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Oxo–Hydrido and Imido–Hydrido Derivatives of Permethyltantalocene. Structures of $(\eta^5\text{-}C_5Me_5)_2Ta({=}O)H$ and $(\eta^5\text{-}C_5Me_5)_2Ta({=}NC_6H_5)H$: Doubly or Triply Bonded Tantalum Oxo and Imido Ligands?

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The syntheses of the complexes $Cp^*_2Ta({=}O)H$, $Cp^*_2Ta({=}NH)H$ and $Cp^*_2Ta({=}NC_6H_5)H$ and the solid-state structures for $Cp^*_2Ta({=}O)H$ and $Cp^*_2Ta({=}NC_6H_5)H$ are reported ($Cp^* = (\eta^5\text{-}C_5Me_5)$). These are formally 18-electron complexes with the oxo or imido ligands donating only one π-electron pair to tantalum. Since these ligands commonly donate both π-electron pairs (i.e. they triply bond) to transition-metal centers, at issue are the Ta–O and Ta–N bond orders. $Cp^*_2Ta({=}NC_6H_5)H$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $Z = 4$. The unit cell dimensions are $a = 15.324$ (3) Å, $b = 9.630$ (3) Å, $c = 17.707$ (5) Å; $\beta = 112.94$ (3)° and $V = 2406$ (2) Å^3. The solid-state structure reveals a linear Ta–N–C unit for $Cp^*_2Ta({=}NC_6H_5)H$. This feature is accommodated on both steric and electronic grounds. $Cp^*_2Ta({=}O)H$ crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $Z = 8$ and two inequivalent but similar molecules in the asymmetric unit. The unit cell dimensions are $a = 13.089$ (9) Å, $b = 19.322$ (11) Å, $c = 15.990$ (11) Å, $\beta = 108.61$ (6)° and $V = 3832$ (5) Å^3. The Ta–N and Ta–O bond distances are intermediate between the values expected for double and triple bonds, and the ν(Ta–O) for $Cp^*_2Ta({=}O)H$ is considerably less than that for other metal oxo compounds. Thus, the tantalum–nitrogen and tantalum–oxygen bond orders for these two compounds are anomalously low.

Introduction

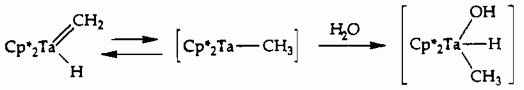
Organotransition-metal compounds containing multiply bonded heteroatom ligands such as oxo, sulfido, and imido ("nitrene") are of increasing interest, since these may provide models for suspected intermediates in catalytic oxidation/deoxygenation, hydrodesulfurization, and hydrodenitrogenation.[3] Although there are presently a relatively large number of compounds containing oxo or imido groups in combination with alkyl ligands (i.e. $L_nM({=}O)R_m$ or $L_nM({=}NR)R'_m$ (R, R′ = alkyl, aryl),[3,4] there are few complexes containing a reducing ligand such as hydride in combination with these functional groups, commonly associated with oxidizing compounds. Indeed, such complexes were unknown prior to our report of $Cp^*_2Ta({=}O)H$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$).[5,6] We describe herein results of an X-ray crystal structure determination for this unusual compound, the synthesis of the closely related imido hydride derivatives $Cp^*_2Ta({=}NR)H$ (R = H, C_6H_5), and the structure of $Cp^*_2Ta({=}NC_6H_5)H$. The nature of the metal–oxygen and metal–nitrogen bonding for these compounds is of particular interest, since for both $Cp^*_2Ta({=}O)H$ and $Cp^*_2Ta({=}NR)H$ the tantalum center is formally 18-electron and hence closed shell with doubly bonded (M=O and M=NR) oxo or imido groups. This bonding arrangement contrasts the more common triply-bonded character ($M^-{\equiv}O^+$ and $M^-{\equiv}N^+R$) observed for oxo and imido derivatives of early transition metals. Thus, at the outset of this study, the Ta–O and Ta–N bond lengths and the Ta–N–(ipso-C) bond angle for $Cp^*_2Ta({=}NC_6H_5)H$ were of special interest.

