10642 *Inorg. Chem.* **2010**, *49*, 10642–10648
DOI: 10.1021/ic1016609

Inorganic Chemistry
Article

Trapping Unstable Terminal M–O Multiple Bonds of Monocyclopentadienyl Niobium and Tantalum Complexes with Lewis Acids

Javier Sánchez-Nieves,*[†,‡] Luis M. Frutos,[§] Pascual Royo,*[†] Obis Castaño,[§] Eberhardt Herdtweck,[‖] and Marta E. G. Mosquera[†]

[†]*Departamento de Química Inorgánica,* [‡]*CIBER-BBN, Departamento de Química Inorgánica, and*
[§]*Departamento de Química Física, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares,*
Madrid, Spain, and [‖]*Anorganisch-Chemisches Institut der Technischen Universität München,*
Lichtenbergstrasse 4, D-85747 Garching bei München, Germany

Received August 17, 2010

Hydrolysis of $[NbCp'Cl_4]$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$) with the water adduct $H_2O\cdot B(C_6F_5)_3$ afforded the oxo-borane compound $[NbCp'Cl_2\{O\cdot B(C_6F_5)_3\}]$ (**2a**). This compound reacted with $[MgBz_2(THF)_2]$ giving $[NbCp'Bz_2\{O\cdot B(C_6F_5)_3\}]$ (**2b**), whereas $[NbCp'Me_2\{O\cdot B(C_6F_5)_3\}]$ (**2c**) was obtained from the reaction of $[NbCp'Me_4]$ with $H_2O\cdot B(C_6F_5)_3$. Addition of $Al(C_6F_5)_3$ to solutions containing the oxo-borane compounds $[MCp^RX_2\{O\cdot B(C_6F_5)_3\}]$ (M = Ta, $Cp^R = \eta^5\text{-}C_5Me_5$ (Cp*), X = Cl **1a**, Bz **1b**, Me **1c**; M = Nb, $Cp^R = Cp'$, X = Cl **2a**) afforded the oxo-alane complexes $[MCp^RX_2\{O\cdot Al(C_6F_5)_3\}]$ (M = Ta, Cp^R = Cp*, X = Cl **3a**, Bz **3b**, Me **3c**; M = Nb, $Cp^R = Cp'$, X = Cl **4a**), releasing $B(C_6F_5)_3$. Compound **3a** was also obtained by addition of $Al(C_6F_5)_3$ to the dinuclear μ-oxo compound $[TaCp^*Cl_2(\mu\text{-}O)]_2$, meanwhile addition of the water adduct $H_2O\cdot Al(C_6F_5)_3$ to $[TaCp^*Me_4]$ gave complex **3c**. The structure of **2a** and **3a** was obtained by X-ray diffraction studies. Density functional theory (DFT) calculations were carried out to further understand these types of oxo compounds.

Introduction

Metal complexes in high oxidation states are stabilized via formation of terminal multiple bonds with ligands such as alkylidene (CR_2), imide (NR), and oxo (O).[1,2] The similarities between these three ligands and the cyclopentadienyl ligand (C_5R_5) has allowed relationships between the fragments $[M(C_5R_5)_2]$ (M = group 4), $[M(C_5R_5)(L)]$ (M = group 5, L = CR_2, NR) and $[M(L)_2]$ (M = group 6, L = CR_2, NR or O) to be established.[3−6] It is noteworthy that while for compounds of group 6 metals, terminal oxo ligands are widely studied,[1,2] in group 5 metals, half-sandwich 16 electron compounds of the type $[M(C_5R_5)(O)R_2]$ (M = group 5) with a terminal oxo ligand have only been unequivocally characterized for vanadium.[7−9] Analogous unstable diiodide and dibromide tantalum compounds are postulated to be mononuclear,[10] but no X-ray structure could be determined, although the corresponding dichloride compound was formulated as a binuclear complex with μ_2-O bridges.[11,12] Related mononuclear 16- and 18-electron imide[1,2,13−22] and alkylidene[1,2,23−30] half-sandwich complexes have been described for vanadium, niobium, and tantalum.

---

*To whom correspondence should be addressed. E-mail: pascual.royo@uah.es (P.R.), javier.sancheznieves@uah.es (J.S.-N.). Fax: 00 34 91 885 4683.

(1) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley Interscience: New York, 1988.

(2) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(3) Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; Oneil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 739.

(4) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *Polyhedron* **1995**, *14*, 103.

(5) Chan, M. C. W.; Cole, J. M.; Gibson, V. C.; Howard, J. A. K.; Lehmann, C.; Poole, A. D.; Siemeling, U. *J. Chem. Soc., Dalton Trans.* **1998**, 103.

(6) Lin, Z. Y.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.

(7) Fischer, E. O.; Vigoureux, S. *Chem. Ber. Recl.* **1958**, *91*, 1342.

(8) Fischer, E. O.; Vigoureux, S.; Kuzel, P. *Chem. Ber. Recl.* **1960**, *93*, 701.

(9) Bottomley, F.; Darkwa, J.; Sutin, L.; White, P. S. *Organometallics* **1986**, *5*, 2165.

(10) Herberhold, M.; Peukert, J.; Milius, W. *J. Prakt. Chem., Chem. Zeitung* **1999**, *341*, 797.

(11) Gibson, V. C.; Kee, T. P. *J. Chem. Soc., Chem. Commun.* **1989**, 656.

(12) Royo, P.; Sánchez-Nieves, J. *J. Organomet. Chem.* **2000**, *597*, 61.

(13) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(14) Royo, P.; Sánchez-Nieves, J.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1998**, *563*, 15.

(15) Alcalde, M. I.; Gómez-Sal, P.; Martín, A.; Royo, P. *Organometallics* **1998**, *17*, 1144.

(16) Alcalde, M. I.; Gómez-Sal, M. P.; Royo, P. *Organometallics* **1999**, *18*, 546.

(17) Humphries, M. J.; Green, M. L. H.; Douthwaite, R. E.; Rees, L. H. *J. Chem. Soc., Dalton Trans.* **2000**, 4555.

(18) Nikonov, G. L.; Mountford, P.; Ignatov, S. K.; Green, J. C.; Leech, M. A.; Kuzmina, L. G.; Razuvaev, A. G.; Rees, N. H.; Blake, A. J.; Howard, J. A. K.; Lemenovskii, D. A. *J. Chem. Soc., Dalton Trans.* **2001**, 2903.

(19) Burckhardt, U.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 6328.

(20) Burckhardt, U.; Casty, G. L.; Gavenonis, J.; Tilley, T. D. *Organometallics* **2002**, *21*, 3108.

(21) Benito, J. M.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R.; Gómez-Sal, P. *J. Organomet. Chem.* **2002**, *664*, 258.

