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Characterization of β-B-Agostic Isomers in Zirconocene Amidoborane Complexes

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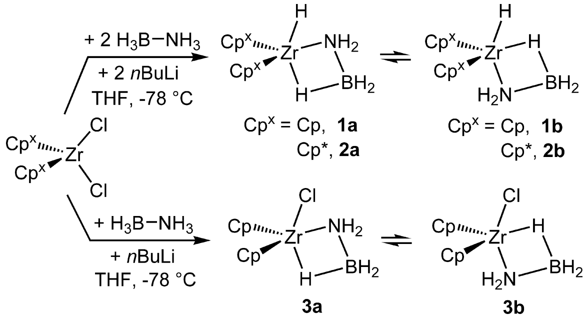
The agostic interaction is a thoroughly documented and well-understood concept in organometallic chemistry that plays an essential role in transition-metal catalysis.[1] In spite of the ubiquity of complexes featuring agostic interactions, to our knowledge no stereoisomers differing with respect to the orientation of the C−H−M bond (agostic isomers) have been reported, although such species are believed to be responsible for determining the outcome of certain catalytic reactions, such as the stereochemistry in olefin polymerization.[2] The pronounced hydridic nature of the B−H moiety renders three-center-two-electron B−H−M bonds considerably less elusive than classical agostic interactions, and numerous transition-metal hydridoborate and related metal σ-borane complexes have been structurally characterized.[3] Although the B−H−M and C−H−M interactions are based on closely related electron-sharing principles, it has been stressed that the term "agostic interaction" should be restricted to hydrocarbon derivatives in order to emphasize that they are unusual.[1d]

The σ-N-binding amidoborane ($NH_2{-}BH_3^-$) ligand is isoelectronic with the ethyl anion, and consequently, it is expected to display in its binding properties certain similarities with this simple organic group. As a result of the potential of ammonia borane as a hydrogen source,[4] amidoborane alkali-, alkaline-earth-,[5] and transition-metal complexes[6] were very recently reported, although no structural details for the transition-metal derivatives are yet available. We were interested in exploring the ligand properties of $NH_2{-}BH_3^-$ and especially in comparing its binding ability to that of the ethyl group.

The reaction of $Cp^x{}_2ZrCl_2$ ($Cp^x = Cp, Cp^*$) with 2 equiv of $H_3N{-}BH_3$ in the presence of *n*-BuLi cleanly produced the zirconocene hydride complexes **1** and **2** (Scheme 1). Reaction of Cp_2ZrCl_2 with 1 equiv of $H_3N{-}BH_3$ and *n*-BuLi yielded **3**, but attempts to prepare $Cp^*{}_2Zr(Cl)NH_2BH_3$ (**4**) produced only mixtures of **2** and unreacted $Cp^*{}_2ZrCl_2$. A plausible mechanism for the formation of **1** via the intermediate **3** would involve salt metathesis and formation of the sterically encumbered complex $Cp_2Zr(NH_2BH_3)_2$, followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp* ligands in **4** could promote β-hydride elimination with formation of $Cp^*{}_2Zr(H)Cl$, which would undergo further salt metathesis to yield the less sterically encumbered complex **2**. All of the complexes were isolated as colorless crystalline solids. The expected byproducts of β-hydride elimination, cyclic borazane oligomers or open-chain polymers, were not identified.[7]

Scheme 1. Synthesis of Derivatives **1**−**3**



The ^1H and ^{13}C NMR spectra of compounds **1**−**3** in benzene-d_6, toluene-d_8, and THF-d_8 feature all of the signals expected for either the Cp or the Cp* ligands in sets of two, in good agreement with the presence of two isomers for each compound. The relative intensities of the signals indicate different ratios for the two isomers, which are strongly solvent-dependent but show little temperature dependence. The pair of ^1H resonances corresponding to the zirconium hydride, one for each isomer, appear at 3.12−3.61 ppm for **1** and 4.08−4.15 ppm for **2**, both of which are slightly upfield from the typical values observed for terminal zirconium hydrides.[8] Two broad ^1H NMR resonances corresponding to the NH_2 groups of **1** (0.10−1.41 ppm), **2** (−0.10 to 0.40 ppm) and **3** (1.48−2.76 ppm) are generally observed, but occasionally these resonances coincide. The very broad quartet signals corresponding to the BH_3 protons in the two isomers of each of **1**, **2**, and **3** overlap at room temperature between −0.15 and 0.44 ppm. Also, the ^{11}B NMR spectra of **1**, **2**, and **3** at room temperature feature two distinct, sharp quartet resonances around −34, −31, and −23 ppm, respectively, with $^1J_{BH} = 88{-}94$ Hz. This is comparable to the value of 92 Hz observed for ammonia borane, confirming that all three hydrogen atoms in each isomer are equivalent on the NMR time scale.