Results

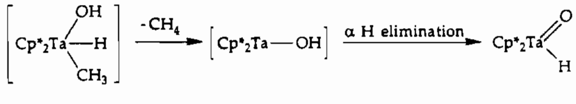
The title compounds, $Cp^*_2Ta({=}O)H$ and $Cp^*_2Ta({=}NC_6H_5)H$, are prepared by treatment of $Cp^*_2Ta({=}CH_2)H$ with water or aniline. The parent imido hydride derivative $Cp^*_2Ta({=}NH)H$ is obtained in low yield in the reaction of $Cp^*_2Ta({=}CH_2)H$ with NH_3. An improved preparation involves treatment of $Cp^*_2TaCl_2$ with excess $NaNH_2$. These new compounds have been isolated and characterized by infrared and ^1H and ^{13}C NMR spectroscopy and by X-ray crystal structure determinations for $Cp^*_2Ta({=}O)H$ and $Cp^*_2Ta({=}NC_6H_5)H$.

Discussion

We have previously reported that the methylidene hydride complex $Cp^*_2Ta({=}CH_2)H$ is a versatile starting material for a variety of permethyltantalocene derivatives.[5] Treatment with water cleanly affords $Cp^*_2Ta({=}O)H$ and methane. The reaction of $Cp^*_2Ta({=}CH_2)H$ with D_2O gives only CH_3D and $Cp^*_2Ta({=}O)D$, consistent with a reaction sequence involving initial tautomerization of $Cp^*_2Ta({=}CH_2)H$ to $[Cp^*_2TaCH_3]$, oxidative addition of water affording $[Cp^*_2Ta(CH_3)(H)(OH)]$ (or $[Cp^*_2Ta(CH_3)(D)(OD)]$), reductive elimination of CH_4 (or CH_3D), and subsequent α-H elimination for the resulting permethyltantalocene hydroxide yielding $Cp^*_2Ta({=}O)H$ (or $Cp^*_2Ta({=}O)D$) (eqs 1 and 2). $Cp^*_2Ta({=}O)H$ is also obtained cleanly by treatment of other $[Cp^*_2TaR]$ precursors, i.e. $Cp^*_2Ta(\eta^2\text{-}CH_2{=}CHR')H$, $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$, $Cp^*_2Ta({=}CHC_6H_5)H$, $Cp^*_2Ta({=}C{=}CH_2)H$, etc., with water.

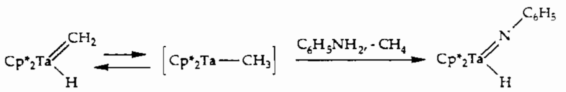


(1)



(2)

In a similar fashion, $Cp^*_2Ta({=}CH_2)H$ reacts with $NH_2C_6H_5$ to eliminate CH_4 and form the phenylimido hydride derivative $Cp^*_2Ta({=}NC_6H_5)H$ (eq 3). The parent imido hydride derivative,



(3)

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(1) Present address: Department of Chemistry, Columbia University, New York, NY 10027.

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(3) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123-175.

(4) (a) Herrmann, W.; Romao, C.; Fischer, R.; Kiprof, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185-187. (b) Zhang, C.; Schlemper, R.; Schrauzer, G. *Organometallics* **1990**, *9*, 1016-1020. (c) Spaltenstein, E.; Erikson, T.; Critchlow, S.; Mayer, J. *J. Am. Chem. Soc.* **1989**, *111*, 617-623. (d) Herrmann, W.; Floel, M.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *358*, 321-338. (e) Legzdins, P.; Rettig, S.; Sanchez, L. *Organometallics* **1985**, *4*, 1470-1471. (f) Herrmann, W.; Serrano, U.; Ziegler, M.; Guggolz, E.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 515. (g) Nugent, W.; Harlow, R. *J. Am. Chem. Soc.* **1980**, *102*, 1759-1760. (h) Beattie, I.; Jones, P. *Inorg. Chem.* **1979**, *18*, 2318-2319.

