

## Communications to the Editor

**A Wonderful Bond That Wasn't There:  
Reformulation of a Compound "Containing a  
Ta–Ta Bond without Bridging Ligands" as  
[(Cy<sub>2</sub>N)<sub>2</sub>CITa(μ-H)]<sub>2</sub>**

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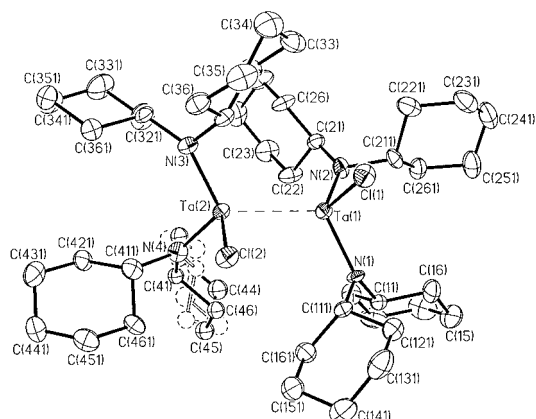
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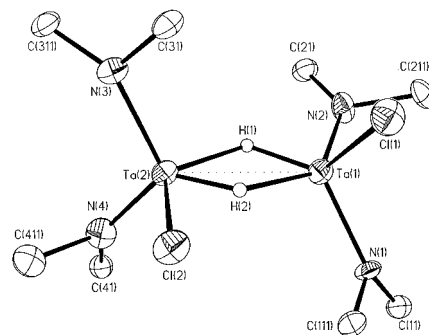
Recently Gambarotta *et al.*<sup>1</sup> reported the X-ray crystal structures of two compounds prepared by the reaction of TaCl<sub>5</sub> and LiNCy<sub>2</sub> (Cy = cyclohexyl). In the [(Cy<sub>2</sub>N)<sub>2</sub>TaCl(CyNC<sub>6</sub>H<sub>10</sub>)] molecule **1**, a pentavalent tantalum atom is surrounded by a chloride ion, two "normal" amido groups and a modified amido group in which one of the hydrogen atoms of a cyclohexyl group is lost to give a Ta–C bond. The formula of the other compound was proposed to be [(Cy<sub>2</sub>N)<sub>2</sub>CITa]<sub>2</sub> (**2**). The latter complex was remarkable in at least three ways: (1) each Ta atom had undergone a 2e reduction, (2) it had an unsupported Ta–Ta bond, and (3) the structure was highly unsymmetrical in the sense that what might have been expected to be chemically equivalent bonds were *very* different in length. For example, according to the published data and those provided as Supporting Information, the Ta–Cl distances were 2.401(3) and 2.453(3) Å, the Ta–N distances varied from 2.05(1) to 2.28(1) Å, and the C–C distances ranged from 0.86 to 1.70 Å. The refinement data indicated that it had been necessary to refine five carbon atoms isotropically.

Because of our interest in the chemistry of metal–metal compounds, especially those of tantalum,<sup>2</sup> the remarkable claim that an unbridged ditantalum unit could exist with a Ta–Ta distance greater than 2.8 Å, and the aforementioned anomalies, we decided to reinvestigate compound **2**.

We report here that a redetermination of the structure,<sup>3</sup> depicted in Figure 1, shows the same qualitative arrangement of the core atoms (Ta, N, Cl) as that previously reported,<sup>1</sup> but all the bond distances are regular and shorter than those reported earlier. The Ta–Cl distances are 2.376(2) and 2.388(2) Å, and the Ta–N distances vary from 1.967(5) to 1.991(6) Å. We believe that the shorter distances are consistent with the presence



**Figure 1.** A drawing of the molecular structure of [(Cy<sub>2</sub>N)<sub>2</sub>CITa(μ-H)]<sub>2</sub>. Ellipsoids are drawn at the 40% probability level. The minor orientation of the disordered cyclohexyl group (45%) is shown as dashed circles. The positions of the bridging hydrido groups are not shown.



**Figure 2.** A drawing of the core in [(Cy<sub>2</sub>N)<sub>2</sub>CITa(μ-H)]<sub>2</sub>. Two bridging hydride ions are shown as arbitrarily sized circles. All other atoms are represented by their 40% probability ellipsoids.

of tantalum atoms in a higher oxidation state.<sup>2</sup> For example, the Ta–Cl distances are 2.392(2) and 2.398(3) Å in the pentavalent tantalum complex TaCl<sub>2</sub>(NPh)(DPhF)(HDPhF)<sup>2d</sup> [HDPhF = *N,N'*-diphenylformamidine], while they are *ca.* 2.42 Å in *mer*-TaCl<sub>3</sub>(py)<sub>3</sub>. However, the most significant indication of the higher oxidation state of the tantalum atom are the Ta–N bond distances which are shorter than expected for a Ta(III)–N(amide) by more than 0.1 Å. Indeed, Ta–N distances which vary from 1.937(8) to 1.969(9) Å are reported for [(Cy<sub>2</sub>N)<sub>2</sub>TaCl(CyNC<sub>6</sub>H<sub>10</sub>)],<sup>1</sup> which contains a pentavalent tantalum atom.

