Acknowledgment. This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), and the National Science Foundation (RII-8922165). Drs. Arthur Diaz and Jean Guay of the IBM Almaden Research Center kindly provided the electrochemical data.

Supplementary Material Available: Experimental details for compounds listed in this paper (6 pages). Ordering information is given on any current masthead page.

Synthesis of an Air-Stable, Moisture-Stable, and Thermally Stable Tungsten(VI) Oxo Alkylidene Complex. Precursor to an Air- and Moisture-Stable ROMP Catalyst

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There has been considerable interest in the chemistry of high-valent tungsten alkylidyne[1,2] and alkylidene[1,3] complexes. Many such complexes have been demonstrated to be catalysts for acetylene[2,5] and olefin metathesis,[3,6] respectively. Tungsten imido alkylidenes have been shown to be extremely active catalysts for the ring opening metathesis polymerization (ROMP) of cyclic olefins[3a-c] and for the metathesis polymerization of acyclic dienes.[4] Until now, all well-characterized, molecular, high-valent tungsten alkylidynes and alkylidenes have proven to be air and moisture sensitive as well as thermally unstable at elevated temperatures.[7] We report here the synthesis and characterization of the first air-stable, moisture-stable, and thermally stable tungsten(VI) alkylidyne and alkylidene complexes and the conversion of the alkylidene complex to an air-stable ROMP catalyst.

Addition of 1 equiv of the tris-chelating monoanionic ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate[8] (Tp′) to a cold, stirring solution of W[≡CC(CH$_3$)$_3$]Cl$_3$(DME)[9] yielded the Tp′ alkylidyne dichloride **1**, eq 1. Compound **1** was recrystallized from toluene, producing small, fine purple needles.[10] The ^{1}H[11] and ^{13}C NMR spectra[12] were consistent with the proposed structure, with the alkylidyne α-carbon resonance appearing 335 ppm downfield of tetramethylsilane in the region characteristic for tungsten(VI) alkylidynes.[13] Remarkably, **1** has been found to be completely air and moisture stable both in the solid phase and in solution indefinitely.[14] No evidence of decomposition was observed when **1** was heated to 275 °C in an open capillary tube.[14b] Due to the extreme, unprecedented thermal stability of **1**, a very clean fragmentation pattern and intense molecular ion envelope (nominal parent ion mass 620.16) were detected by high-resolution mass spectroscopy.[15]

1

(1)

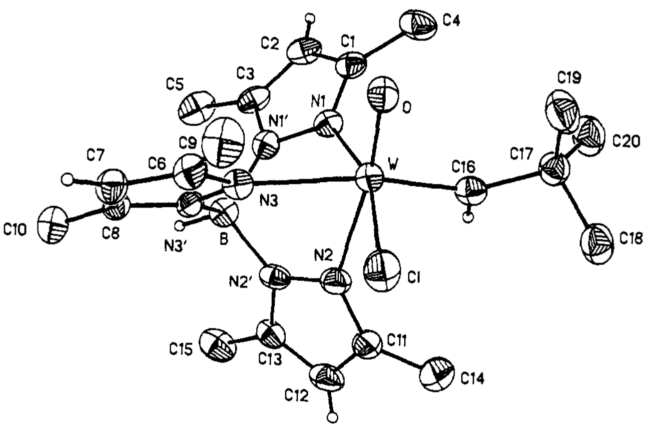

Figure 1. The structure of Tp′W═C(H)CMe$_3$(O)Cl (**2**), showing 50% thermal ellipsoids and the atom-labeling scheme. Selected bond distances (Å): W–Cl, 2.363 (2); W–O, 1.685 (8); W–C(16), 1.949 (8); W–N(1), 2.174 (5); W–N(2), 2.359 (9); W–N(3), 2.285 (6). Selected bond angles (deg): Cl–W–O, 96.2 (2); Cl–W–N(1), 161.2 (2); O–W–N(1), 96.8 (3); Cl–W–N(2), 85.1 (2); O–W–N(2), 172.7 (2); N(1)–W–N(2), 80.3 (3); Cl–W–N(3), 85.0 (2); O–W–N(3), 94.5 (3); N(1)–W–N(3), 80.5 (2); N(2)–W–N(3), 78.4 (3); Cl–W–C(16), 96.6 (2); O–W–C(16), 99.8 (4); N(1)–W–C(16), 94.5 (3); N(2)–W–C(16), 87.2 (4); N(3)–W–C(16), 165.3 (4).