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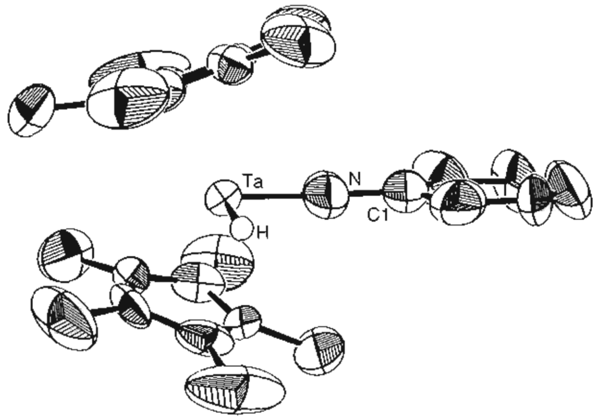
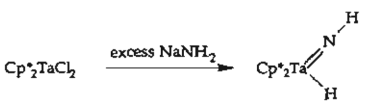


Figure 1. ORTEP drawing of $Cp^*_2Ta(=NC_6H_5)H$ with 50% probability ellipsoids. Hydrogen atoms on the methyl groups have been omitted.

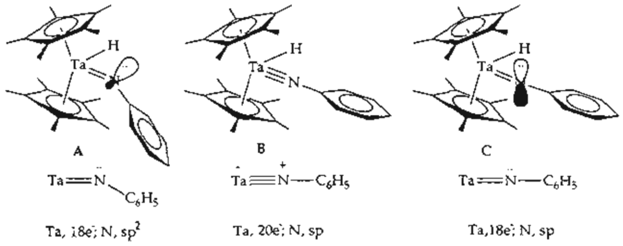
$Cp^*_2Ta(=NH)H$, is generated only in poor yield by the reaction of $Cp^*_2Ta(=CH_2)H$ with NH_3. The preferred method of preparation is via reaction of $Cp^*_2TaCl_2$ with $NaNH_2$ (eq 4).



$$Cp^*_2TaCl_2 \xrightarrow{\text{excess } NaNH_2} Cp^*_2Ta(=NH)H \qquad (4)$$

Although the mechanism for this unusual reaction is not clear, it is probably analogous to that which yields $Cp^*_2Ta(=CH_2)H$ from $Cp^*_2TaCl_2$ and 2.5 equiv of CH_3Li.[5a] $Cp^*_2Ta(=NH)H$ is characterized by a N–*H* resonance at δ 10.39 and a Ta–*H* resonance at δ 6.38 in the ^1H NMR spectrum and a strong band at 3430 cm^{-1} in the IR spectrum assignable to ν(N–H). The imido hydride complex $Cp^*_2Ta(=NH)H$ can be compared to the methylidene hydride complex $Cp^*_2Ta(=CH_2)H$; however, unlike $Cp^*_2Ta(=CH_2)H$, an α-H migration from Ta to N to generate $[Cp^*_2Ta\text{-}NH_2]$ does not occur on the NMR time scale at room temperature.

On the basis of its electron count and the accepted MO description of bent bis(η^5-cyclopentadienyl) metal derivatives,[7] $Cp^*_2Ta(=NC_6H_5)H$ may be expected to have a structure with a bent [Ta=N—(ipso-C)] arrangement (bonding picture A), since with (only) one Ta=N π interaction tantalum achieves a closed-shell, 18-electron configuration. Hence, the imido nitrogen should be sp^2 hybridized and the phenyl substituent oriented out of the equatorial plane toward one of the cyclopentadienyl ligands, as observed for the closely related benzylidene derivatives $Cp_2Ta(=CHC_6H_5)CH_2C_6H_5$ (Cp = (η^5-C_5H_5))[8] and $Cp^*_2Ta(=CHC_6H_5)H$.[9] The structures of the phosphinidene derivatives of molybdenocene and tungstenocene, $Cp_2M{=}PR$ (M = Mo, W, R = 2,4,6-$C_6H_2(CMe_3)_3$; M = W; R = $CH(SiMe_3)_2$), bear out these expectations, with the phosphorus substituent bent ca. 64° out of the equatorial plane toward one of the cyclopentadienyl ligands for $Cp_2Mo{=}P(2,4,6\text{-}C_6H_2(CMe_3)_3)$.[10] On the other hand, linear M–N–C geometries are observed for virtually all transition-metal imido complexes,[3] including related, formally 19-electron cases such as $Cp^*_2V{\equiv}NC_6H_5$[11] and $Cp^*_2V{\equiv}N(2,6\text{-}Me_2C_6H_3)$.[12] The observation of only one Cp* resonance in the ^1H NMR spectrum for $Cp^*_2Ta(=NC_6H_5)H$ places a bent tantalum–imido bonding arrangement in further doubt,[13] and so an X-ray crystal structure determination was undertaken. As can be seen in Figure 1, the rather unexpected finding is a nearly linear (177.8 (9)°) Ta–N–(ipso-C) arrangement, with the phenyl group lying neatly in the equatorial plane. The hydride atom was also located in the same symmetry plane between the two Cp* ligands. Interestingly, the hydride and phenylimido ligands are asymmetrically situated in the $[Cp^*_2Ta]$ wedge: while the Ta–N bond is displaced 21° to one side of the plane containing the two Cp* centroids and tantalum atom, the Ta–H bond is 61° to the other side (N–Ta–H = 81.6 (18)°). Such an asymmetric arrangement probably results from the preference for the bulkier phenylimido ligand to occupy a more spacious, more centrally located site (vide infra).