The very unstable oxo halide compounds $[M(C_5Me_5)(O)X_2]_n$ (n = 1, X = Br, I; n = 2, X = Cl) were obtained by exposure of carbonyl complexes to air in halogenated solvents,[10] oxygen abstraction from CO_2 by $[TaCp^*Cl_2(PMe)_3]$[11] and oxo-imido exchange.[12] Any attempt to introduce the terminal oxo ligand via hydrolysis reactions of monocyclopentadienyl compounds $[M(C_5R_5)X_4]$ (M = Nb, Ta) gave polynuclear oxo-bridged complexes.[15,31-33] Conversely, in previous work by our group, we successfully isolated stable 18 electron monocyclopentadienyl tantalum compounds $[TaCp^*Cl(O)\{\eta^2\text{-}C(Me)NR\}]$ by intramolecular exchange between imide and acyl groups.[34,35] For niobium, the transfer of an oxo group from oxythiolate compounds yields terminal oxo complexes.[36,37] These are to our knowledge the only examples of fully characterized (X-ray diffraction studies) terminal oxo monocyclopentadienyl compounds reported for tantalum and niobium, while terminal oxo complexes are easily achieved for dicyclopentadienyl compounds of both tantalum and niobium.[1,38] Very few other examples of non cyclopentadienyl terminal oxo tantalum complexes have been described, while for niobium it is a more common ligand.[1]

We have reported that hydrolysis of Ta−Cl and Ta−C bonds with the water adduct $H_2O\cdot B(C_6F_5)_3$ was an efficient method to generate mononuclear oxo compounds of the type $[TaCp^*R_2\{O\cdot B(C_6F_5)_3\}]$ (R = Cl **1a**, CH_2Ph **1b**, Me **1c**),[39] stabilized by the presence of the strong Lewis acid $B(C_6F_5)_3$[40-42] which avoids molecular aggregation via adduct formation.[43] These complexes showed similar behavior in insertion reactions[44] of CO and CNR than related monocyclopentadienyl imido complexes $[TaCp^*R_2(NR)]$,[34,35,45,46] although the presence of the oxo ligand helped to stabilize the new acyl derivatives.

Terminal oxo-borane adducts have been previously synthesized for Ti,[47] V,[47,48] Mo,[49-52] W,[52] Re,[51-53] and U[54] compounds starting from the stable terminal oxo complexes in reactions with the Lewis acid $B(C_6F_5)_3$, also by trapping a non-detected oxo Ti derivative,[55] meanwhile Al[43] and Ta[39,56] complexes have been obtained by hydrolysis of M-alkyl bonds with $H_2O\cdot B(C_6F_5)_3$ and Zr[57] complexes by hydrolysis with $[NEt_3H][HOB(C_6F_5)_3]$. However, similar oxo-adduct compounds with the related Lewis acid $Al(C_6F_5)_3$ are unknown.

Continuing with our aim to synthesize group 5 mononuclear oxo complexes, we have explored the reactivity of monocyclopentadienyl niobium compounds $[NbCp'X_4]$ (Cp^R = $C_5H_4SiMe_3$, X = Cl, Me) with the water adduct $H_2O\cdot B(C_6F_5)_3$, analogous reactions of these complexes and related monocyclopentadienyl tantalum derivatives with the alane adduct $H_2O\cdot Al(C_6F_5)_3$, and finally borane-alane exchange processes.

Results and Discussion

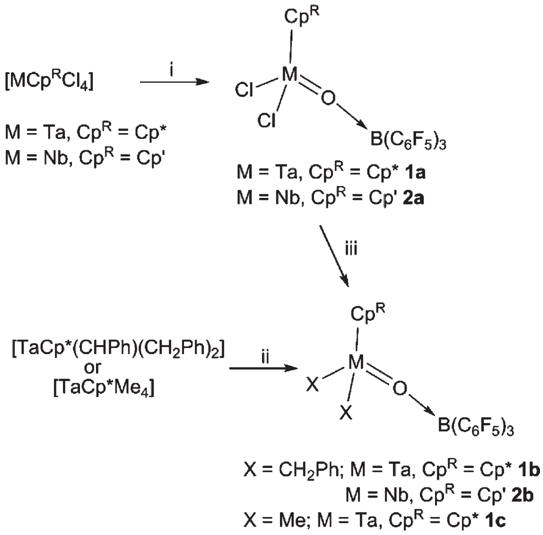
Hydrolysis with $H_2O\cdot E(C_6F_5)_3$ (E = B, Al). The same method reported to obtain the oxo-borane tantalum complexes $[TaCp^*R_2\{O\cdot B(C_6F_5)_3\}]$ (R = Cl **1a**, CH_2Ph **1b**, Me **1c**)[39] has been used to isolate the related niobium derivatives. Thus, a hydrolysis reaction of $[NbCp'Cl_4]$ (Cp' = η^5-$C_5H_4SiMe_3$) with 1 equiv of $H_2O\cdot B(C_6F_5)_3$ afforded the green mononuclear oxo-borane complex $[NbCp'Cl_2\{O\cdot B(C_6F_5)_3\}]$ (**2a**) in a moderate yield upon heating in toluene at 90 °C for 3 h (Scheme 1). Similar hydrolysis of $[NbCp'Me_4]$ with $H_2O\cdot B(C_6F_5)_3$ gave $[NbCp'Me_2\{O\cdot B(C_6F_5)_3\}]$ (**2c**), whereas the corresponding benzyl derivative could not be obtained following this procedure for $[NbCp'(CHPh)Bz_2]$, where a mixture of unidentified compounds resulted.

However, complex $[NbCp'Bz_2\{O\cdot B(C_6F_5)_3\}]$ (**2b**) was accessible in low yield by reaction of **2a** with $[MgBz_2(THF)_2]$