Although **1** proved to be stable to protonation by triflic acid, tetrafluoroboric acid, and hydrochloric acid, it was quantitatively converted to an oxo alkylidene monochloride, **2**, in essentially quantitative yield by stirring with neutral, activity 1 alumina,[16] eq 2. After filtration from alumina, **2** was pure (by ^{1}H NMR) and was dried under reduced pressure, giving a bright yellow, air-stable powder. Compound **2** also has remarkable thermal stability since it can be heated to reflux in cyclooctene solution

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[1] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience, 1988 and references therein.

[2] Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

[3] (a) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5384. (b) Schrock, R. R.; De Pue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (c) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899. (d) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298. (e) Legzdins, P.; Phillips, E. C.; Sāchez, L. *Organometallics* **1989**, *8*, 940.

[4] (a) Wagener, K. B.; Boncella, J. M.; Nel, J. G.; Duttweiler, R. P.; Hillmyer, M. A. *Makromol. Chem.* **1990**, *191*, 365. (b) Wagener, K. B.; Nel, J. G.; Konzelman, J.; Boncella, J. M. *Macromolecules* **1990**, *23*, 5155. (c) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649.

[5] Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; Verlag Chemie: Weinheim, 1988.

[6] See ref 1, pp 304–307, and references therein.

[7] The most stable compounds of this type were six-coordinate tungsten oxo neopentylidene complexes that have been characterized as "relatively stable thermally and only slightly sensitive to water and oxygen". Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

[8] Prepared by published procedure. Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

[9] Prepared by published procedure. Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645.

[10] Calculated for C$_{20}$H$_{31}$BCl$_2$N$_6$W: C, 38.08; H, 5.05; N, 13.57. Found: C, 38.34; H, 4.94; N, 13.34. Yield, 49%. Complete experimental details can be found in the supplementary material.

[11] ^{1}H NMR data (300 MHz) for **1** (C$_6$D$_6$, 22 °C): δ 5.58, 5.38 (each s, 1:2 H, Tp′ ring H's); 2.76, 2.61, 2.09, 1.83 (each s, 3:6:3:6 H, Tp′CH$_3$'s); 1.56 (s, 9 H, C(CH$_3$)$_3$].

[12] ^{13}C NMR data (300 MHz) for **1** (C$_6$D$_6$, 22 °C): δ 335.33 [$^1J_{CW}$ = 212, *C*C(CH$_3$)$_3$]; 153.09, 152.40, 145.86, 141.62 (substituted Tp′ ring C's); 107.49 (unsubstituted Tp′ ring C's, overlapping); 47.69 [C*C*(CH$_3$)$_3$]; 33.30 [CC(*C*H$_3$)$_3$]; 19.30, 13.56, 12.16, 11.62 (Tp′ CH$_3$'s).

[13] Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342. See also ref 1, pp 135–136.

[14] (a) No change in the physical appearance or ^{1}H NMR spectrum of **1** could be detected after 3 months' storage of the solid in air or 3 weeks' stirring in THF or C$_6$D$_6$ solution. (b) There was no change in the ^{1}H NMR spectrum of the sample following heating of the sample to 275 °C.

[15] The complex mass envelopes generated for each peak are a consequence of the large number of atoms in **1** with relatively abundant isotopes. Modeling calculations accounting for five tungsten isotopes, two boron isotopes, and the usual carbon, hydrogen, and chlorine isotopes have successfully reproduced the parent ion envelope and the envelope around 551.082 which corresponds to loss of alkylidyne. Further analysis of the fragmentation pattern is currently underway.

[16] (a) The reaction of **1** with alumina was facilitated by the presence of undried solvents. Such reactivity has precedent for group VI Tp′ compounds, but has not been reported for high-valent alkylidenes. Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 504. (b) The transformation of **1** to **2** can also be carried out by using 1 equiv of H$_2$O and NEt$_3$ in THF solvent, but the transformation is very slow (only 34% conversion after 5 days at 25 °C). No reaction was observed between **1** and LiOH in THF at 25 °C after 2 days.

