DOI: 10.1002/anie.201204634

Actinide Complexes

Giant Spin-Orbit Effects on NMR Shifts in Diamagnetic Actinide Complexes: Guiding the Search of Uranium(VI) Hydride Complexes in the Correct Spectral Range**

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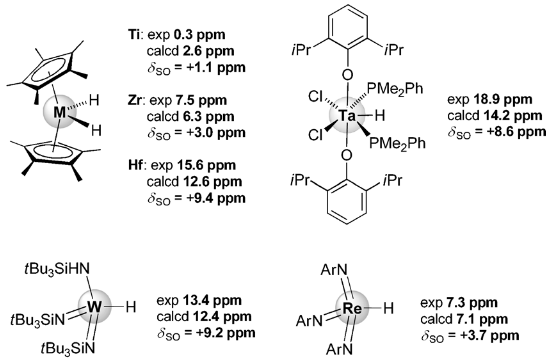
Transition- and inner-transition metal hydride complexes are crucial reagents in a great variety of stoichiometric and catalytic transformations, including C−H bond activation.[1] As hydrogen atoms near heavy-metal centers are difficult to locate by X-ray diffraction, often their prime characterization is by ^1H NMR spectroscopy, sometimes augmented by IR spectroscopy. A significant part of the utility of ^1H NMR spectroscopy in this field arises from the fact that the chemical shifts of metal-bound protons are characteristic and occupy extreme positions in the proton shift range, even for diamagnetic compounds. For instance, complexes with d^6 or d^8 metal configuration exhibit shifts below $\delta = 0$ ppm, in record cases down to below $\delta = -50$ ppm for iridium hydride complexes.[2,3] While this phenomenon was explained as early as the 1960s by Buckingham and Stephens as being due to off-center paramagnetic ring currents[4] (see Ref. [5] for the earliest DFT results), we have recently shown that the largest low-frequency shifts of this kind are, to an appreciable part, caused by relativistic spin-orbit (SO) effects.[2] These heavy-atom induced SO effects are mediated through the Fermi contact mechanism to which proton shifts are particularly susceptible, owing to the large hydrogen 1s-orbital contributions to bonding (the transfer of SO-induced spin polarization to the NMR nucleus is decisive in this situation).[6] In contrast, d^{10} metal hydride complexes of mercury or gold exhibit large high-frequency shifts up to $\delta = +17$ ppm, again predominantly because of SO coupling.[2] Some d^0 metal hydrides have been studied by ^1H NMR spectroscopy as well. Similarly to d^{10} systems they often also exhibit shifts in the very high-frequency range (Scheme 1).[7] As shown in Scheme 1, SO effects again play a very important role in these NMR shift values, increasingly so moving down a group in the periodic table (cf. ^1H NMR shifts within the $[H_2MCp^*_2]$ series, M = Ti, Zr, Hf, $Cp^* = \eta\text{-}C_5Me_5$). Probably the largest known shift value of such a d^0 complex is the $\delta = +18.9$ ppm of the tantalum complex in Scheme 1.



Scheme 1. Experimental and calculated ^1H NMR shifts (in ppm vs. TMS) in pertinent d^0 transition-metal hydride complexes. SO contributions, δ_{SO}, to the NMR shifts are also indicated. 2c-ZORA-SO/PBE0/TZ2P results (see Methods Section).

We note in passing, that deshielding SO shifts are generally related to high-lying occupied orbitals with σ-symmetry relative to the bond between the SO center and NMR atom (e.g. for the abovementioned d^{10} and d^0 metal hydride complexes), whereas π-type occupied orbitals provide shielding SO contributions (e.g. in the d^6 and d^8 hydride complexes or for heavy halogen substituents).[8]

In view of these observations, we wondered about the magnitude of hydride shifts when the d^0 transition-metal center is replaced by an actinide ion to form the corresponding f^0 species, as SO effects should be particularly large in this case. A literature survey provided only a few diamagnetic hydride complexes: the thorium systems **1**–**3** shown in Scheme 2[9] and a few borohydride complexes of Th^{IV} and UO_2^{2+}.[10] The hydride shifts in **1**–**3** are in the high-frequency range, comparable to the abovementioned Ta complex (only some protons involved in low-barrier hydrogen bonds feature similar shifts; for example, in hydrogen maleate, $\delta = +20.3$ ppm),[11] thus defining the upper limits of currently known ^1H shifts of diamagnetic compounds. The experimental value of **3** ($\delta = +0.9$ ppm)[9d] was most likely misassigned, as the analogous Zr complex exhibits a hydride shift of $\delta = +9.6$ ppm.[12] This situation indicates the usefulness of relativistic quantum-chemical calculations when assigning signals in NMR spectra for systems containing such heavy atoms. Our

