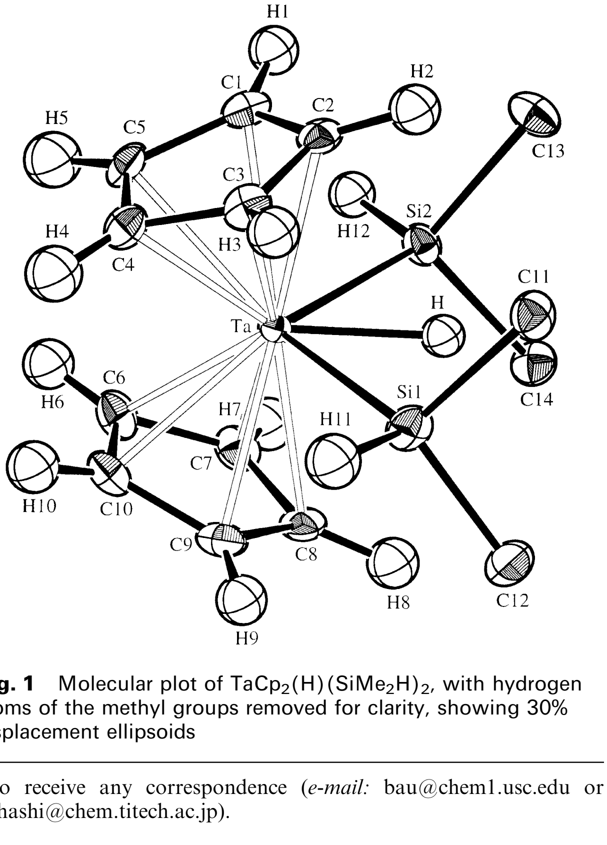


Fig. 1 Molecular plot of $TaCp_2(H)(SiMe_2H)_2$, with hydrogen atoms of the methyl groups removed for clarity, showing 30% displacement ellipsoids

A plot of $TaCp_2(H)(SiMe_2H)_2$ (**1**) is given in Fig. 1 and selected distances and angles are listed in Table 1. Within experimental error, the unique hydride ligand is symmetrically located between the two silicon atoms: the Ta–H distance is 1.785(15) Å, the non-bonding H···Si distances are 2.189(18) and 2.190(17) Å, and the H–Ta–Si angles are 55.2(5) and 55.5(5)°. All distances and angles in the molecule are normal: the aforementioned Ta–H distance agrees quite well with that found in TaH_3Cp_2 [average 1.774(3) Å],[8] while both single-bonded Si–H distances (of the $SiMe_2H$ ligands) have the expected value of 1.48(2) Å.

In the original X-ray structure determination of the title compound,[6] the Si–Ta–Si angle (110° in the X-ray analysis and 111° in the present neutron analysis) was cited as a piece of evidence favouring the non-classical structure, since it seemed much smaller than the corresponding H–Ta–H

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†The intensity of each reflection was obtained by summing up the intensities of the individual pixels. Only reflections with intensities greater than five times that of the surrounding background fluctuations were used in this integration. Data were collected using a monochromatic neutron beam of wavelength 1.060 Å. A total of 3649 reflections were measured and merged [*R*(int) = 6.8%] to give 1295 unique reflections used in the subsequent structural analysis. Crystal data for $TaC_{14}H_{25}Si_2$: space group $P2_12_12_1$ (orthorhombic); $a = 7.989(2)$, $b = 8.822(2)$, $c = 23.100(3)$ Å; $V = 1628.1(6)$ Å^3; $Z = 4$. Complete listings of the atomic coordinates, distances and angles in the molecule can be found in the full text version of this paper.

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Table 1 Selected distances and angles in $TaCp_2(H)(SiMe_2H)_2$

Bond lengths/Å			
Ta–Si(1)	2.644(14)	Ta–Si(2)	2.631(12)
Ta–H	1.785(15)		
Si(1)–C(11)	1.937(16)	Si(2)–C(13)	1.909(14)
Si(1)–C(12)	1.851(17)	Si(2)–C(14)	1.911(15)
Si(1)–H(11)	1.483(22)	Si(2)–H(12)	1.485(18)
Si(1)···H	2.189(18)	Si(2)···H	2.190(17)
Bond angles/°			
Si(1)–Ta–Si(2)	110.8(4)		
Si(1)–Ta–H	55.2(5)	Si(2)–Ta–H	55.5(5)
Ta–Si(1)–C(11)	113.7(6)	Ta–Si(2)–C(13)	114.9(6)
Ta–Si(1)–C(12)	117.0(7)	Ta–Si(2)–C(14)	115.8(6)
Ta–Si(1)–H(11)	113.0(10)	Ta–Si(2)–H(12)	113.6(8)
C(11)–Si(1)–H(11)	101.2(11)	C(13)–Si(2)–H(12)	104.6(9)
C(12)–Si(1)–H(11)	108.1(11)	C(14)–Si(2)–H(12)	103.1(9)
C(11)–Si(1)–C(12)	102.3(8)	C(13)–Si(2)–C(14)	103.3(6)
H···Si(1)–H(11)	154.1(12)	H···Si(2)–H(12)	155.8(9)

angle in the classical structure TaH_3Cp_2 (126°).[8] It was argued that the shorter H···Si distances corresponding to the non-classical model (**I** or **II**) would result in a smaller Si–Ta–Si "bite" than the classical model **III**. In retrospect, it is now clear that these angles can be rationalized by a consideration of steric effects. In TaH_3Cp_2 the necessity of maintaining normal H···H contact distances (1.847 and 1.855 Å)[6]] "pushes" the H atoms apart, while in **1** the steric problems around the core of the molecule are less severe: the much longer Ta–Si distances [2.644(14) and 2.631(12) Å] allow the Si–Ta–Si angle to "shrink" while still maintaining comfortably large nonbonding H···Si contact distances [2.189(18) and 2.190(17) Å].

The classical structure of $TaCp_2(H)(SiMe_2H)_2$ reported here is consistent with the NMR spectrum of the compound, which essentially shows the two dimethylsilyl ligands as being equivalent.[6] Our result does not, of course, imply that all complexes of the type $MCp_2(H)R_2$ (M = Nb, Ta) are classical, although we note that one other compound originally thought to have an unsymmetrical geometry, $NbCp_2(H)(SiMe_2Cl)_2$,[9] has recently had its structure revised in favour of a symmetrical one.[10]

This research was supported by the National Science Foundation (Grants CHE-94-21769 and CHE-98-16294 to RB and DMR-96-32598 to DHB) and the American Chemical Society (Grant PRF-29196-AC3 to RB).

Technique used: Neutron diffraction

References: 10

Table: 1

Figures: 1

Appendix: Atomic coordinates, distances and angles in **1**

Received, 24th August 1998; Accepted, 21st September 1998
Paper E/8/06646I

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