The immediate implication from the linear Ta–N–(ipso-C) arrangement is that nitrogen is sp (not sp^2) hybridized. However, such sp nitrogen hybridization does *not* necessarily imply a triple $[Ta{\equiv}NC_6H_5]$ bond by donation of the nitrogen lone pair into an out-of-plane orbital of the $[Cp^*_2Ta(H)]$ moiety and thus a 20-electron configuration at Ta (B). If steric interactions force the phenyl ring into the equatorial plane, a linear Ta–N–(ipso-C), sp-hybridized N with a double $[Ta{=}NC_6H_5]$ bond and the lone electron pair localized in a nitrogen p orbital could result. Bonding situation C is the best limiting picture in this alternate description.

A decision between bonding descriptions B and C then rests not on the Ta–N–(ipso-C) bond angle, but on the tantalum–nitrogen bond order. Moreover, since in the 20-electron alternative B the electron pair on nitrogen would be donated into an orbital which is Ta–Cp* antibonding in character, a comparison of the Ta–Cp* bond lengths to those for other bona fide 18-electron permethyltantalocene derivatives might be informative. The Ta–N bond length for $Cp^*_2Ta(=NC_6H_5)H$ of 1.831 (10) Å is longer than that observed for $(Me_2N)_3Ta{=}NCMe_3$ (1.77 (2) Å)[14] and $(PEt_3)(THF)Cl_2Ta{\equiv}NC_6H_5$ (1.765 (5) Å),[15] where there can be little doubt that Ta≡NR triple bonding is the best description. Moreover, the expected Ta≡N bond length for octahedral complexes has been estimated to be 1.75 Å.[3b] Hence, we may conclude that the Ta–N bond length for $Cp^*_2Ta(=NC_6H_5)H$ is ca. 0.07 (1) Å longer than expected for the limiting description B. In the absence of crystal structure determinations for reference compounds with true Ta=NR double bonds, we estimate this bond length as ca. 1.89 Å.[16] The Ta–N bond length for $Cp^*_2Ta(=NC_6H_5)H$ (1.831 (10) Å) is thus ca. 0.06(1) Å shorter than expected for the limiting description C, and we conclude from bond length arguments that the tantalum-nitrogen bond order is roughly halfway between 2 and 3, with the true bonding situation for $Cp^*_2Ta(=NC_6H_5)H$ intermediate between the limiting descriptions B and C.

Both Bergman[17] and Schrock[18] have recently reported X-ray

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[7] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

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[12] Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 7945–7952.

[13] An alternate bent arrangement with equivalent pentamethylcyclopentadienyl ligands would have the phenyl ring in the equatorial plane of the $[(\eta^5\text{-}C_5Me_5)_2Ta]$ moiety; however, such an orientation places the π-symmetry orbital on N perpendicular to that on Ta, i.e. as for 90° twisted ethylene.

[14] Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579.

[15] Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 223.