---

(22) Dubberley, S. R.; Ignatov, S. K.; Rees, N. H.; Razuvaev, A. G.; Mountford, P.; Nikonov, G. I. *J. Am. Chem. Soc.* **2003**, *125*, 642.
(23) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744.
(24) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.
(25) Hessen, B.; Meetsma, A.; Vanbolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925.
(26) de Castro, I.; de la Mata, J.; Gómez, M.; Gómez-Sal, P.; Royo, P.; Selas, J. M. *Polyhedron* **1992**, *11*, 1023.
(27) Cockcroft, J. K.; Gibson, V. C.; Howard, J. A. K.; Poole, A. D.; Siemeling, U.; Wilson, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1668.
(28) Buijink, J. K. F.; Kloetstra, K. R.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 2523.
(29) Mashima, K.; Tanaka, Y.; Kaidzu, M.; Nakamura, A. *Organometallics* **1996**, *15*, 2431.
(30) Courtenay, S.; Stephan, D. W. *Organometallics* **2001**, *20*, 1442.
(31) Andreu, A. M.; Jalón, F. A.; Otero, A.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1987**, 953.
(32) Jernakoff, P.; de Bellefon, C. D.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362.
(33) de la Mata, J.; Fandos, R.; Gómez, M.; Gómez-Sal, P.; Martínez-Carrera, S.; Royo, P. *Organometallics* **1990**, *9*, 2846.
(34) Gómez, M.; Gómez-Sal, P.; Jiménez, G.; Martín, A.; Royo, P.; Sánchez-Nieves, J. *Organometallics* **1996**, *15*, 3579.
(35) Sánchez-Nieves, J.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **2000**, *19*, 3161.
(36) Lindsell, W. E.; Rosair, G. M.; Spence, M. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3281.
(37) Dersch, R. K.; Jungclas, H.; Lindsell, W. E.; Rosair, G. M. *J. Chem. Soc., Dalton Trans.* **2003**, 126.
(38) Wigley, D. E.; Gray, S. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. *5*, p 121.
(39) Sánchez-Nieves, J.; Frutos, L. M.; Royo, P.; Castaño, O.; Herdtweck, E. *Organometallics* **2005**, *24*, 2004.
(40) Vagedes, D.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3362.
(41) Blackwell, J. M.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 1400.
(42) Dash, A. K.; Jordan, R. F. *Organometallics* **2002**, *21*, 777.
(43) Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Walfort, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4294.
(44) Sánchez-Nieves, J.; Royo, P.; Mosquera, M. E. G. *Eur. J. Inorg. Chem.* **2006**, 127.
(45) Royo, P.; Sánchez-Nieves, J.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1998**, *563*, 15.
(46) Castro, A.; Galakhov, M. V.; Gómez, M.; Gómez-Sal, P.; Martín, A.; Sánchez, F. *J. Organomet. Chem.* **2000**, *595*, 36.
(47) Galsworthy, J. R.; Green, M. L. H.; Muller, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1997**, 1309.
(48) Wolff, F.; Choukroun, R.; Lorber, C.; Donnadieu, B. *Eur. J. Inorg. Chem.* **2003**, 628.
(49) Doerrer, L. H.; Galsworthy, J. R.; Green, M. L. H.; Leech, M. A.; Muller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3191.
(50) Doerrer, L. H.; Galsworthy, J. R.; Green, M. L. H.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2483.
(51) Galsworthy, J. R.; Green, J. C.; Green, M. L. H.; Muller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 15.
(52) Barrado, G.; Doerrer, L.; Green, M. L. H.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1061.
(53) Han, Y.; Harlan, C. J.; Stoessel, P.; Frost, B. J.; Norton, J. R.; Miller, S.; Bridgewater, B.; Xu, Q. *Inorg. Chem.* **2001**, *40*, 2942.
(54) Sarsfield, M. J.; Helliwell, M. *J. Am. Chem. Soc.* **2004**, *126*, 1036.
(55) Kilgore, U. J.; Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2006**, *45*, 487.
(56) Bo, C.; Fandos, R.; Feliz, M.; Hernández, C.; Otero, A.; Rodríguez, A.; Ruiz, M. J.; Pastor, C. *Organometallics* **2006**, *25*, 3336.
(57) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491.

Scheme 1. Synthesis of Oxo-Borane Compounds[a]



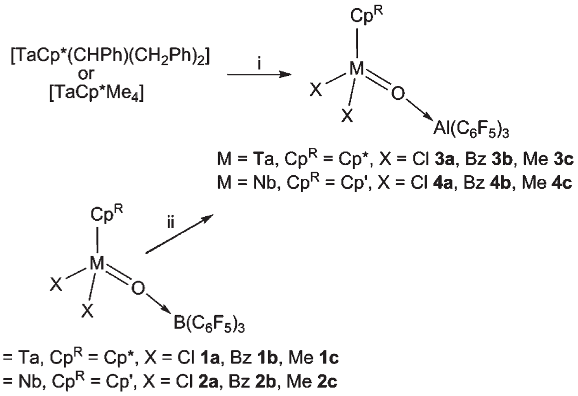
[a] (i) $H_2O\cdot B(C_6F_5)_3$, toluene, reflux; (ii) $H_2O\cdot B(C_6F_5)_3$, toluene, −78°C; $[MgBz_2(THF)_2]$, toluene, −78°C, only for **2b**.

in toluene at low temperature. In contrast, we were unable to detect the formation of the corresponding dimethyl derivative using different alkylating agents. Compounds **2** are soluble in halogenated and aromatic solvents but insoluble in alkanes. Compound **2a** is thermally stable and air stable in solution for a few hours, whereas the alkyl derivatives **2b** and **2c** were thermally unstable decomposing in solution within a few hours.

Analogous hydrolytic reactions of both Nb and Ta compounds were studied using the adduct $H_2O\cdot Al(C_6F_5)_3$. Addition of this water adduct to the tantalum complexes $[TaCp^*(CHPh)Bz_2]$ or $[TaCp^*Me_4]$ at low temperature allowed us to isolate the oxo-alane complexes $[TaCp^*R_2\{O\cdot Al(C_6F_5)_3\}]$ (R = CH_2Ph **3b**, Me **3c**) in low yield. Unfortunately, any attempt to obtain the corresponding chloro derivatives $[MCp^RCl_2\{O\cdot Al(C_6F_5)_3\}]$ (M = Ta, Nb) or the alkyl niobium derivatives $[NbCp'R_2\{O\cdot Al(C_6F_5)_3\}]$ (R = B, Al) by hydrolysis reactions of $[MCp^RCl_4]$ and $[NbCp'(CHPh)Bz_2]$ or $[NbCp'Me_4]$, respectively, failed; a mixture of unidentified compounds being obtained.

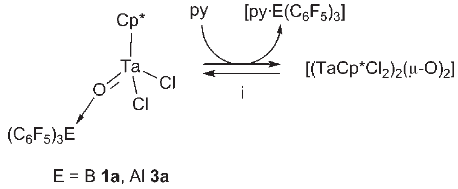
Exchange from M−O−B to M−O−Al. The higher oxophilicity of $Al(C_6F_5)_3$ led us to try borane-alane exchange reactions. Thus, the oxo-borane compounds $[MCp^RX_2\{O\cdot B(C_6F_5)_3\}]$ (M = Ta, Cp^R = η^5-C_5Me_5 (Cp*), X = Cl **1a**, Bz **1b**, Me **1c**; M = Nb, Cp^R = Cp′, X = Cl **2a**, Bz **2b**) reacted with one equiv of $Al(C_6F_5)_3$ affording the corresponding oxo-alane derivatives $[MCp^RX_2\{O\cdot Al(C_6F_5)_3\}]$ (M = Ta, Cp^R = Cp*, X = Cl **3a**, Bz **3b**, Me **3c**; M = Nb, Cp^R = Cp′, X = Cl **4a**, Bz **4b**) (Scheme 2). This process rendered the more thermodynamically stable compound, as has been inferred from theoretical calculations (see below). The $B(C_6F_5)_3$ released in these reactions did not abstract any alkyl group from the metal center. However, all of these compounds were thermally unstable even in the solid state, contrasting with the inertness shown by the corresponding oxo-borane derivatives, probably as consequence of the higher oxophilicity of the aluminum atom.

Scheme 2. Synthesis of Oxo-Alane Compounds[a]



[a] (i) $H_2O\cdot Al(C_6F_5)_3$, toluene, −78°C; ii) $Al(C_6F_5)_3$, toluene.

Scheme 3. Synthesis of Mononuclear Oxo Adducts from a Dinuclear Compound[a]



[a] (i) $E(C_6F_5)_3$ (E= B, Al), toluene.

Finally, the mononuclear oxo-alane derivative **3a** was also achieved upon addition of $Al(C_6F_5)_3$ to the dinuclear μ-oxo compound $[TaCp^*Cl_2(\mu\text{-}O)]_2$, in an analogous way to its reaction with $B(C_6F_5)_3$ (Scheme 3).