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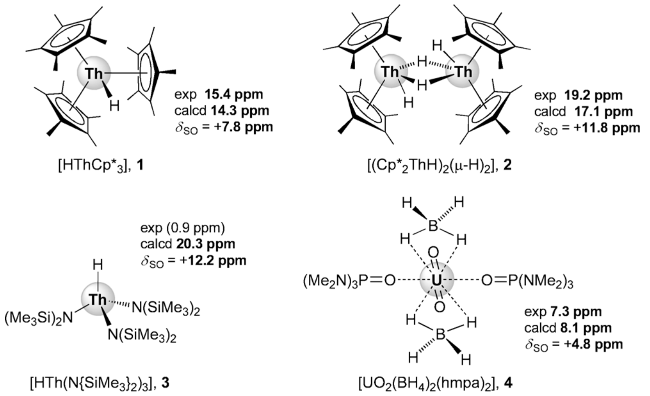
[**] This work has been supported by the Berlin DFG cluster of excellence on "Unifying Concepts in Catalysis" (UniCat) and Slovak grant agency APVV (0483-10). P.H. gratefully acknowledges the Alexander von Humboldt Foundation for a research fellowship. Katarína Starinská is thanked for help in the preparation of the Inside Cover picture.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204634.



Scheme 2. Experimental and calculated ^{1}H NMR shifts (in ppm vs. TMS) in known f^0 actinide hydride complexes. SO contributions, δ_{SO}, to the NMR shifts are also indicated. 2c-ZORA-SO/PBE0/TZ2P results (see Methods Section).

computations show again, that SO effects are very important (Scheme 2). Similarly to the d^0 case, paramagnetic shift contributions already make the ^{1}H shifts positive, but SO effects enhance them significantly, by about 12 ppm in **2** and **3**.

Owing to the stronger involvement of f orbitals in bonding, we expected U^{VI} hydride complexes to exhibit particularly large SO effects, but except for a matrix-isolation IR report of H_2UO_2,[13] such complexes are presently unknown. The only diamagnetic uranium complex with a direct U···H interaction studied so far by NMR spectroscopy is the uranyl borohydride complex **4** (Scheme 2).[10c] It does exhibit an unusually large ^{1}H NMR shift ($\delta = +7.3$ ppm) for a BH_4 ligand (typical shifts in transition-metal BH_4 complexes range from $\delta = -0.1$ to $+2.0$ ppm, up to $\delta = +4.2$ ppm in the extreme case of a Th^{IV} complex).[10a] Our calculations show that this high-frequency signal is again largely due to appreciable SO effects (+4.8 ppm).[14] Given that the bond order of the U···H interaction in **4** is relatively low (d(U···H) = 2.28 Å compared to ca. 2.0 Å in the uranium(VI) hydrides presented in Table 1), we expected much more dramatic SO effects for true U^{VI} hydride complexes.

Computations on a series of complexes $[HAnL_5]^q$ (An = Th, Pa, U; L = F, CH_3, OCH_3), and of uranyl dihydride complexes (Table 1; data for analogous transition-metal d^0 complexes are given for comparison) confirm this assumption: while the value for the Th^{IV} model is in the range of d^0 systems, in line with the relatively weak involvement of the 5f orbitals in bonding (cf. Table 2), the Pa^V model complex, and even more so the U^{VI} complexes in Table 1, are predicted to exhibit giant high-frequency shifts arising from SO effects. These values are completely outside the known ^{1}H shift range of diamagnetic compounds. In the case of H_2UO_2, SO effects strongly depend on the geometry, as a result of the different f-orbital participation in U−H bonding (two minima of C_{2v} and D_{2h} symmetry, respectively, are found; the C_{2v} form is energetically preferred by ca. 22 kJ mol^{-1} and exhibits much less 5f-orbital participation in bonding, see Table 2). Closer analyses using a perturbation treatment of SO coupling (see Table S1 in Supporting Information) indicate that the presence of low-lying unoccupied orbitals with predominant metal 5f character and favorable symmetry properties relative to the An−H bond (Figure S2, S3) is responsible for these unusually large positive SO shifts.