[16] The estimate is based on the following arguments: the difference in the W=C double bond and W≡C triple bond lengths = 0.16 Å in the complex $W(dmpe)(CH_2R)(=CHR)(\equiv CR)$ (dmpe = $Me_2PCH_2CH_2PMe_2$; R = CMe_3) (see: Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2054), close to the difference in C=C and C≡C bond lengths, 0.14 Å. Hence, we may estimate the difference in Ta=N and Ta≡N from the difference in C=N and C≡N bond lengths, 0.13 Å, which implies the Ta=NR bond length is approximately 1.76 (1) Å + 0.13 Å = 1.89 (1) Å.

[17] Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

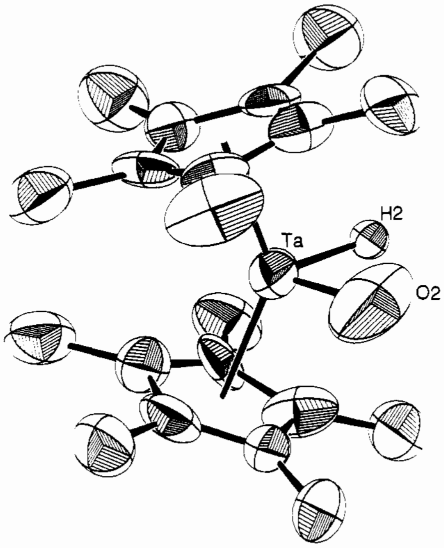

Figure 2. ORTEP drawing of molecule 2 of $Cp^*_2Ta({=}O)H$ with 50% probability ellipsoids. Hydrogen atoms on the methyl groups have been omitted.

crystal structures for compounds with linear [M–N–R] arrangements that would formally result in 20-electron species, if the imido ligand is triply bonded to the metal. These results further challenge the notion that linearity of an imido ligand implies donation of the electron pair on nitrogen to the metal. For $Os[N\text{-}2,6\text{-}C_6H_3(CHMe_2)_2]_3$ there is an occupied MO consisting of a linear combination of nitrogen p_z orbitals, which is essentially Os–N *non*bonding; a similar situation may obtain for the related (also otherwise formally 20-electron) compound $Os(N\text{-}2,6\text{-}(CHMe_2)_2C_6H_3)_2(PMe_2Ph)_2$.

We have also determined the structure for $Cp^*_2Ta({=}O)H$ by X-ray methods (Figure 2). The two independent molecules in the unit cell are similar, with Ta–O distances (Ta1–O1A = 1.73 (2) Å, Ta1–O1B = 1.69 (4) (the oxygen atom is disordered) and Ta2–O2 = 1.683 (18) Å). Results from an earlier study of ours showed distances that are somewhat longer (Ta1–O1 = 1.762 (12) Å and Ta1–O2 = 1.735 (10) Å). The thermal ellipsoids for O1 and O2 have their largest principal axes in the equatorial plane of the permethyltantalocene moiety, with O1 showing such a large motion that we had to represent it by two partial oxygen atoms; this disorder precludes our locating the hydrogen atom on Ta1. Although this motion brings the exact positions of O1 and O2 into some doubt, less asymmetry for the hydride and oxo ligands within the $[Cp^*_2Ta]$ wedge is observed for $Cp^*_2Ta({=}O)H$ than for the hydride and phenylimido ligands for $Cp^*_2Ta({=}NC_6H_5)H$ (vide supra). Thus, Ta1–O1A, Ta1–O1B, and Ta2–O2 bonds are directed 31, –23, and 25° to one side of the plane containing the two Cp* centroids and tantalum atom. It is likely that the small size of the hydride ligand relative to oxo and especially phenylimido is responsible for this asymmetry.