NMR Characterization. The ^{11}B- and ^{19}F-NMR spectroscopy of complexes **2** indicated that the boron atom was tetracoordinated, by means of a broad peak in the ^{11}B-NMR spectra around δ 0 and by the shift to higher field of the resonances corresponding to the *meta*-fluorine nuclei of the C_6F_5 groups with regard to free $B(C_6F_5)_3$.[39,43,44,47−53,56,57] A comparison for compounds **1** and **2** of the ^{11}B NMR chemical shifts and of the $\delta(m\text{-F}) - \delta(p\text{-F})$ differences ($\Delta\delta$) in the ^{19}F-NMR spectra showed a shifting to higher field of the ^{11}B resonances and a decrease of the $\Delta\delta$ values when the chloro ligands were replaced by alkyl substituents, indicating a slightly stronger interaction of the oxygen atom with the borane as consequence of the lower electronegative and higher inductive effect of the alkyl group.

The ^{1}H and ^{13}C NMR spectra of compounds **3**−**4** were very close to those of the related compounds **1**−**2**, with no significant change in their chemical shifts. More information can be obtained from ^{19}F NMR spectroscopy of the borane-alane exchange reaction, which clearly showed resonances corresponding to free $B(C_6F_5)_3$, whereas the resonances corresponding to the $Al(C_6F_5)_3$ moiety were as expected for this type of tetracoordinated aluminum derivative.

X-ray Characterization. The X-ray structure of compound **2a** is depicted in Figure 1, and selected bond distances and angles are collected in Table 1. The molecular structure of compound **2a** corresponds to a three-legged piano stool disposition with the cyclopentadienyl ring at

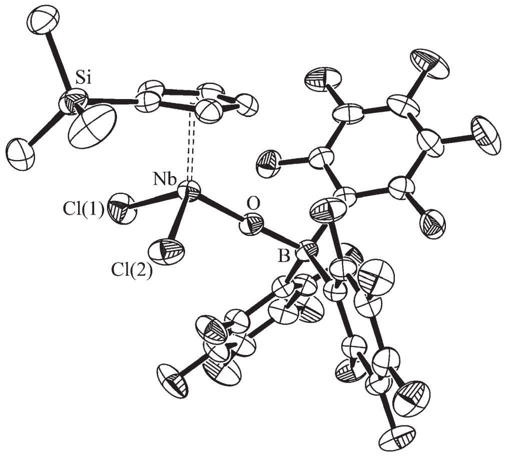


Figure 1. X-ray structure of compound **2a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds **1a**,[39] **2a**, and **3a**

	1a	2a	3a
M−O	1.784(2)	1.765(1)	1.788(3)
O−E	1.546(4)	1.558(3)	1.807(4)
M−Cl(1)	2.283(1)	2.2829(7)	2.278(1)
M−Cl(2)	2.284(1)	2.2840(7)	2.279(1)
M−O−E	169.6(2)	177.0(1)	165.0(2)
Cl(1)−M−Cl(2)	104.88(4)	106.77(2)	105.30(4)
Cl(1)−M−O	104.49(8)	102.12(5)	105.01(1)
Cl(2)−M−O	101.30(8)	103.14(5)	103.3(1)

the top. The distribution of the ligands about the Nb atom is similar to that found in the tantalum oxo-borane compound **1a**[39] and analogues half-sandwich imido complexes,[3,58] with three short M−C bonds and two long M−C-cyclopentadienyl bonds and a slightly distorted cyclopentadienyl ring. The SiMe$_3$ group of the cyclopentadienyl ring points away from the $B(C_6F_5)_3$ ligand, as in related imido compounds.

The Nb−O bond length of 1.765(1) Å is in the high region of the range found for terminal Nb−O bonds (1.678−1.783 Å), similar to the one in the oxo-alane complex $[NbCl_4(O)\cdot AlCl_3]_2^{2-}$ (1.768 Å), longer than the values reported for monocyclopentadienyl oxo compounds $[Nb_2Cp^R{}_2(\mu\text{-}\eta^1{:}\eta^2\text{-edt})_2(\text{edt})(O)]$[36] (mean 1.735 Å) and $[NbCp^R(O)\{\text{edt}_2O\}]$[37] (1.734(3) and 1.735(3) Å) ($Cp^R = C_5H_4Me$, edt = SC_2H_4), and dicyclopentadienyl compounds $[NbCp^R{}_2X(O)]$ (1.718−1.752 Å), but clearly shorter than the bond length found in the oxo-borane adduct $[NbCp_2'Cl(O\cdot BF_3)]$[59] (1.830(4) Å). The O−B bond distance of 1.558(3) Å is within the range observed for neutral compounds of the type $M{-}O\cdot B(C_6F_5)_3$ (1.496−1.591 Å), although clearly longer than the O−B bond distance in $[NbCp_2'Cl(O\cdot BF_3)]$ (1.486(3) Å), this difference is attributed to softer Lewis acidity of $B(C_6F_5)_3$ and also to a stronger interaction of the oxygen atom with the metal center in compound **2a**. Finally, the M−O−B angle is close to linearity (177.0(1)°), indicative of π delocalization through the Nb−O−B system. With respect to the boron atom environment, it presents a distorted tetrahedral geometry with three closer O−B−C angles about 104° and three more open C−B−C angles about 113°, as consequence of the steric demand of the C_6F_5 groups.

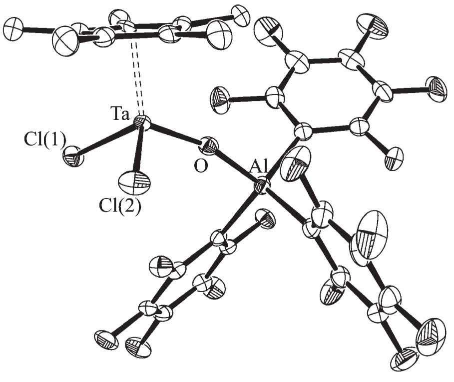


Figure 2. X-ray structure of compound **3a**.

The X-ray structure of compound **3a** is depicted in Figure 2, and selected bond distances and angles are collected in Table 1. The disposition of the substituents about the Ta atom is as expected, as in compounds **1a** and **2a**. The Ta−O bond length of 1.788(3) Å is very similar to that in compound **1a** (1.784(2) Å). This value is longer than those reported for mononuclear tantalum complexes containing terminal free Ta−O multiple bonds, ranging from 1.730 to 1.760 Å,[34,60] but shorter than the related oxo-borane adduct $[TaCp^*\{(\kappa^3\text{-}OCH_2CH_2)_2O\}\{O\cdot B(C_6F_5)_3\}]$ (1.829(2) Å),[56] which is coordinatively saturated, and also shorter than bridging Ta−O−Ta (1.82−2.10 Å). The O−Al bond distance of 1.807(4) Å is shorter than that found in the water adduct $H_2O\cdot Al(C_6F_5)_3$ (1.857(3) Å),[61] where interactions of both oxygen lone pairs with the aluminum were proposed from the oxygen sum of angles (360°), although this compound also presented intermolecular H−F interactions. However, the O−Al bond distance in **3a** is similar to the one in the adduct $[WBr(CH_2{}^tBu)_3(O)\cdot AlBr_3]$ (1.794(3) Å), containing a third period transition metal, but longer than those in the niobium and titanium adduct complexes $[NbCl_4(O)\cdot AlCl_3]_2^{2-}$ (1.772 Å) and $[TiLCl_2(O)\cdot AlCl_3]$ (1.758 Å), respectively. Conversely, all these values are longer than the O−Al bond distances in bridging M−O−Al containing complexes (1.710−1.727 Å). The Ta−O−Al angle value of 165.0(2) is slightly smaller than the corresponding angle in **1a** (169.6(2)°) but clearly smaller than the Nb−O−B angle in **2a**. This difference may be attributed to the steric demand of the Cp* ligand in **1a** and **3a** when compared with the Cp′ ligand in **2a**. With respect to the geometry around the aluminum atom, the pseudotetrahedral disposition of the substituents is slightly different to the disposition around the boron atom in **2a** but analogous to the environment about the boron atom in **1a**, observing for **1a** and **3a** one O−X−C and one C−X−C angle (X = B, Al) closer to 109° than in **2a**, whereas the remaining O−X−C and C−X−C angle