Table 1: Calculated ^{1}H NMR shifts (in ppm vs. TMS) in f^0 actinide hydride model complexes and their d^0 transition-metal analogues.[a,b]

Complex	Symm.	d(M−H) [Å]	δ_{SR}	δ_{SO}	δ_{total}
$[HHfF_5]^{2-}$	C_{4v}	2.028	4.7	4.8	9.6
$[HTaF_5]^{-}$	C_{4v}	1.834	4.6	10.3	14.9
HWF_5	C_s	1.683	7.2	23.5	30.7
$HWMe_5$	C_s[c]	1.673	8.6	11.0	19.6
$HW(OMe)_5$	C_s[c]	1.730	4.2	11.2	15.4
H_2WO_2	C_{2v}	1.729	4.6	17.7	22.3
$[HThF_5]^{2-}$	C_{4v}	2.364	6.0	10.5	16.5
$[HPaF_5]^{-}$	C_{4v}	2.076	6.3	57.3	63.6
HUF_5	C_{4v}	1.911	0.7	254.1	254.8
$HUMe_5$	C_{4v}[c]	1.997	14.4	155.8	170.2
$HU(OMe)_5$	C_{4v}[c]	1.957	3.8	176.1	179.9
H_2UO_2	C_{2v}	1.965	13.1	50.6	63.7
H_2UO_2	D_{2h}	2.000	5.0	215.9	220.9
$[HHfF_5]^{2-}$	C_{4v}	2.028	4.7	4.8	9.6

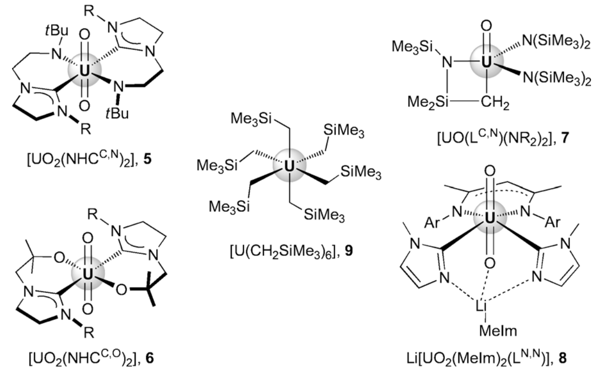
[a] 2c-ZORA-SO results at the PBE0/TZ2P level (see Methods Section). [b] δ_{SR} stands for NMR shifts calculated using scalar relativistic effects only, and δ_{SO} for the SO contribution. [c] In this case the symmetry of the HML_5 core without hydrogen atoms of the methyl group is denoted (the symmetry of the full system is lower).

Table 2: Hydride NPA charges and NLMO hybridization analysis of the M−H bonds in f^0 actinide hydrides and their d^0 transition metal analogues.[a]

Complex	Symm.	q(H)	%M	s	p	d	f
$[HHfF_5]^{2-}$	C_{4v}	−0.674	17.2	34.6	0.8	64.3	0.4
$[HTaF_5]^{-}$	C_{4v}	−0.469	28.6	27.3	0.8	71.6	0.2
HWF_5	C_s	−0.100	47.2	15.5	0.5	83.9	0.2
$HWMe_5$	C_s[b]	+0.030	49.9	7.6	0.1	92.2	0.1
$HW(OMe)_5$	C_s[b]	−0.196	41.4	15.9	0.2	83.8	0.1
H_2WO_2	C_{2v}	−0.269	36.4	27.6	1.2	71.0	0.2
$[HThF_5]^{2-}$	C_{4v}	−0.717	14.3	31.8	1.5	44.0	22.7
$[HPaF_5]^{-}$	C_{4v}	−0.439	28.0	18.7	0.3	34.7	46.3
HUF_5	C_{4v}	−0.064	47.2	10.6	0.2	22.4	66.8
$HUMe_5$	C_{4v}[b]	−0.223	39.3	13.5	0.8	31.9	53.8
$HU(OMe)_5$	C_{4v}[b]	−0.099	44.2	10.6	0.2	26.1	63.1
H_2UO_2	C_{2v}	−0.305	34.9	23.5	0.2	52.6	23.7
H_2UO_2	D_{2h}	−0.344	32.8	14.9	0.5	31.9	52.7

[a] Results obtained at the PBE0/def-TZVPP level (see Methods Section). [b] In this case the symmetry of the HML_5 core without hydrogen atoms of the methyl group is denoted (the symmetry of the full system is lower).