As previously discussed, the tantalum–oxygen bond order and tantalum electron count for $Cp^*_2Ta({=}O)H$ are of considerable interest. Unfortunately, there appears to be only one tantalum–oxygen bond length of a tantalum oxo compound reported for comparison (d(Ta–O) = 1.725 (7) Å for $Ta({=}O)\{N(CHMe_2)_2\}_3$).[19] $Cp_2Nb({=}O)\{C_7H_5(CF_3)_2\}$ (d(Nb–O) = 1.63 (3) Å) is the most closely related structure;[20] however, the comparatively large uncertainty is this very short niobium–oxygen bond length brings it into question as a basis for comparison.[21] Moreover, the poor quality of the bond length data from the structure determination for $Cp^*_2Ta({=}O)H$ and the large variance in tantalum–oxygen bond lengths for the two independent molecules obtained (1.73 (2), 1.69 (4), and 1.68 (2) Å) do not allow for accurate assessment of the tantalum–oxygen bond order for $Cp^*_2Ta({=}O)H$ based on d(Ta–O) (including our earlier measurements, the Ta–O bond length averages to 1.72 (3) Å). On the other hand, the metal–oxygen stretching frequency does provide a reliable indicator of bond strength, unlike the energy for the metal–nitrogen stretch for metal imido derivatives, since the latter is strongly coupled to other modes, particularly ν(N–C). The relatively low-energy stretching frequency ν(Ta–O) = 850 cm^{-1} is perhaps the best indicator that the bond order is substantially less than 3 (cf. the range of 905–935 cm^{-1} for "typical" monooxo complexes of Ta).[22]

To the extent that structure B (and its oxo counterpart) contribute, the Ta–Cp* bonds should be weakened by donation of the out-of-plane nitrogen or oxygen lone pair into the antibonding b_1 orbital for the $[Cp^*_2Ta]$ unit.[8] The Ta–C(Cp*) bond lengths for $Cp^*_2Ta({=}NC_6H_5)H$ (average = 2.461 (14) Å) and $Cp^*_2Ta({=}O)H$ (averages = 2.489 (9), 2.480 (8) Å) are not statistically different from those for $Cp^*_2Ta({=}CH_2)CH_2Ph$ (2.476 (5) Å),[23] O-*anti*-$Cp^*_2Ta(OCHC_6H_5CH_2)CH_3$ (2.503 (17) Å),[24] $Cp^*_2Ta(\eta^2\text{-}O_2)CH_2C_6H_5$ (2.509 (10) Å),[25] $Cp^*_2Ta(\eta^2\text{-}OCH_2)H$[26] (2.456 (10) Å), and $Cp^*_2Ta(\eta^2\text{-}CH_2CH_2\cdot AlEt_3)H$ (2.44 (2) Å),[27] so that triple Ta≡NR or Ta≡O bonding is not apparent using this criterion. Admittedly, the reduction in Ta–Cp* bond order should result in only a very small change in the average Ta–C(Cp*) distance, since the effect is spread over 10 tantalum–carbon bonds. We do note that a significant trans influence has been clearly observed for unsymmetrical compounds such as $Cp^*(OC_5Me_5)WO_2$,[28] $Cp^*(\eta^1\text{-}C_5Me_5)WO_2$,[29] $Cp^*ReO_2(CH_3)_2$, and $Cp^*ReO_2Cl_2$.[30]

Conclusions

The structural data for $Cp^*_2Ta({=}O)H$ and $Cp^*_2Ta({=}NC_6H_5)H$ suggest tantalum–oxygen and tantalum–nitrogen bond orders between 2 and 3. Thus, neither limiting picture, B or C, adequately depicts the true bonding situation. We conclude that the second Ta–O or Ta–N π interaction is relatively weak, resulting in a modest shortening of bond lengths and such a small lengthening of Ta(Cp*) distance as to be statistically insignificant. The relatively low energy for the ν(Ta–O) for $Cp^*_2Ta({=}O)H$ affirms the importance of the doubly bonded (class b)[31] character of the metal–oxygen bond.

Experimental Section

General Considerations. All manipulations were carried out with glovebox or high vacuum line techniques described previously.[32] Solvents were dried over $LiAlH_4$ or sodium benzophenone ketyl and stored over titanocene. Elemental analyses were performed at the Caltech Analytical Laboratory by Fenton Harvey. Infrared spectra were measured either as Nujol mulls on KBr plates or as KBr pellets and recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Jeol GX400Q (399.78 MHz) instrument in C_6D_6 (δ 7.15) solutions.