---

(58) Galakhov, M.; Gómez, M.; Jiménez, G.; Pellinghelli, M. A.; Royo, P.; Tiripicchio, A. *Organometallics* **1994**, *13*, 1564.

(59) Thiyagarajan, B.; Kerr, M. E.; Bollinger, J. C.; Young, V. G.; Bruno, J. W. *Organometallics* **1997**, *16*, 1331.

(60) Parkin, G.; Asselt, A. v.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82.

(61) Chakraborty, D.; Chen, E. Y. X. *Organometallics* **2003**, *22*, 207.

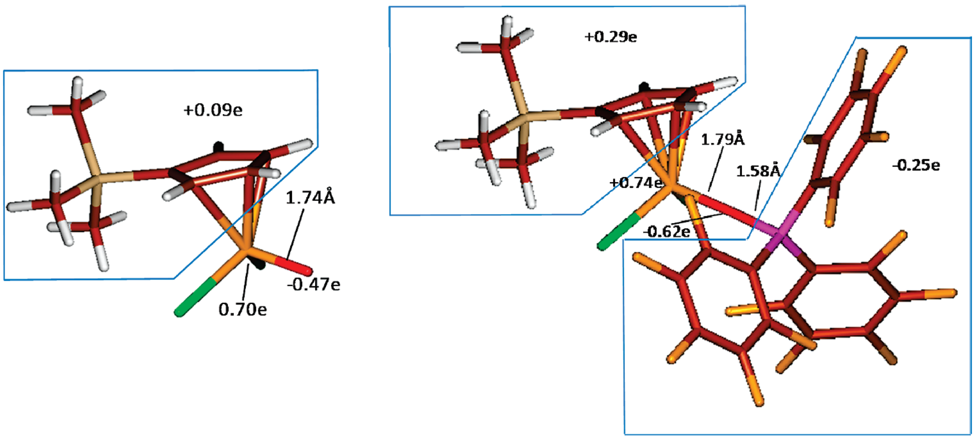


Figure 3. Optimized structures for compounds **A** and **2a**. Different bond distances and atom (O, Nb) and molecular fragment (η^5-$C_5H_4SiMe_3$ and $B(C_6F_5)_3$) charges are displayed.

values are similar to those in **2a**. This situation is also probably influenced by the different steric requirements of each type of monocyclopentadienyl ligands.

Theoretical Calculations

Optimizations of **2a**, **4a**, [NbCp$_2$′Cl(O)] (**A**), $B(C_6F_5)_3$ (**B**) and $Al(C_6F_5)_3$ (**C**) were carried out to determine the minimum energy structures of these species.[62] The data obtained for **2a** are in quantitative agreement with those obtained by X-ray diffraction (see Supporting Information for details).

The formation of **2a** as well as **4a** implies a stabilization of 19.3 and 38.1 kcal/mol, respectively, with respect to isolated compounds **A** and **B** or **C**, with formation of complex **4a** being more energetically favorable. In the following discussion, we analyze the electronic structure of these complexes.

The formation of complex **2a** (Figure 3) provokes a reorganization of the electronic structure compared with complex **A**. The Nb−O bond is enlarged from 1.74 Å to 1.79 Å and, moreover, the bond order is reduced from 2.1 to 1.5. Also, the charge separation between both atoms increases because of the slight increase of the positive charge in the Nb atom (from +0.70 in **A** to +0.73 in **2a**), and the increase of the negative charge on the oxygen atom (from −0.47 in **A** to −0.62 in **2a**). The charge separation is explained in terms of total charge of $B(C_6F_5)_3$, which is raised from 0 (**B**) to −0.25e in **2a**. Therefore the Nb−O covalent character is lowered and the ionic character increased with a net loss of bond order of about 0.6.

In contrast, the [$B(C_6F_5)_3$] moiety has an electronic withdrawing effect when complex **2a** is formed, provoking an electronic deficit in the Nb center which is compensated for by the other ligands; this effect is clearly seen in the shortening of the bond distances with both Cl and Cp′ ligands. The Nb−Cl bond distances are reduced from 2.40 Å in **A** to 2.37 Å in **2a**. Also, the average Nb−C distance in the Cp′ moiety is slightly shortened from 2.53 in **A** to 2.49 Å in **2a**. Not only are the bond distances shortened, but the bond orders are increased because of the decrease of Nb−O bond order in **2a**. In effect, the Nb−Cl bond order is 1.17 in **A** and 1.28 in **2a**, while the total Nb−Cp bond order is 1.51 in **A** and 1.70 in **2a**.

The formation of complex **4a** (Figure 4) occurs in a similar way to **2a**. The main difference is the electronic withdrawing effect of the [$Al(C_6F_5)_3$] fragment in **4a**, which is lower than that of the corresponding [$B(C_6F_5)_3$] moiety in compound **2a**. This is reflected in the charge of the [$Al(C_6F_5)_3$] moiety in **4a** (−0.12 e) compared with that of the [$B(C_6F_5)_3$] moiety in **2a** (−0.25 e). Because of this slight difference, the Al−O bond order is lower (0.25) than the B−O bond order (0.51). This effect has only a slight effect on the Nb−O bond, the distance and the bond order remain almost unaffected compared with complex **2a**, with only a small increase in the ionic contribution of the Nb−O character because of the increase of the negative charge in oxygen from −0.62e in **2a** to −0.76e in **4a**. Finally, the Nb−Cp′ and Nb−Cl bonds are shortened, increasing the bond order of the corresponding bonds, as was observed for **2a**.

Conclusions

Mononuclear monocyclopentadienyl oxo niobium and tantalum complexes [$MCp^RX_2\{O\cdot E(C_6F_5)_3\}$] can be obtained by hydrolysis of M−Cl and M−C bonds with the water adducts $H_2O\cdot E(C_6F_5)_3$ (E = B, Al). The higher oxophilicity of $Al(C_6F_5)_3$ with respect to $B(C_6F_5)_3$ produces the displacement of the coordinated borane ligand in complexes [$MCp^RX_2\{O\cdot B(C_6F_5)_3\}$] and the formation of the corresponding alane derivatives [$MCp^RX_2\{O\cdot Al(C_6F_5)_3\}$]. The presence of the Lewis acid coordinated to the oxygen atom is responsible of the complex's mononuclearity.