In the absence of experimental data, we need to find out how reliable the predicted ^{1}H shifts in Table 1 are. Previously a large dependence on the exact-exchange admixture in the functional for the ^{19}F shifts in U^{VI} fluoro-chloro complexes has been found.[15] In contrast to d^0 analogues, this dependence is even more pronounced for both hydride ^{1}H shifts and methyl ^{13}C shifts in U^{VI} systems, as demonstrated for the $HUMe_5$ model complex (cf. Tables S2 and S3 in Supporting Information). As ^{13}C shifts of metal-bound ligand atoms are also affected appreciably by SO effects and depend as much



Scheme 3. U^{VI} Complexes with direct U–C σ-bonds.

on the exact-exchange admixture as the hydride ^{1}H shifts, we thus have a way to select the most reliable functional by evaluating the ^{13}C shifts for a number of recently synthesized U^{VI} complexes with direct U–C σ-bonds (Scheme 3).

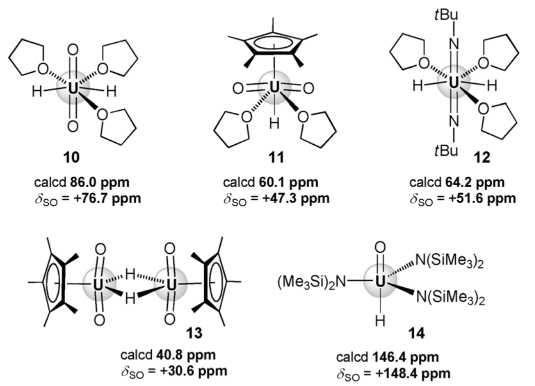
While the carbene ^{13}C shifts in **5** and **6** are affected only moderately by the exact-exchange admixture, a strong dependence is found in complexes **7**–**9** (cf. Table 3). In all but one case, a 40% exact-exchange admixture provides consistently excellent agreement with experimental shifts. While a detailed understanding of this performance for actinide systems is beyond the scope of the present study and will be addressed elsewhere, it appears that 40% exact exchange provides the optimum compromise between reduced self-interaction errors (favored at high exact exchange) and simulation of left–right correlation (favored at low exact exchange). The only outlier is the hexaalkyl U^{VI} complex **9**, where a shift of $\delta = 34$ ppm had been assigned to the uranium-bonded carbon atoms.[16] This situation is in striking disagreement with the large computed shifts, which are certainly more in line with, for example, the SO-induced high-frequency shift for **8**. Closer inspection of the experimental data for **9** shows that a) this compound had been generated in situ and was measured as a mixture, and b) the ^{13}C NMR spectra were taken only in the range from $\delta = -125$ ppm to $+300$ ppm, far from the computationally obtained values (as confirmed to us by the author, experimental reevaluation is in progress).[17] This possible misassignment is understandable, as the predictions are in the highest-frequency ^{13}C shift range for diamagnetic compounds.[18] We note that the other ^{1}H and ^{13}C NMR shifts computed for **9** at the PBE0-40HF level agree excellently with experiment (Table S4 in Supporting Information) while also exhibiting unprecedentedly large SO shifts for atoms several bonds remote from a heavy-metal center, up to $\delta_{SO} = -6.2$ ppm for ^{1}H (CH$_2$ group) and $+11.5$ ppm for ^{13}C (SiMe$_3$ group). A similar but less-pronounced SO-induced shielding effect is also found for the ^{1}H shift of the methylene group in **7**.

Table 3: Calculated and experimental ^{13}C NMR shifts (in ppm vs. TMS) of the uranium-bonded carbon atoms in U^{VI} complexes.[a]

Complex	GGA	hybrid functionals			Expt.
	PBE	PBE0	40HF	50HF	
[UO$_2$(NHC^{C,N})$_2$] (**5**)	267.1 (64.7)	271.3 (60.8)	270.7 (56.7)	270.4 (53.9)	262.8[b]
[UO$_2$(NHC^{C,O})$_2$] (**6**)	281.7 (55.7)	286.7 (48.7)	287.5 (43.6)	289.3 (42.2)	283.6[c]
[UO(L^{C,N})(NR$_2$)$_2$] (**7**)	208.3 (55.0)	257.3 (86.4)	303.2 (123.6)	350.3 (164.9)	317.4[d]
Li[UO$_2$(MeIm)$_2$(L^{N,N})] (**8**)	365.8 (141.8)	351.4 (131.3)	336.2 (119.9)	320.3 (108.1)	329.4[e]
[U(CH$_2$SiMe$_3$)$_6$] (**9**)	256.0 (101.7)	357.5 (195.2)	529.1 (347.9)	809.9 (599.5)	(34.0)[f]