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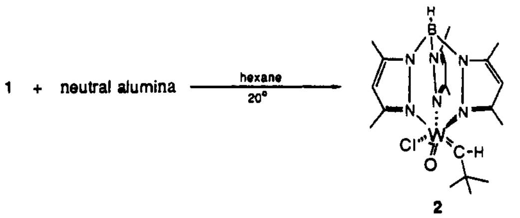


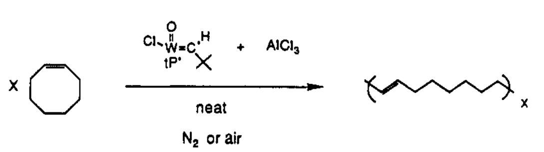
(2)

2

(145 °C) overnight in the air with no evidence of decomposition as observed by ^{1}H NMR spectroscopy. The ^{1}H NMR α-proton resonance of the alkylidene was detected at 10.41 ppm ($^2J_{HW}$ = 2.9 Hz), and the ^{13}C NMR alkylidene α-carbon resonance was found at 303.5 ppm ($^1J_{CW}$ = 158 Hz). Both resonances were in the expected region for such alkylidenes.[17] All other ^{1}H NMR[18] and ^{13}C NMR[19] resonances were in agreement with the structure shown. The composition of **2** was further verified by elemental analysis,[20] high-resolution mass spectroscopy[21] (nominal mass parent ion 602.193), and infrared spectroscopy ($\nu_{W=O}$ = 973 cm^{-1}),[22] as well as by a single-crystal X-ray diffraction study.[23]

Slow, room temperature evaporation of a diethyl ether solution of **2** yielded small, bright yellow crystals that were suitable for a single-crystal X-ray diffraction study. The structure consists of well-separated molecules with pseudooctahedral coordination geometry at tungsten as shown in the ORTEP drawing in Figure 1. The Tp′ ligand forces the oxo, alkylidene, and chloride ligands to be mutually cis[24] with the O–W–C(16) angle 99.8 (4)°.[25] The W=O bond length of 1.685 (8) Å was of interest in confirming the strong π-donating character of the oxo ligand for this complex.[1,26] Both previously crystallographically characterized six-coordinate tungsten oxo alkylidenes $W(O)[=C(H)C(CH_3)_3]Cl_2[P(CH_2CH_3)_3]_2$ (**3**)[27] and $W(O)[C(CH_2)_4]Cl_2[P(CH_3)Ph_2]_2$ (**4**)[3d] have identical formal electron counts[28] at tungsten and have similar W=O bond lengths of 1.697 (**3**) and 1.708 Å (**4**). Also of interest was the W=C(16) bond length of 1.949 (8) Å and the W–C(16)–C(17) angle of 136.0 (6)°, both of which are characteristic of undistorted tungsten alkylidene linkages[29] and are comparable with values for known species **3** (1.986 Å, 142.4°) and **4** (1.980 Å, 132.2°). The alkylidene was oriented with the neopentyl group slightly bent toward the oxo, precluding oxo–alkylidene interaction.[30] The N–W distances vary from 2.174 (5) Å to 2.359 (9) Å and are consistent with a decreasing trans influence of the ligands oxo > alkylidene > chloride.[31]

Since oxo alkylidenes have been implicated as catalysts in the olefin metathesis reaction,[32] the interaction of **2** with cyclooctene and norbornene was investigated. When 1 equiv of $AlCl_3$ was added to **2** in cyclooctene at 25 °C, rapid ring opening polymerization of cyclooctene occurred, giving high molecular weight, solid polyoctenomer within 15 min, eq 3. This polymerization reaction may be performed either in an inert atmosphere or in the air, producing polymer with essentially the same molecular weight and polydispersity.[33] The polymerization catalyst remained active after the initial reaction mixture solidified since subsequent additions of monomer to the solid polymer–catalyst mixture resulted in dissolution of the polymer followed by resolidification as the polymerization reaction continued.



(3)

Norbornene could also be polymerized by a mixture of **2** and 1 equiv of $AlCl_3$ in toluene solution either in the air or under an inert atmosphere, producing polymers with similar though not identical properties.[34] It is significant that this polymerization can be carried out in the air since it demonstrates that the catalyst that is generated by mixing **2** and $AlCl_3$ is active in solution in the air for at least 15 min (the time of the reaction). It is possible that the active species in this polymerization is simply more reactive toward monomer than O_2 or H_2O. We do not expect this catalyst to have the long-term air stability observed for **1** or **2**, especially since $AlCl_3$ degrades rapidly in moist air. Studies are underway to find a more suitable cocatalyst.