X-ray diffraction studies showed that the M−O bonds are longer than in complexes of the type [$MCp^R{}_2(O)$] and [$MCp^R(O)$], with terminal non-coordinated oxo ligands, for

---

[62] Frisch, J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.

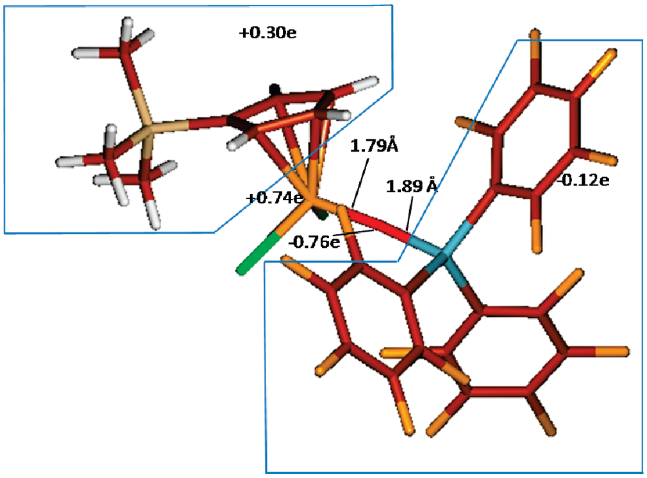


Figure 4. Optimized structures for **4a** complex. Bond distances and atom (O, Nb) and molecular fragment (η^5-$\mathrm{C_5H_4SiMe_3}$ and $\mathrm{Al(C_6F_5)_3}$) charges are displayed.

which bond orders of two and three respectively are proposed, to conform with the 18 electron rule. The oxygen atom environments indicate that the bond order in these oxo-adduct complexes could be higher than two, comparing the M−O−E angle in these compounds with that found in $[\mathrm{NbCp_2'Cl(O{\cdot}BF_3)}]$ (140.07°), where the free electron pair on the oxygen atom forces this situation. Also, the linear M−O−E indicates π delocalization through this system.

Experimental Section

All manipulations were carried out under an argon atmosphere, and solvents were distilled from appropriate drying agents. NMR spectra were recorded at 300.13 (^{1}H), 282.2 (^{19}F), 75.47 (^{13}C), and 128.4 (^{11}B) at room temperature on a Varian Unity 300 (^{1}H, ^{13}C, ^{19}F) or Bruker Advance 400 (^{11}B), and chemical shifts (δ) are given in parts per million (ppm). ^{1}H and ^{13}C resonances were measured relative to solvent peaks considering TMS = 0 ppm, and ^{19}F and ^{11}B were measured relative to external $\mathrm{CFCl_3}$ and $\mathrm{BF_3{\cdot}OEt_2}$, respectively. Elemental analyses were performed on a Perkin-Elmer 240C. The compounds $[\mathrm{TaCp^*Cl_4}]$,[63] $[\mathrm{NbCp'Cl_4}]$,[31] $[\mathrm{NbCp'Me_4}]$,[64] $[\mathrm{TaCp^*Me_4}]$,[63] $[\mathrm{TaCp^*(CHPh)(CH_2Ph)_2}]$,[23] $[\mathrm{TaCp^*R_2\{O{\cdot}B(C_6F_5)_3\}}]$ (R = Cl **1a**, $\mathrm{CH_2Ph}$ **1b**, Me **1c**),[39] $\mathrm{H_2O{\cdot}B(C_6F_5)_3}$,[65] (0.5 toluene)$\cdot\mathrm{Al(C_6F_5)_3}$[66] and $\mathrm{H_2O{\cdot}Al(C_6F_5)_3}$[61] were prepared by literature methods.

$[\mathrm{NbCp'Cl_2\{O{\cdot}B(C_6F_5)_3\}}]$ (2a). A solution of $[\mathrm{H_2O{\cdot}B(C_6F_5)_3}]$ (0.70 g, 1.33 mmol) in toluene (15 mL) was added slowly to a suspension of $[\mathrm{NbCp'Cl_4}]$ (0.50 g, 1.33 mmol) in toluene (10 mL) at ambient temperature. When the addition was complete, the solution was refluxed for 3 h when the solution was filtered and the volatiles removed under vacuum. The green solid was washed with hexane (2 × 20 mL) yielding **2a** (0.80 g, 73%). Data for **2a**: ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 0.38 (s, 9 H, $\mathrm{Si}Me_3$), 6.67 (m, 2 H, $\mathrm{C_5}H_4$), 7.14 (m, 2 H, $\mathrm{C_5}H_4$); ^{11}B NMR (δ, $\mathrm{CDCl_3}$): 4.68; ^{13}C NMR (δ, $\mathrm{CDCl_3}$): −1.0 ($\mathrm{Si}Me_3$), 117.5 (i-$C_5\mathrm{H_4}$), 119.5 ($C_5\mathrm{H_4}$), 128.4 ($C_5\mathrm{H_4}$), 137.1 ($C_6\mathrm{F_5}$), 141.4 ($C_6\mathrm{F_5}$), 147.6 ($C_6\mathrm{F_5}$); ^{19}F NMR (δ, $\mathrm{CDCl_3}$): −132.3 (o-$\mathrm{C_6F_5}$), −155.3 (p-$\mathrm{C_6F_5}$), −162.4 (m-$\mathrm{C_6F_5}$). $\mathrm{C_{26}H_{13}BCl_2F_{15}NbOSi}$ (829.07): calcd C 37.67, H 1.58; found C 37.83, H 1.69.

$[\mathrm{NbCp'(CH_2Ph)_2\{O{\cdot}B(C_6F_5)_3\}}]$ (2b). A solution of $[\mathrm{Mg(CH_2Ph)_2(THF)_2}]$ (0.26 g, 0.72 mmol) in toluene (15 mL) was slowly added to a solution of $[\mathrm{NbCp'Cl_2\{O{\cdot}B(C_6F_5)_3\}}]$ (**2a**) (0.60 g, 0.72 mmol) in toluene (15 mL) at −78 °C. When the addition was complete, the solution was allowed to reach ambient temperature and stirred for 2 h. The solution was then filtered and the volatiles removed under vacuum leaving a yellow oil that was washed with cold hexane (10 mL) to yield **2b** (0.10 g., yield 28%). Data for **2b**: ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 0.26 (s, 9 H, $\mathrm{Si}Me_3$), 1.37 (d, ^2J(H−H) = 10.0 Hz, 2 H, Nb−$C H_2$Ph), 3.00 (d, ^2J(H−H) = 10.0 Hz, 2 H, Nb−CH_2Ph), 5.58 (m, 2 H, $\mathrm{C_5}H_4$), 5.83 (m, 2 H, $\mathrm{C_5}H_4$), 6.54 (d, ^3J(H−H) = 7.5 Hz, 4 H, o-$\mathrm{C_6}H_5$), 7.24 (m, 4 H, m-$\mathrm{C_6}H_5$), 7.43 (t, ^3J(H−H) = 6.3 Hz, 2 H, p-$\mathrm{C_6}H_5$); ^{11}B NMR (δ, $\mathrm{CDCl_3}$): −0.35; ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 0.0 ($\mathrm{Si}Me_3$), 59.8 (Nb-CH_2Ph), 114.7 ($C_5\mathrm{H_4}$), 118.4 ($C_5\mathrm{H_4}$), 126.7 (i-$C_5\mathrm{H_4}$), 130.5 ($C_6\mathrm{H_5}$), 131.1 ($C_6\mathrm{H_5}$), 132.1 ($C_6\mathrm{H_5}$), 137.3 ($C_6\mathrm{F_5}$), 141.1 ($C_6\mathrm{F_5}$), 147.6 ($C_6\mathrm{F_5}$); ^{19}F NMR (δ, $\mathrm{CDCl_3}$): −131.3 (o-$\mathrm{C_6F_5}$), −157.0 (p-$\mathrm{C_6F_5}$), −163.1 (m-$\mathrm{C_6F_5}$). $\mathrm{C_{40}H_{27}BF_{15}NbOSi}$ (940.42): calcd C 51.10, H 2.89; found C 50.73, H 2.99.