[a] 2c-ZORA-SO results. Spin-orbit contributions to the NMR shifts are given in parentheses (see Methods Section). [b] Ref. [19]. [c] Ref. [20]. [d] Ref. [21]. [e] Ref. [22]. [f] Ref. [16]; value probably misassigned, see text.

Having thus established the high predictive power of quasirelativistic 2-component PBE0-40HF/TZ2P/ZORA calculations for the ^{13}C shifts of uranium-bound carbon atoms (and also for ^{1}H shifts in **7** and **9**), we may now confidently apply the same level of theory to the prediction of the presently unknown ^{1}H hydride shifts for a series of larger, synthetically realistic U^{VI} hydride complexes **10**–**14** (Scheme 4).



Scheme 4. ^{1}H NMR shifts (in ppm vs. TMS) predicted for a series of uranium(VI) hydride complexes. 2c-ZORA-SO results at the PBE0-40HF/TZ2P level. SO contributions to the total NMR shifts are also indicated.

In agreement with the simpler model complexes in Table 1 (see also Table S5 in Supporting Information for 2c-ZORA-SO results at the PBE0-40HF/TZ2P level), the predicted ^{1}H hydride shifts range from around $\delta = +40$ ppm (for the hydride-bridged complex **13** with a somewhat longer U–H bond) to almost $\delta = +150$ ppm for complex **14**. These values correspond to an unprecedented ^{1}H shift range for diamagnetic compounds! We may in fact consider the possibility that the current complete lack of diamagnetic U^{VI} hydride complexes characterized under normal conditions (i.e. not in a matrix-isolation IR study) may be due to the fact that their ^{1}H NMR shifts are so far outside the known range.

As the identification by ^{1}H NMR spectroscopy should be exceedingly characteristic, we suggest to experimental workers in the field to consider in their studies the extreme high-frequency shift range predicted herein when they study reactions that may have led to uranium(VI) hydride complexes. Reductive elimination to form paramagnetic U^{IV} complexes is the most likely obstacle to isolation of the U^{VI} hydrides, and preliminary computational studies (data not shown) suggest that such reactions may often be exothermic. Nevertheless, at least metastable species should be accessible if sufficiently large barriers exist. Such species have already been assumed as intermediates in the mechanisms of some unusual transformations to rationalize the observed chemistry.[23]

In conclusion, record spin-orbit effects on ligand shifts in diamagnetic actinide complexes have been found in relativistic computations, extending both the predicted ^{13}C and ^{1}H shift ranges of diamagnetic compounds, dramatically so for the latter. Strong deshielding spin–orbit effects should also be kept in mind for the shifts of other atoms directly bonded to high-valent closed-shell actinide centers with U−L bonding orbitals exhibiting appreciable s-character on the NMR atom (this excludes, e.g., ^{19}F or ^{17}O shifts, but ^{29}Si or ^{31}P shifts in U^{VI} complexes may also feature dramatic spin-orbit-induced high-frequency shifts). State-of-the-art relativistic quantum-chemical calculations provide a means to predict the expected shift ranges in such cases, thus offering an important tool to help researchers characterize new types of coordination compounds and organometallic complexes of the actinides.