In an attempt to observe the catalytically active species in these polymerizations, the reaction of **2**, $AlCl_3$, and 2 equiv of cyclooctene was carried out in an NMR tube in CD_2Cl_2. At −60 °C,

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(17) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. See also ref 1, pp 135–136.

(18) ^{1}H NMR data (300 MHz) for **2** (C_6D_6): δ 10.41 [s, 1 H, $^2J_{HW}$ = 2.9 Hz, $C(H)C(CH_3)_3$]; 5.47, 5.46, 5.41 (each s, 1:1:1 H, Tp′ ring H's); 2.93, 2.68, 2.38, 2.04, 1.99, 1.97 (each s, 3:3:3:3:3:3 H, Tp′ CH_3's); 1.63 [s, 9 H, $CC(CH_3)_3$].

(19) ^{13}C NMR data (300 MHz) for **2** (C_6H_6): δ 303.53 [$^1J_{CW}$ = 158 Hz, $^1J_{CH}$ = 123 Hz, $C(H)C(CH_3)_3$]; 153.42, 151.78, 152.80, 145.86, 143.48 (Tp′ substituted ring C's, only five peaks are observed because the peak at 143.48 ppm consists of two overlapping resonances); 107.25, 107.49, 107.86 (Tp′ unsubstituted ring C's); 43.77 [$C(H)C(CH_3)_3$]; 33.33 [$C(H)C(CH_3)_3$]; 17.79, 15.86, 14.79, 12.38, 11.91, 11.61 (Tp′ CH_3's).

(20) Calculated for $C_{20}H_{32}BClN_6OW$: C, 39.86; H, 5.36; N, 13.95. Found: C, 39.79; H, 5.36; N, 13.89. Yield: 98%. Complete experimental details can be found in the supplementary material.

(21) The mass spectrum of **2** was not as clean as the spectrum for **1**, and the parent ion envelope was much less intense. These differences in mass spectroscopic behavior may be attributed to the decreased thermal stability of **2** resulting in decomposition prior to vaporization.

(22) W=O stretching frequencies in this region are characteristic of a terminal "W≡O" stretch. Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369.

(23) $C_{20}H_{32}BClN_6OW$: triclinic, $P\bar{1}$, a = 10.319 (2) Å, b = 10.773 (3) Å, c = 12.338 (3) Å, α = 68.61 (2)°, β = 82.05 (2)°, γ = 71.28 (2)°, V = 1209.2 (5) Å^3, Z = 2, D_{calcd} = 1.68 cm^{-3}, Mo Kα (λ = 0.71069 Å, T = 298 K. The structure was solved by the heavy-atom method (Patterson on SHELXTL), which revealed the position of the W atom. The rest of the atoms in the asymmetric unit were obtained from subsequent difference Fourier maps. Blocked-cascade least-squares refinement converged to R = 0.0528 and R_2 = 0.0501 using 3757 reflections with $I > 3\sigma(I)$. Sheldrick, G. M.; *SHELXTL*; Nicolet XRD Corporation, Madison, WI, 1986.

(24) Geometric constraints of the Tp′ ligand as well as electronic constraints for d^0 tungsten with multiple π-bonding ligands require that W=O and W=C are mutually cis. Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203. Tatsumi, K.; Hoffman, R. *Inorg. Chem.* **1980**, *19*, 2656. See also ref 2.

(25) This O–W–C angle is typical for such complexes. All other angles follow from the bond lengths and geometric constraints of the ligands. See ref 1, pp 157–185 and ref 3d, 27.

(26) In transition-metal–oxo compounds, if the formal electron count of the metal is less than 18 electrons, the oxo–metal bond length is appropriately short, and a π-symmetry metal orbital in the appropriate orientation is available, a triply bonded "W≡O" is the preferred valence-bond description of the metal–oxo interaction.

(27) (a) Churchill, M. R.; Rheingold, A. L. *Inorg. Chem.* **1982**, *21*, 1357. (b) Churchill, M. R.; Rheingold, A. L.; Youngs, W. J.; Schrock, R. R.; Wengrovius, J. H. *J. Organomet. Chem.* **1981**, *204*, C17. (c) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

(28) The electron count at tungsten(VI) in **2**, **3**, and **4** is 18 electrons if the oxo is counted as a six-electron donor (2−) and the alkylidene is counted as a four-electron donor (2−).