$[\mathrm{NbCp'Me_2\{O{\cdot}B(C_6F_5)_3\}}]$ (2c). A Teflon-valved NMR tube was charged with a solution of $[\mathrm{NbCp'Me_4}]$ (0.012 g, 0.041 mmol) in $\mathrm{C_6D_6}$, and a solution of $\mathrm{H_2O{\cdot}B(C_6F_5)_3}$ (0.022 g, 0.041 mmol) in $\mathrm{C_6D_6}$ was added; a bubble of a gas was immediately observed. NMR spectroscopy showed formation of **2c** as the main reaction product. Data for **2c**: ^{1}H NMR (δ, $\mathrm{C_6D_6}$): −0.20 (s, 9 H, $\mathrm{Si}Me_3$), 0.90 (s, 6 H, $\mathrm{Nb}Me_2$), 5.28 (m, 2 H, $\mathrm{C_5}H_4$), 5.66 (m, 2 H, $\mathrm{C_5}H_4$); ^{11}B NMR (δ, $\mathrm{C_6D_6}$): −0.58; ^{13}C NMR (δ, $\mathrm{C_6D_6}$): −1.0 ($\mathrm{Si}Me_3$), 48.9 ($\mathrm{Nb}Me$), 117.5 (i-$C_5\mathrm{H_4}$), 119.5 ($C_5\mathrm{H_4}$), 128.4 ($C_5\mathrm{H_4}$), 137.1 ($C_6\mathrm{F_5}$), 141.4 ($C_6\mathrm{F_5}$), 147.6 ($C_6\mathrm{F_5}$); ^{19}F NMR (δ, $\mathrm{C_6D_6}$): −132.7 (o-$\mathrm{C_6F_5}$), −156.4 (p-$\mathrm{C_6F_5}$), −162.9 (m-$\mathrm{C_6F_5}$).

$[\mathrm{TaCp^*Cl_2\{O{\cdot}Al(C_6F_5)_3\}}]$ (3a). A solution of $[\mathrm{TaCp^*Cl_2\{O{\cdot}B(C_6F_5)_3\}}]$ (**1a**) (0.30 g, 0.33 mmol) and $\mathrm{Al(C_6F_5)_3}$ (0.20 g, 0.33 mmol) in toluene (5 mL) was stirred for 1 h when the volatiles were removed under vacuum and the yellow solid remaining was washed with hexane (2 × 5 mL) yielding **3a** (0.20 g, 68%).

Data for **3a**: ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 2.44 (s, 15 H, $\mathrm{C_5}Me_5$); ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 12.01 ($\mathrm{C_5}Me_5$), 129.0 ($C_5\mathrm{Me_5}$), 136.5 ($C_6\mathrm{F_5}$), 141.7 ($C_6\mathrm{F_5}$), 149.5 ($C_6\mathrm{F_5}$);^{19}F NMR (δ, $\mathrm{CDCl_3}$): −121.6 (o-$\mathrm{C_6F_5}$), −153.0 (p-$\mathrm{C_6F_5}$), −161.1 (m-$\mathrm{C_6F_5}$). $\mathrm{C_{28}H_{15}AlCl_2F_{15}OTa}$ (931.23): calcd C 36.11, H 1.62; found C 35.89, H 1.69.

$[\mathrm{TaCp^*(CH_2Ph)_2\{O{\cdot}Al(C_6F_5)_3\}}]$ (3b). Method (A): A solution of $[\mathrm{TaCp^*Bz_2\{O{\cdot}B(C_6F_5)_3\}}]$ (**1b**) (0.30 g, 0.29 mmol) and $\mathrm{Al(C_6F_5)_3}$ (0.17 g, 0.29 mmol) in toluene (5 mL) was stirred for 1 h when the solution was filtered, volatiles were removed under vacuum, and the yellow solid remaining was washed with hexane (2 × 5 mL) yielding **3b** (0.12 g, 40%).

Method (B): A solution of $[\mathrm{H_2O{\cdot}Al(C_6F_5)_3}]$ (0.140 g, 0.25 mmol) in toluene (5 mL) was added slowly to a solution of $[\mathrm{TaCp^*(CHPh)(CH_2Ph)_2}]$ (0.150 g, 0.25 mmol) in toluene (5 mL) at −78 °C. When the addition was complete, the solution was warmed to room temperature and stirred for an additional 1 h when the volatiles were partially removed under vacuum to about 5 mL. The solution was then filtered and volatiles removed under vacuum, and the yellow remaining solid was washed with hexane (2 × 5 mL) yielding **3b** (0.060 g, 23%).

Data for **3b**: ^{1}H NMR (δ, $\mathrm{C_6D_6}$): 1.32 (s, 15 H, $\mathrm{C_5}Me_5$), 1.73 (d, ^2J(H−H) = 12.9 Hz, 2 H, Ta−CH_2Ph), 2.70 (d, ^2J(H−H) = 12.9 Hz, 2 H, Ta−CH_2Ph), 6.72 (m, 4 H, o-$\mathrm{C_6}H_5$), 7.03 (m, 4 H, m-$\mathrm{C_6}H_5$), 7.12 (m, 2 H, p-$\mathrm{C_6}H_5$); ^{13}C NMR (δ, $\mathrm{C_6D_6}$): 9.3 ($\mathrm{C_5}Me_5$), 68.8 (Ta- CH_2Ph), 122.8 ($C_5\mathrm{Me_5}$), 123.4 ($\mathrm{C_6H_5}$), 127.0 ($\mathrm{C_6H_5}$), 128.2 ($\mathrm{C_6H_5}$), 135.1 (m, $C_6\mathrm{F_5}$), 139.0 (m, $C_6\mathrm{F_5}$), 149.7 (m, $C_6\mathrm{F_5}$); ^{19}F NMR (δ, $\mathrm{C_6D_6}$): −122.1 (o-$\mathrm{C_6F_5}$), −150.3 (p-$\mathrm{C_6F_5}$), −159.9 (m-$\mathrm{C_6F_5}$). $\mathrm{C_{42}H_{29}AlF_{15}OTa}$ (1042.58): calcd C 48.38, H 2.80; found C 48.19, H 2.69.

---

(63) Sanner, R. D.; Carter, S. T.; Bruton, W. J. *J. Organomet. Chem.* **1982**, *240*, 157.