Methods

The structures of all complexes were fully optimized at the PBE0 level[24] with def-TZVPP Gaussian-type orbital (GTO) basis sets and small-core quasirelativistic effective core potentials (ECPs) for the metal centers,[25] using the Turbomole program package.[26] The optimizations started from X-ray structures, where available, retrieved from the Cambridge Structural Database (see Supporting Information for comparison of calculated and experimental geometric parameters in selected complexes). Stationary points on the potential-energy surface were characterized by harmonic vibrational frequency analyses. Quasirelativistic all-electron DFT calculations of the nuclear shieldings have been performed using the Amsterdam Density Functional (ADF) program suite,[27] employing Slater-type orbital (STO) basis sets of triple-zeta doubly polarized (TZ2P) quality and an integration accuracy of 7.0 as a reasonable compromise between accuracy and computational time. Both scalar and SO relativistic effects were treated by the two-component zero-order regular approximation (ZORA).[28] To assess the effect of exact Hartree–Fock (HF) exchange admixture, several PBE-based exchange-correlation functionals have been tested (PBE within the generalized gradient approximation (GGA) with 0%, PBE0 the global hybrid with 25%, PBE0-40HF with 40%, and PBE0-50HF with 50% exact-exchange admixture). The computed ^{1}H and ^{13}C nuclear shieldings were converted into chemical shifts (δ, in ppm) relative to the shielding of tetramethylsilane (TMS), obtained at the same computational level. Natural localized molecular orbital (NLMO) hybridization analyses were performed in the Gaussian 09 program package[29] at the PBE0/def-TZVPP/ECP level of theory, using built-in NBO subroutines.[30]

Received: June 14, 2012
Revised: August 7, 2012

Keywords: actinides · chemical shifts · hydride complexes · relativistic effects · uranium

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[1] See for example: a) R. G. Bergman, *Nature* **2007**, *446*, 391–393; b) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514; c) T. J. Marks, *Science* **1982**, *217*, 989–997; d) A. E. Shilov, G. B. Shulpin, *Chem. Rev.* **1997**, *97*, 2879–2932; e) H. D. Kaesz, R. B. Saillant, *Chem. Rev.* **1972**, *72*, 231–281; f) D. Grant, T. J. Stewart, R. Bau, K. A. Miller, S. A. Mason, M. Gutmann, G. J. McIntyre, L. Gagliardi, W. J. Evans, *Inorg. Chem.* **2012**, *51*, 3613–3624; g) W. J. Evans, K. A. Miller, A. G. DiPasquale, A. L. Rheingold, T. J. Stewart, R. Bau, *Angew. Chem.* **2008**, *120*, 5153–5156; *Angew. Chem. Int. Ed.* **2008**, *47*, 5075–5078.

[2] P. Hrobarik, V. Hrobarikova, F. Meier, M. Repisky, S. Komorovsky, M. Kaupp, *J. Phys. Chem. A* **2011**, *115*, 5654–5659.

[3] The lowest-frequency ^{1}H NMR shift value observed to date for a diamagnetic compound is, to our knowledge, $\delta = -59.1$ ppm for $[HIr(H_2O)(TMPS)]^{8-}$, TMPS = tetra(3,5-disulfonatomesityl)porphyrin; see: S. Bhagan, B. B. Wayland, *Inorg. Chem.* **2011**, *50*, 11011–11020.

[4] a) A. D. Buckingham, P. J. Stephens, *J. Chem. Soc.* **1964**, 4583–4587; b) A. D. Buckingham, P. J. Stephens, *J. Chem. Soc.* **1964**, 2747–2759.

[5] Y. Ruiz-Morales, G. Schreckenbach, T. Ziegler, *Organometallics* **1996**, *15*, 3920–3923.

[6] M. Kaupp, O. L. Malkina, V. G. Malkin, P. Pyykkö, *Chem. Eur. J.* **1998**, *4*, 118–126.

[7] Experimental ^{1}H NMR shifts of d^0 systems given in Scheme 1 were taken from the following references; (Ti, Zr, Hf): J. E. Gozum, G. S. Girolami, *J. Am. Chem. Soc.* **1991**, *113*, 3829–3837; (Ta): B. C. Parkin, J. R. Clark, V. M. Visciglio, P. E. Fanwick, I. P. Rothwell, *Organometallics* **1995**, *14*, 3002–3013; (W): D. F. Schafer, P. T. Wolczanski, E. B. Lobkovsky, *Organometallics* **2011**, *30*, 6539–6561; (Re): D. S. Williams, R. R. Schrock, *Organometallics* **1993**, *12*, 1148–1160.

[8] M. Kaupp, *Relativistic Effects on NMR Chemical Shifts in Relativistic Electronic Structure Theory II*: *Applications* (Ed.: P. Schwerdtfeger), Elsevier, Amsterdam, **2004**, pp. 552–597.