(29) Undistorted linkage refers to an sp^2 geometry at the alkylidene α carbon with no electronic donation from the α-H or the C–H bond to the metal center. Distorted alkylidenes have shortened bond lengths and large (<151°) W=C–C angles. Such distorted alkylidenes are not active metathesis catalysts. See ref 1, p 155, and footnotes 13 and 17.

(30) This orientation of the alkylidene and oxo ligands is like that reported by Schrock (see ref 27c) but unlike that reported by Mayer (see ref 3d).

(31) see ref 1, pp 156–157.

(32) (a) Rappi, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448. (b) Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G. A.; Fellmann, J. D. *J. Mol. Catal.* **1980**, *8*, 73. (c) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515.

(33) Cyclooctene polymerization reactions were performed neat at room temperature with a 500:1 monomer:catalyst ratio. Polymer samples were dissolved in hot toluene, precipitated with methanol, and then dried under reduced pressure. Molecular weights were determined by GPC and corrected[4a] to polystyrene standards. Polymer prepared in N_2 atmosphere: $\bar{M}_n$ = 58900, $\bar{M}_w/\bar{M}_n$ = 1.3. Polymer prepared in air on benchtop: $\bar{M}_n$ = 49 350, $\bar{M}_w/\bar{M}_n$ = 1.3. No evidence for cross-linking or vinyl addition chemistry was found by APT ^{13}C NMR of these polymers.

(34) Polynorbornylene was prepared by weighing equimolar quantities of **2** and $AlCl_3$ into a test tube in an N_2-filled drybox followed by dissolution in toluene in air or under an inert atmosphere. Addition of 500 equiv of norbornene resulted in the rapid formation of polynorbornene, which was isolated in a manner similar to that used for the polyoctenomer.[33] Polymer prepared in N_2 atmosphere: $\bar{M}_n$ = 75 800, $\bar{M}_w/\bar{M}_n$ = 1.8. Polymer prepared in air: $\bar{M}_n$ 67 200, $\bar{M}_w/\bar{M}_n$ = 2.2. Molecular weights were determined by GPC and referenced to polystyrene standards and are uncorrected.

signals assignable to three new alkylidene species (9.56, 9.90, 10.17 ppm) were observed in the ^1H NMR spectrum as were signals due to polyoctenomer (5.35 ppm) and possibly a metallacyclobutane species (6.4, 0.45 ppm). The complexity of the mixture prevents any assignment of the active species at this time. Clearly, more work will be necessary to understand how **2** is converted into a catalytically active species.

Compound **2** is not a ROMP catalyst in the absence of Lewis acid, presumably due to its electronic and coordinative saturation. The addition of Lewis acid cocatalysts to similar systems has succeeded in generating olefin metathesis catalysts previously,[32c,35] but these catalysts do not appear to operate in air. Recently, several ruthenium complexes have been shown to be catalyst precursors for the ROMP of substituted norbornenes in aqueous solution,[36] but the nature of the active species in these reactions remains elusive. The nature of the interaction between $AlCl_3$ and **2** is currently under investigation, but it is suspected to involve attack by $AlCl_3$ at the chloride ligand,[35b,37] generating a five-coordinate cationic alkylidene as the active species.

Acknowledgement is made to the National Science Foundation (Grant No. DMR-8912026) for support of this research.

Supplementary Material Available: Experimental details for the synthesis of **1** and **2** as well as for the polymerization reactions, tables of thermal parameters, positional parameters, and bond lengths and angles for **2**, and details of the X-ray crystal structure determination of **2** (13 pages); table of observed and calculated structures for **2** (27 pages). Ordering information is given on any current masthead page.

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(36) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

(37) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6546.

Thermochemical Comparison of Organolithium Bases

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Organolithium reagents play an important role in synthetic organic chemistry.[1] Although several research groups have determined the strengths of many types of weak acids or their strong conjugate bases in solution[2-4] and in the gas phase,[5] we are unaware of any report that compares the bases used most often for synthetic operations.