(64) Sánchez-Nieves, J.; Tabernero, V.; Camejo, C.; Royo, P. *J. Organomet. Chem.* **2010**, *695*, 2469.

(65) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325.

(66) Feng, S. G.; Roof, G. R.; Chen, E. Y. X. *Organometallics* **2002**, *21*, 832.

[TaCp*Me$_2${O·Al(C_6F_5)$_3$}] (3c). Method (A): A solution of [TaCp*Me$_2${O·B(C_6F_5)$_3$}] (**1c**) (0.120 g, 0.14 mmol) and Al(C_6F_5)$_3$ (0.080 g, 0.14 mmol) in toluene (5 mL) was stirred for 1 h when the solution was filtered, volatiles were removed under vacuum and the yellow solid remaining was washed with hexane (2 × 5 mL) yielding **3c** (0.070 g, 52%).

Method (B): A solution of [H_2O·Al(C_6F_5)$_3$] (0.140 g, 0.25 mmol) in toluene (5 mL) was added slowly to a solution of [TaCp*Me$_4$] (0.096 g, 0.25 mmol) in toluene (5 mL) at −78 °C. When the addition was finished the solution was warmed to room temperature and stirred for an additional 1 h when the volatiles were partially removed under vacuum to about 5 mL. Then, the solution was filtered, volatiles removed under vacuum, and the yellow solid remaining was washed with hexane (2 × 5 mL) yielding **3c** (0.070 g, 30%).

Data for **3c**: ^{1}H NMR (δ, $CDCl_3$): 0.72 (s, 6 H, Ta-*Me*), 2.08 (s, 15 H, C_5*Me*$_5$); ^{13}C NMR{^{1}H} (δ, $CDCl_3$): 11.0 (C_5*Me*$_5$), 62.7 (Ta-*Me*), 123.0 (*C*$_5$Me$_5$), 136.9 (m, *C*$_6$F$_5$), 141.0 (m, *C*$_6$F$_5$), 149.9 (m, *C*$_6$F$_5$); ^{19}F NMR (δ, $CDCl_3$): −122.1 (*o*-C_6F_5), −153.7 (*p*-C_6F_5), −161.3 (*m*-C_6F_5). $C_{30}H_{21}AlF_{15}OTa$ (890.39): calcd C 40.47, H 2.38; found C 40.39, H 2.29.

[NbCp′Cl$_2${O·Al(C_6F_5)$_3$}] (4a). A solution of [NbCp′Cl$_2${O·B(C_6F_5)$_3$}] (**2a**) (0.100 g, 0.120 mmol) and 0.5(toluene)·Al(C_6F_5)$_3$ (0.070 g, 0.120 mmol) in toluene (5 mL) was stirred for 1 h. The solution was filtered, the volatiles were removed under vacuum, and the brown oil was washed with hexane (2 × 3 mL), obtaining **4a** as a yellowish solid (0.025 g, 25%).

Data for **4a**: ^{1}H NMR (δ, C_6D_6): −0.13 (s, 9 H, Si*Me*$_3$), 5.94 (m, 2 H, C_5*H*$_4$), 6.05 (m, 2 H, C_5*H*$_4$); ^{13}C NMR (δ, C_6D_6): −1.56 (Si*Me*$_3$), 121.9 (*C*$_5$H$_4$), 125.6 (*i*-*C*$_5$H$_4$), 129.3 (*C*$_5$H$_4$), 137.3 (*C*$_6$F$_5$), 142.2 (*C*$_6$F$_5$), 148.2 (*C*$_6$F$_5$); ^{19}F NMR (δ, C_6D_6): −121.8 (*o*-C_6F_5), −151.5 (*p*-C_6F_5), −160.3 (*m*-C_6F_5). $C_{26}H_{13}AlCl_2F_{15}NbOSi$ (845.24): calcd C 36.95, H 1.55; found C 36.55, H 1.39.

Table 2. Crystallographic Data of Compounds **2a** and **3a**

	2a	**3a**
formula	$C_{26}H_{13}BCl_2F_{15}NbOSi$	$C_{28}H_{15}AlCl_2F_{15}TaO$
M_w	829.07	931.23
T (K)	173	150
λ (Å)	0.71073	0.71073
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
crystal size, mm^3	0.10 × 0.13 × 0.18	0.49 × 0.40 × 0.38
a (Å)	10.9783(1)	10.7086(10)
b (Å)	11.7477(1)	11.2122(10)
c (Å)	12.4249(1)	14.0319(14)
α (deg)	88.2373(5)	90.945(9)
β (deg)	86.5981(5)	110.889(7)
γ (deg)	70.7876(3)	104.017(8)
V (Å^3)	1510.42(2)	1517.3(2)
D(Mg/m^3)	1.823	2.038
μ(mm^{-1})	0.730	3.944
F (000)	812	892
θ range for data collection (deg)	1.64−25.38	3.05−27.50
reflections collected	32416	12838
independent reflections	5534 [R(int) = 0.036]	6811 [R(int) = 0.072]
R_1, wR_2 [$I > 2\sigma(I)$]	0.0251, 0.0604	0.0322, 0.0724
R_1, wR_2 [all data]	0.0251, 0.0626	
largest diff. peak and hole (e Å^{-3})	0.24−0.47	1.57−1.92
GOF	1.052	1.066

X-ray Diffraction Studies. Crystal data and details of the structure determination are presented in Table 2. Suitable single crystals of **2a** for the X-ray diffraction study were grown from toluene/hexane. A clear orange crystal was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 5517 reflections. Data collection was performed at 173 K (OXFORD CRYOSYSTEMS) within a θ-range of 1.64° < θ < 25.38°. The data were collected with nine sets in rotation scan modus with $\Delta\varphi/\Delta\omega$ = 1.0°. A total number of 32416 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay, and absorption effects. After merging (R_{int} = 0.036) a sum of 5534 (all data) and 5075 [$I > 2\sigma(I)$], respectively, remained and all data were used. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the final difference Fourier maps and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements with 476 parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features.[67−72]

A suitable single crystal of **3a** for the X-ray diffraction study was selected (Table 2), covered with perfluorinated ether and mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer. Data collection was performed at 150(2) K. The structure was solved, using the WINGX package,[73] by direct methods (SHELXS-97) and refined by using full-matrix least-squares against F^2 (SHELXL-97).[69] All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were geometrically placed and left riding on their parent atoms.

Acknowledgment. We gratefully acknowledge Ministerio de Educación y Ciencia (projects MAT2007-60997 and CTQ2009-07120) and DGUI-Comunidad de Madrid (programme S-0505/PPQ-0328, COMAL-CM) (Spain) for financial support. L.M.F. acknowledges Spanish MEC for a “Ramón y Cajal” contract.

Supporting Information Available: Tables and figures giving computational details. Crystallographic data for compounds **2a** and **3a** are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-785359 (**2a**) and CCDC-794327 (**3a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

---

(67) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2010.

(68) *Data Collection Software for Nonius CCD devices*; Nonius BV: Delft, The Netherlands, 2001.

(69) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1998.

(70) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(71) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(72) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. *C*, Tables 6.1.1.4.

(73) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.