An interesting result of our re-examination of the crystal structure is that our fractional coordinates for the Ta<sub>2</sub>Cl<sub>2</sub>N<sub>4</sub> core are essentially the same as those reported in ref 1, as are the lengths of the *b* and *c* axes and the value of the β angle, but the length of the *a* axis is *ca.* 6.6 Å shorter than the one reported. While this is, evidently, the origin of some of the difficulties experienced by the previous authors, the structure they obtained is rife with inconsistencies that indicate error. To confirm that the difference between their work and ours originates, as proposed, in their incorrect cell, we used our data together with the incorrect unit cell and obtained their incorrect result.

Since unbridged metal–metal bonds between metal atoms in high (>III) oxidation states are very rare<sup>4</sup> and considering also the rather long Ta to Ta distance, it was reasonable to suspect the presence of bridging hydrogen atoms. Given the

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(1) Scoles, L.; Ruppia, K. B. P.; Gambarotta, S. *J. Am. Chem. Soc.* **1996**, *118*, 2529.

(2) For example, see: (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *J. Am. Chem. Soc.* **1996**, *118*, 4830. (b) Cotton, F. A.; Murillo, C. A.; Wang, X. *Inorg. Chim. Acta* **1996**, *245*, 15. (c) Cotton, F. A.; Matonic, J. H.; Murillo, C. A.; Wang, X. *Bull. Soc. Chim. Fr.* **1996**, *133*, 711. (d) Cotton, F. A.; Daniels, L. M.; Matonic, J. H.; Murillo, C. A.; Wang, X. *Polyhedron* In press.

(3) The compound was prepared according to ref 1, and dark red crystals (as reported) were obtained from a concentrated diethyl ether solution at –5 °C. Crystal data: monoclinic *C2/c*, *a* = 42.234(5) Å, *b* = 10.804(1) Å, *c* = 22.765(2) Å, β = 94.702(8)°, *V* = 10353(2) Å<sup>3</sup>, *Z* = 8, *T* = –60 °C, *R*<sub>1</sub> (on *F*<sub>o</sub>) = 0.032, *wR*<sub>2</sub> (on *F*<sub>o</sub><sup>2</sup>) = 0.080, GOF = 1.09 for 809 parameters and 5388 unique data (5055 with *I* > 2σ(*I*)). One cyclohexyl ring was disordered as two interpenetrating chair conformers (C41–C46), and all other non-hydrogen atoms were refined anisotropically. The final refinement cycles included positions and isotropic displacement parameters for all nondisordered hydrogen atoms. The cell dimensions were also determined from a second crystal at –150 °C and were found to be *a* = 42.06(1) Å, *b* = 10.753(3) Å, *c* = 22.261(5) Å, β = 94.83(2)°, *V* = 10032(4) Å<sup>3</sup>.

(4) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610.

heavy scattering by the large Ta atoms, their presence might be difficult or impossible to detect by X-ray diffraction (but not necessarily impossible<sup>5</sup>), but an effort was made. We did, in fact, find two credible electron density peaks in bridging positions, and the positions and  $U_{\text{iso}}$  for the H atoms were included in the refinement. The result is shown in Figure 2.

The presence of two hydrogen atoms was also indicated by the  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ).<sup>6</sup> A sharp signal at 7.06 ppm had an integrated intensity that corresponded to 2.0 H when ratioed to the intensity of the complex multiplets arising from the hydrogen atoms (88) of the cyclohexyl groups. When the crystals were placed into  $\text{CD}_2\text{Cl}_2$ , immediate bubbling was observed, the signal at 7.06 ppm disappeared, and other signals appeared in the cyclohexyl region, but the spectrum was not clean.

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(5) For example, in  $\text{W}_2(\mu\text{-O}_2\text{CPh})_2(\mu\text{-H})(\mu\text{-Cl})\text{Cl}_2[\text{P}(n\text{-Bu})_3]_2$ , (Cotton, F. A.; Mott, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5978), there are two independent molecules, and the  $\mu\text{-H}$  atom was found and refined isotropically in each one. There are other, admittedly rare, examples of this kind.

(6)  $^1\text{H}$  NMR (from dissolution of crystals in  $\text{C}_6\text{D}_6$ , 200 MHz, 22 °C):  $\delta$  7.06 (s, 2 H, hydride ions), 3.87 (m, 8 H, CH cyclohexyl groups), 2.3 to 1.1 (series of multiplets, 80 H,  $\text{CH}_2$  cyclohexyl groups). When bulk material instead of crystalline material was used, other signals appeared including those at  $\delta$  3.48, 3.35, and 2.6 ppm, ascribed in ref 1 to compound 2.

It is pertinent to point out that other ditantalum compounds having the  $[\text{Ta}_2(\mu\text{-H})_n]$  core ( $n = 2, 3, 4$ ) have been described.<sup>7</sup> In the present case the source of the hydrogen atoms is not known, but the nature of compound 1 suggests that they may have been removed from cyclohexyl groups.

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**Supporting Information Available:** Tables of crystallographic data including diffractometer and refinement data, final coordinates, bond lengths, bond angles, and anisotropic displacement parameters (11 pages). See any current masthead page for ordering and Internet access instructions.

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(7) For example, see: Scioly, A. J.; Luetkens, M. L., Jr.; Wilson, R. B., Jr.; Huffman, J. C.; Sattelberger, A. P. *Polyhedron* **1987**, *6*, 741.