Single-crystal X-ray diffraction (XRD) for samples of **1** revealed two coexisting polymorphs, **1bI** and **1bII**. Their metric parameters are very similar, and only the former will be discussed here. The crystal structures of **2b** and **3a** were also determined, but the former suffered from significant disorder of the Cp* ligands, preventing the location of the hydrogen atoms even at −150 °C, and will not be discussed. The molecular structure of **2b** is nevertheless similar to the structure of **1b**. The most important feature in all of the structures is the chelating $NH_2BH_3^-$ ligand, which binds to the metal through a Zr−N bond and a Zr−H−B bridge (Figure 1). The resulting planar MNBH ring has been observed as a structural element in several main-group[5e,9] and transition-metal complexes,[10] among them one zirconium derivative containing the Cp_2ZrCl fragment [Zr−N, 2.211(2) Å; B−N, 1.360(3) Å; Zr···B, 2.627(2) Å][10c] and one derivative featuring a tetracoordinated nitrogen [B−N, 1.52(4) Å].[10a,b] Very recently, a nickel(II) complex, (N-heterocyclic carbene)Ni(H)NH_2BH_3, featuring the amidoborane ligand in a very similar bonding environment, was proposed as an

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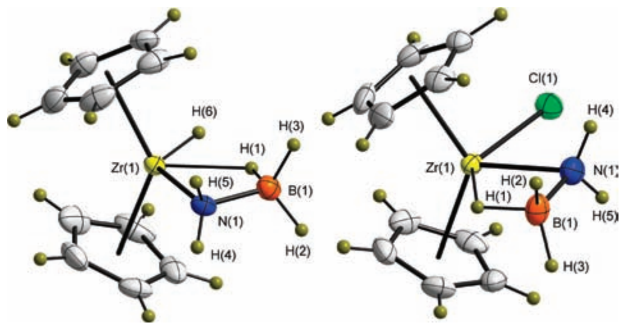

Figure 1. Solid-state molecular structures of (left) **1bI** and (right) **3a**, with thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg), with values for the polymorph **1bII** given in curly brackets and calculated values in square brackets: **1bI** {**1bII**}: Zr−H(6), 1.71(4) {1.74(3)} [1.823]; Zr−N, 2.286(4) {2.284(2)} [2.297]; Zr···B, 2.665(5) {2.657(2)} [2.643]; N−B, 1.539(7) {1.531(3)} [1.544]; N−H, 0.81(5), 0.81(6) {0.84(3), 0.86(3)} [1.008]; B−H_{term}, 1.09(5), 1.10(4) {1.11(3), 1.11(3)} [1.208]; B−H(1), 1.22(4) {1.24(4)} [1.301]; Zr−H(1), 2.02(4) {1.98(2)} [2.004]; H(6)−Zr−N, 125.1(14) {123.0(8)} [122.85]; Zr−N−B, 86.0(3) {85.86(12)} [84.55]; N−B−H(1), 105(2) {103.9(11)} [107.21]; Zr−H(1)−B, 108(2) {109(2)} [104.19]. **3a**: Zr−Cl, 2.5742(8) [2.520]; Zr−N, 2.268(3) [2.272]; Zr···B, 2.685(4) [2.681]; N−B, 1.523(5) [1.526]; N−H, 0.93(5), 0.98(4) [1.010]; B−H_{term}, 1.09(4), 1.13(3) [1.207]; B−H(1), 1.24(3) [1.306]; Zr−H(1), 2.02(3) [2.015]; Cl−Zr−N, 78.68(8) [78.73]; Zr−N−B, 87.89(19) [87.49]; N−B−H(1), 102.8(15) [104.13]; Zr−H(1)−B, 108(2) [105.69].