Synthesis of $Cp^*_2Ta({=}NC_6H_5)H$. A solution of $Cp^*_2Ta({=}CH_2)H$

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Table I. Crystallographic Data for $Cp^*_2Ta({=}NC_6H_5)H$ and $Cp^*_2Ta(O)H$

	$Cp^*_2Ta({=}NC_6H_5)H$	$Cp^*_2Ta({=}O)H$
formula	$TaNC_{26}H_{36}$	$TaOC_{20}H_{31}$
fw	543.53	468.41
a, Å	15.324 (3)	13.089 (9)
b, Å	9.630 (3)	19.322 (11)
c, Å	17.707 (5)	15.990 (11)
β, deg	112.94 (3)	108.68 (2)
V, Å^3	2406 (2)	3832 (5)
Z	4	8
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
T, °C	23	24
λ, Å	0.71073	0.71073
ρ_{calc}, g cm^{-3}	1.50	1.62
μ, cm^{-1}	45.23	56.71
transm coeff: max; min	0.62; 0.24	0.55; 0.26
R^a	0.045	0.054

[a] $R = (|\sum|F_o| - \sum|F_c||)/\sum|F_o|$ for all $F_o^2 > 0$.

(250 mg, 0.48 mmol) in benzene (ca. 2 mL) was treated with $C_6H_5NH_2$(170 μL) and left at room temperature for 18 h. The solvent was removed in vacuo, and the residue was extracted into pentane and filtered. The filtrate was concentrated and cooled to −78 °C, giving $Cp^*_2Ta({=}NC_6H_5)H$ as orange crystals (130 mg, 50% yield). Anal. Found: C, 57.0; H, 6.8; N, 2.4. Calcd: C, 57.5; H, 6.7; N, 2.6. ^1H NMR data (C_6D_6): δ 1.92 [s, $C_5(CH_3)_5$], 6.31 [s, Ta–H], 6.50 [d, $^3J_{H-H}$ = 7.5 Hz, ortho C_6H_5], 6.95 [t, $^3J_{H-H}$ = 7.5 Hz, para C_6H_5], 7.21 [t, $^3J_{H-H}$ = 7.5 Hz, meta C_6H_5]. ^{13}C NMR data (C_6D_6): δ 12.5 [q, $^1J_{C-H}$ = 125 Hz, $C_5(CH_3)_5$], 113.7 [s, $C_5(CH_3)_5$], 115.5 [d, $^1J_{C-H}$ = 159 Hz, para C_6H_5], 118.4 [d, $^1J_{C-H}$ = 155 Hz, ortho or meta C_6H_5], 160.9 [s, ipso C_6H_5]. IR data (Nujol mull, cm^{-1}): 1790 ν(Ta–H).

Structure Determination of $Cp^*_2Ta({=}NC_6H_5)H$. A single crystal needle was sealed in a capillary under argon. A total of 2244 independent reflections were collected over a range of 2θ of 4–40° on a CAD-4 diffractometer. Cell dimensions were determined from the setting angles of 25 reflections with $19° < 2\theta < 22°$. Two equivalent sets of data were collected; intermittent diffractometer failure caused 188 reflections to be set incorrectly and to measure zero. The data were corrected for a linear decay of 1.6%, and absorption corrections were done by Gaussian integration over an 8 × 8 × 8 grid. Space group $P2_1/c$ (No. 14) was chosen based on the systematic absences of $h0l$, where $l = 2n + 1$, and $0k0$, where $k = 2n + 1$, in the intensity data. See Table I for crystallographic data.

The tantalum atom coordinates were found from a Patterson map, and the remaining atoms were located by successive structure factor calculations and Fourier maps. All non-hydrogen atoms were refined by full-matrix least-squares methods with anisotropic thermal parameters. The phenyl hydrogen atoms were included at calculated positions as fixed contributions; their positions were adjusted twice during the refinement; the Cp methyl group hydrogen atoms were modeled by a 2-fold disorder, with six half-hydrogens around each carbon atom. The hydride atom appeared as a prominent peak in a late difference map. Its coordinates and B were included in the refinement. Several cycles of full-matrix least-squares refinement led to convergence with $R = 0.0451$ when $F_o^2 > 3\sigma(F_o^2)$ (1711 reflections). The final goodness of fit $([\sum w(F_o^2 - F_c^2)/(n-p)]^{1/2})$ is 1.79.