Table I. Enthalpies of Deprotonation, $-\Delta H_{(dep)}$ (kcal/mol), of Isopropyl Alcohol by Organolithium Bases, with and without 1 equiv of Lithium *tert*-Butoxide, in 90:10 Hexane–Ether at 25 °C

organolithium base	$-\Delta H_{(dep)}{}^a$	+1 equiv of *t*-BuOLi $-\Delta H_{(dep)}{}^a$
tert-butyllithium	56.2 ± 1.8	56.0 ± 0.5
sec-butyllithium	52.8 ± 1.0	51.9 ± 0.7
n-butyllithium	50.0 ± 0.7	49.3 ± 0.4
phenyllithium	42.3 ± 0.3	42.8 ± 0.3
methyllithium	41.6 ± 0.7[b]	41.6 ± 2.2[b]
((trimethylsilyl)methyl)lithium	40.0 ± 0.6	41.5 ± 0.3
lithium dicyclohexylamide	31.8 ± 0.2	32.0 ± 0.3
lithium 2,2,6,6-tetramethylpiperidide	30.4 ± 1.6	30.5 ± 1.6
lithium isopropylcyclohexylamide	29.6 ± 0.5	29.8 ± 0.4
lithium diisopropylamide	28.6 ± 1.0	28.7 ± 0.3
lithium diethylamide	23.4 ± 0.3	23.7 ± 0.4
lithium cyclohexylamide	insoluble	21.8 ± 0.1
lithium isopropylamide	insoluble	21.3 ± 0.2
lithium *tert*-butylamide	21.2 ± 0.3	20.5 ± 0.2
lithium *n*-octylamide	18.9 ± 0.1	19.4 ± 0.5
lithium bis(trimethylsilyl)amide	12.1 ± 0.6	12.3 ± 0.5
lithium pinacolonate	3.4 ± 1.2[c]	
lithium *tert*-butoxide	2.1 ± 0.6[d]	

[a] Values are calculated on the basis of the known amount of isopropyl alcohol added to an excess of base. Errors are reported at the 95% confidence level. [b] Solvent was 100% diethyl ether to maintain solubility. [c] Value is calculated on the basis of the measured difference of $\Delta H_{(dep)}$'s for LiHMDS + *i*-PrOH (−12.1) and LiHMDS + pinacolone (−8.7). [d] Value is calculated on the basis of the measured difference of $\Delta H_{(dep)}$'s for LiHMDS + *i*-PrOH (−12.1) and LiHMDS + *t*-BuOH (−10.0).

Table II. Enthalpies of Deprotonation, $-\Delta H_{(dep)}$ (kcal/mol), of Isopropyl Alcohol by Organometallic Bases Reacting in 85:15 THF–Toluene at 25 °C

organometallic base[a]	$-\Delta H_{(dep)}$
LiHMDS	15.2 ± 0.5
1:1 mixture of LiHMDS and *t*-BuOLi	15.8 ± 0.4
1:1 mixture of LiHMDS and *t*-BuOK	7.3 ± 0.3
1:1 mixture of KHMDS and *t*-BuOLi	7.3 ± 0.3
KHMDS	2.9 ± 0.3
1:1 mixture of KHMDS and *t*-BuOK	3.3 ± 0.2

[a] LiHMDS = lithium bis(trimethylsilyl)amide. KHMDS = potassium bis(trimethylsilyl)amide. *t*-BuOLi = lithium *tert*-butoxide. *t*-BuOK = potassium *tert*-butoxide.

This report presents enthalpies of deprotonation, $\Delta H_{(dep)}$, of isopropyl alcohol (*i*-PrOH) by eighteen organolithium bases in a 90:10 by volume mixture of hexane–diethyl ether at 25 °C. The solvent system was chosen because of its inertness to strongly basic reagents[6] while still possessing ether oxygens for lithium solvation.[7] This thermochemical method provides the enthalpic driving force for the organolithium bases to deprotonate a common acid and incorporates the differential contributions from solvation, ion-

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(6) THF was attempted but decomposed visibly in the presence of *tert*-butyllithium at 25 °C.

(7) (a) The concentration of organolithium base was approximately 0.05 M, which gives about 15 ether oxygens per lithium. (b) The employment of vapor pressure osmometry to determine aggregation numbers as before[9] was rendered essentially useless due to a combination of a mixed solvent system, high instability of many of the organolithiums, and unknown exact concentrations of commercially available solutions used both as an organolithium base and as a reagent to generate all lithium amides. Information regarding aggregation of these species is available. See ref 8.

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