intermediate in the catalytic decomposition of ammonia borane.[11] The coordination of the NH_2BH_3 fragment is strikingly similar to that of the isoelectronic ethyl group in the seven β-agostic ethyl−metal complexes that have been structurally characterized to date.[12] The metric parameters in the only zirconium derivative, $(\eta^5\text{-MeC}_5H_4)_2Zr(PMe_3)Et^+$,[12d] are similar to those observed in **1b** and **3a** [Zr−C_α, 2.290(9) Å; C_α−C_β, 1.47(2) Å; Zr···C_β, 2.629(9) Å vs Zr−N, 2.268(3)−2.286(4) Å; B−N, 1.523(5)−1.539(7) Å; Zr···B, 2.657(2)−2.685(4) Å]. The slight shortening of the B−N bond upon coordination [vs the B−N bond in ammonia borane, 1.597(3) Å][13] mirrors the shortening of the C_α−C_β bond in β-agostic ethyl complexes [vs the C−C bond in ethane, 1.532(2) Å].[14] One of the structural trademarks of the β-agostic interaction in these derivatives is the unusually narrow M−C_α−C_β angle (74.3−84.5°), with the early metals Ti and Zr situated at the wider end of the range and the late metals Co, Ni, and Pt at the narrow end. With Zr−N−B angles of 85.9−87.9°, complexes **1b** and **3a** fit the model very well, and the term "β-B-agostic" has been chosen to describe the bonding in these compounds in order to emphasize the similarity to that in β-agostic ethyl complexes.

The vibrational spectra of **1**, **2**, and **3** confirmed the findings of the structural measurements, exhibiting characteristic vibrations for terminal and bridging BH bonds at 2397−2304 and 1899−1792 cm^{-1}, respectively.[15] In addition, NH vibrations were observed at 3430−3280 cm^{-1} and Zr−H vibrations (in **1** and **2**) at 1553 and 1531 cm^{-1}.

As in other pentacoordinate zirconocene complexes (with Cp considered as a mondodentate ligand), the Zr−H and Zr−Cl bonds in **1b** and **3a**, respectively, are situated in the plane of the ZrNBH ring, which in turn lies symmetrically between the cyclopentadienyl rings. This raises the possibility of the existence of two stereoisomers, **a** and **b**; in the solid state, the metal hydride in **1b** is indeed situated trans to the nitrogen atom, while the chloride in **3a** is situated trans to the boron atom. The presence of pairs of resonances with solvent-dependent relative ratios in the NMR spectra of **1**, **2**, and **3** indicates that for each compound, the two isomers coexist and are in equilibrium. The cross-peaks for the Cp protons in the EXSY NMR spectra of **1** and **3** in toluene-d_8 confirm this supposition, and the exchange rates were estimated to be 0.27 s^{-1} at 20 °C and 0.05 s^{-1} at −20 °C for the former and 0.01 s^{-1} at 20 °C for the latter. Powder XRD showed that **1bI** is the main constituent of **1** in the solid state, with no detectable amount of **1bII** being present (Figure 2). No other major crystalline constituents were observed, and elemental analysis proved the purity of the sample.

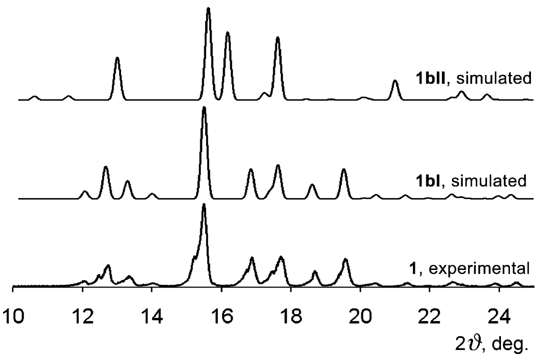

Figure 2. Simulated and experimental powder XRD patterns for **1**.