Synthesis of $Cp^*_2Ta({=}NH)H$. A mixture of $Cp^*_2TaCl_2$ (500 mg, 0.96 mmol) and $NaNH_2$ (200 mg, 5.1 mmol) in toluene (30 mL) was heated at 80 °C for 2 days. The mixture was filtered and the solvent removed from the filtrate in vacuo. The residue was extracted into pentane and filtered and the solvent removed in vacuo giving $Cp^*_2Ta({=}NH)H$ as a yellow solid (ca. 200 mg, 45% yield). Anal. Found: C, 49.3; H, 6.5; N, 3.3. Calcd: C, 51.4; H, 6.9; N, 3.0. ^1H NMR data (C_6D_6): δ 1.95 [s, $C_5(CH_3)_5$], 6.38 [s, Ta—H], 10.39 [s, Ta=NH]. ^{13}C NMR data (C_6D_6): δ 12.7 [q, $^1J_{C-H}$ = 125 Hz, $C_5(CH_3)_5$], 112.8 [s, $C_5(CH_3)_5$]. IR data (Nujol mull, cm^{-1}): 1790 ν(Ta–H), 3420 ν(N–H).

Synthesis of $Cp^*_2Ta({=}O)H$. Fourteen equivalents of H_2O (0.200 mL, 11.1 mmol) were added via syringe to a benzene (15 mL) solution of $Cp^*_2Ta({=}CHPh)H$ (419 mg, 0.77 mmol). The solution was stirred for 20 h at room temperature whereupon the color had faded to light orange (the reaction mixture may be heated using a warm water bath in order to drive it to completion in a shorter period). The benzene was removed, and petroleum ether was added, removed in vacuo, and added again. Cooling the petroleum ether solution to −78 °C resulted in pale yellow crystals of $Cp^*_2Ta({=}O)H$ (125 mg, 30% yield).

Structure Determination of $Cp^*_2Ta({=}O)H$. A single crystal grown by slow evaporation of petroleum ether was sealed in a thin-walled glass capillary under argon. The crystal was optically centered on a CAD-4 diffractometer and 9003 independent reflections ($3° < 2\theta < 40°$) were recorded. A decrease of 11% in the check reflection intensities was observed over the 131.03 h of data collection; the intensities were scaled accordingly. The data were corrected for absorption based on ψ scans, with transmission factors from 0.26 to 0.55. Space group $P2_1/n$, a nonstandard setting of No. 14, was chosen based on the systematic absences of $h0l$, where $h + l = 2n + 1$, and $0k0$, where $k = 2n + 1$, in the intensity data. See Table I for crystallographic data.

The positions of the tantalum atoms were determined from a Patterson map. From Fourier and difference Fourier maps, all the remaining atoms were located. The tantalum, ordered oxygen, and the carbon atoms in the Cp* groups were given anisotropic Gaussian parameters while the disordered oxygen and hydrogen atoms were given isotropic B's. Several cycles of full-matrix least-squares refinement varying all the parameters of the heavy atoms led to convergence with $R = 0.074$ for 3309 reflections with $F_o^2 > 0$ and $R = 0.054$ for 2520 reflections with $F_o^2 > 3\sigma F_o^2$. Hydrogen atoms were positioned by calculation, assuming a 2-fold disorder on each Cp* methyl group, and their parameters were not refined. The population of O1A refined to 0.63 (2), with O1B being 1 − 0.63. The final goodness of fit $([\sum w(F_o^2 - F_c^2)/(n-p)]^{1/2})$ is 2.38.

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Supplementary Material Available: A table of crystallographic data for $Cp^*_2Ta({=}NC_6H_5)H$ and $Cp^*_2Ta({=}O)H$, an ORTEP drawing for the phenylimido hydride, tables of final parameters, assigned hydrogen parameters, anisotropic displacement parameters, and complete distances and angles for the phenylimido hydride, ORTEP drawings for the Ta1 and Ta2 complexes of the oxo hydride, and tables of final refined parameters, assigned hydrogen parameters, distances and angles not involving hydrogen, and anisotropic displacement parameters for the oxo hydride (20 pages); tables of observed and calculated structure factors for both complexes (26 pages). Ordering information is given on any current masthead page.