[9] a) W. J. Evans, G. W. Nyce, J. W. Ziller, *Organometallics* **2001**, *20*, 5489–5491; b) P. J. Fagan, J. M. Manriquez, E. A. Maatta, A. M. Seyam, T. J. Marks, *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667; c) R. W. Broach, A. J. Schultz, J. M. Williams, G. M. Brown, J. M. Manriquez, P. J. Fagan, T. J. Marks, *Science* **1979**, *203*, 172–174; d) H. W. Turner, S. J. Simpson, R. A. Andersen, *J. Am. Chem. Soc.* **1979**, *101*, 2782–2782.

[10] a) S. R. Daly, P. M. B. Piccoli, A. J. Schultz, T. K. Todorova, L. Gagliardi, G. S. Girolami, *Angew. Chem.* **2010**, *122*, 3451–3453; *Angew. Chem. Int. Ed.* **2010**, *49*, 3379–3381; b) T. M. Trnka, J. B. Bonanno, B. M. Bridgewater, G. Parkin, *Organometallics* **2001**, *20*, 3255–3264; c) C. Villiers, P. Thuery, M. Ephritikhine, *Inorg. Chem. Commun.* **2007**, *10*, 891–893.

[11] P. A. Frey, S. A. Whitt, J. B. Tobin, *Science* **1994**, *264*, 1927–1930.

[12] C. C. Cummins, G. D. Vanduyne, C. P. Schaller, P. T. Wolczanski, *Organometallics* **1991**, *10*, 164–170.

[13] B. Liang, R. D. Hunt, G. P. Kushto, L. Andrews, J. Li, B. E. Bursten, *Inorg. Chem.* **2005**, *44*, 2159–2168.

[14] The terminal and bridging B−H units exchange rapidly on the NMR time scale, and thus only one broad quartet is observed for BH_4^-. Hydrogen atoms with direct U···H interaction experience somewhat larger SO effects (cf. Figure S1 in Supporting Information).

[15] a) G. Schreckenbach, *Int. J. Quantum Chem.* **2005**, *101*, 372–380; b) M. Straka, M. Kaupp, *Chem. Phys.* **2005**, *311*, 45–56.

[16] S. Fortier, J. R. Walensky, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2011**, *133*, 11732–11743.

[17] T. W. Hayton, personal communication.

[18] The most deshielded carbon shifts (up to $\delta = +486$ ppm) in diamagnetic compounds known to date were reported for

interstitial “carbides” in metal clusters. See: J. Mason, *J. Am. Chem. Soc.* **1991**, *113*, 6056–6062.

[19] S. A. Mungur, S. T. Liddle, C. Wilson, M. J. Sarsfield, P. L. Arnold, *Chem. Commun.* **2004**, 2738–2739.

[20] P. L. Arnold, I. J. Casely, Z. R. Turner, C. D. Carmichael, *Chem. Eur. J.* **2008**, *14*, 10415–10422.

[21] S. Fortier, N. Kaltsoyannis, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2011**, *133*, 14224–14227.

[22] M. F. Schettini, G. Wu, T. W. Hayton, *Chem. Commun.* **2012**, *48*, 1484–1486.

[23] J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, *Chem. Commun.* **2002**, 30–31.

[24] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868; b) C. Adamo, V. Barone, *Chem. Phys. Lett.* **1998**, *298*, 113–119.

[25] a) X. Y. Cao, M. Dolg, *J. Mol. Struct. THEOCHEM* **2004**, *673*, 203–209; b) D. Andrae, U. Haussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.

[26] TURBOMOLE, version 6.3.1, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, **1989**–**2007**, TURBOMOLE GmBH since **2007**; available from http://www.turbomole.com.

[27] Amsterdam Density Functional (ADF), version 2012.01, SCM, Theoretical Chemistry, Vrije Univeriteit, Amsterdam, Netherlands, **2012**; available from http://www.scm.com.

[28] a) S. K. Wolff, T. Ziegler, *J. Chem. Phys.* **1998**, *109*, 895–905; b) S. K. Wolff, T. Ziegler, E. van Lenthe, E. J. Baerends, *J. Chem. Phys.* **1999**, *110*, 7689–7698. For a recent survey of relativistic DFT calculations of NMR parameters, see also: J. Autschbach, S. Zheng, *Annu. Rep. NMR Spectrosc.* **2009**, *67*, 1–95.

[29] Gaussian 09 (Revision A.02), M. J. Frisch, et al., Gaussian, Inc.: Wallingford, CT, **2009**. See the Supporting Information for full citation.

[30] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.