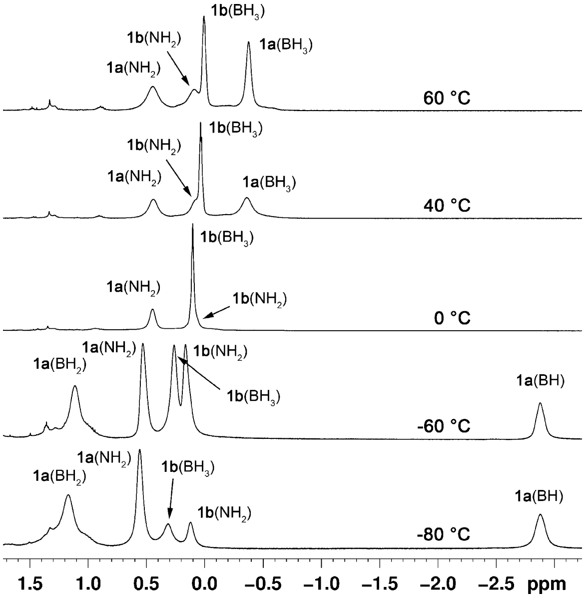

Figure 3. Variable-temperature $^1H\{^{11}B\}$ NMR spectra of **1** in toluene-d_8, showing the area featuring the resonances corresponding to the protons in the NH_2BH_3 ligand.

A variable-temperature boron-decoupled ^1H NMR study of **1** in toluene-d_8 allowed for a more precise assignment of the resonances corresponding to the hydrogen atoms attached to boron (Figure 3). At 60 °C, these hydrogen atoms are equivalent on the NMR time scale and generate a sharper resonance at 0.01 ppm (**1b**) and a broader one at −0.38 ppm (**1a**). The resonance at 0.01 ppm broadens upon cooling and shifts slightly downfield, reaching 0.31 ppm at −80 °C. The broader resonance at −0.38 ppm coalesces at ~0 °C and splits upon further cooling, yielding two signals in a 2:1 ratio at 1.17 and −2.88 ppm at −80 °C, corresponding to the terminal (BH_2) and bridging (B−H−Zr) hydrogen atoms, respectively, in **1a**. This behavior indicates a noticeably lower free energy of activation with respect to rotation of the BH_3 moiety around the BN bond in **1b** than in **1a**, where $\Delta G^{\ddagger}_{273K}$ was estimated to be 48 kJ mol^{-1} using NMR data. A lower free energy of activation would be expected in **1b**, where the BH_3 moiety experiences less steric strain from the Cp groups than in **1a**, in which the tilted Cp groups sandwich the BH_3 moiety more tightly. A computational study confirmed this supposition, yielding estimates for the enthalpy of activation with respect to rotation of the BH_3 moiety around the BN bond of 46 kJ mol^{-1} in **1a** and 19 kJ mol^{-1} in **1b**, allowing for the correlation between the solid-state structures and the NMR signals. Between −80 and −90 °C, the NMR spectra reveal that **1b** starts to crystallize out of the toluene-d_8 solution, in good agreement with the results of the solid-state structural studies.

The low-temperature ^1H NMR spectra of **1a** and **1b** featured broad signals corresponding to the BH protons, preventing the determination of the $^1J_{BH}$ coupling constant. Similarly, the $^1J_{BH}$ coupling was not resolved in the low-temperature ^{11}B NMR spectra. COSY NMR was used for the assignment of the peaks in the ^1H NMR spectra of **1a** and **1b**. Cross-peaks were observed between the resonances assigned to the terminal zirconium hydride and those corresponding to the NH_2 protons, as well as to those corresponding to the bridging BH and temperature-averaged BH_3 protons in the two isomers. The scalar coupling confirmed that the β-B-agostic interaction is preserved in solution in both **1a** and **1b**. An open-chain isomer would be expected to be considerably higher in energy, and its relative concentration would be expected to be strongly temperature-dependent. A computational analysis showed the structurally characterized derivatives **1b** and **2b** to be, in vacuum, energetically on par with their isomers **1a** and **2a**, respectively, with the energy differences between them being less than the expected accuracy of the employed method. Under the same conditions, the crystallized isomer **3a** was ~25 kJ mol^{-1} more stable than **3b**. In all cases, the energy minima were very shallow because of the low energy barrier for the rotation of the Cp/Cp* groups; more importantly, the improbable open-chain isomers featuring monodentate amidoborane ligands were not found to constitute stable minima on the potential energy surface.

In conclusion, we report herein the first structural characterization of transition-metal amidoborane complexes. All of the complexes feature chelating $NH_2BH_3^-$ ligands binding through a Zr−N bond and a classical Zr−H−B bridge, and their structural and spectroscopic properties mirror the properties of their isoelectronic β-agostic ethyl analogues. The relative position of the amidoborane ligand with respect to the chloride or hydride ligand on zirconium gives rise to stereoisomers that have not been characterized in the chemistry of the less robust β-agostic derivatives. The parallel between the more stable β-B-agostic amidoborane complexes and their isoelectronic β-agostic ethyl analogues should allow for a better understanding of both systems. In addition, the structure and dynamics of the derivatives characterized herein is relevant to the thriving field of catalytic hydrogen generation from ammonia borane.

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Supporting Information Available: Experimental details and complete spectroscopic data for **1**−**3**, crystallographic details (including CIF files) for **1bI**, **1bII**, and **3a**, powder XRD data for **1**, and computational details for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124. (c) Scherer, W.; McGrady, G. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1782–1806. (d) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908–6914.

(2) (a) Fan, L.; Harrison, D.; Deng, L.; Woo, T. K.; Swerhone, D.; Ziegler, T. *Can. J. Chem.* **1995**, *73*, 989–998. (b) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85–93.

(3) (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263–293. (b) Greenwood, N. N. *Coord. Chem. Rev.* **2002**, *226*, 61–69. (c) Lin, Z. *Struct. Bonding (Berlin)* **2008**, *130*, 123–148. (d) Besora, M.; Lledós, A. *Struct. Bonding (Berlin)* **2008**, *130*, 149–202. (e) Alcaraz, G.; Sabo-Etienne, S. *Coord. Chem. Rev.* **2008**, *252*, 2395–2409.

(4) (a) Marder, T. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8116–8118. (b) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613–2626. (c) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279–293.

(5) (a) Myers, A. G.; Yang, B. H.; Kopecky, D. J. *Tetrahedron Lett.* **1996**, *37*, 3623–3626. (b) Diyabalanage, H. V. K.; Shrestha, R. P.; Semelsberger, T. A.; Scott, B. L.; Bowden, M. E.; Davis, B. L.; Burrell, A. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 8995–8997. (c) Xiong, Z.; Yong, C. K.; Wu, G.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F. *Nat. Mater.* **2008**, *7*, 138–141. (d) Xiong, Z.; Wu, G.; Chua, Y. S.; Hu, J.; He, T.; Xu, W.; Chen, P. *Energy Environ. Sci.* **2008**, *1*, 360–363. (e) Spielmann, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6290–6295. (f) Wu, H.; Zhou, W.; Yildirim, T. *J. Am. Chem. Soc.* **2008**, *130*, 14834–14839.

(6) (a) Shrestha, R. L.; Diyabalanage, H. V. K.; Semelsberger, T. A.; Scott, B. L.; Burrell, A. K. Presented at the 236th ACS National Meeting, Philadelphia, PA, Aug 17−21, 2008. (b) Baker, R. T. Presented at the 13th International Conference on Boron Chemistry, Platja d'Aro, Spain, Sept 21−25, 2008. (c) Burrell, A. K.; Davis, B. J.; Thorn, D. L.; Gordon, J. C.; Baker, R. T.; Semelsberger, T. A.; Tumas, W.; Diyabalanage, H. V. K.; Shrestha, R. P. U.S. Patent Appl. 0311017 A1, 2008.

(7) (a) Corfield, P. W. R.; Shore, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 1480–1487. (b) Shaw, W. J.; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Camaioni, D. M.; Baker, R. T.; Autrey, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7493–7496. (c) Pons, V.; Baker, R. T. *Angew. Chem., Int. Ed.* **2008**, *47*, 9600–9602.

(8) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724. (b) Kot, W. K.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1987**, *26*, 1339–1341. (c) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255–3256. (d) Chen, X.; Liu, S.; Plečnik, C. E.; Liu, F.-C.; Fraenkel, G.; Shore, S. G. *Organometallics* **2003**, *22*, 275–283. (e) Liu, F.-C.; Chen, J.-H.; Chen, S.-C.; Chen, K.-Y.; Lee, G.-H.; Peng, S.-M. *J. Organomet. Chem.* **2005**, *690*, 291–300.

(9) (a) Nöth, H.; Thomas, S.; Schmidt, M. *Chem. Ber.* **1996**, *129*, 451–458. (b) Dornhaus, F.; Bolte, M. *Acta Crystallogr.* **2007**, *E63*, m39–m40. (c) Spielmann, J.; Harder, S. *J. Am. Chem. Soc.* **2009**, *131*, 5064–5065.

(10) (a) Fachinetti, G.; Floriani, C.; Mellini, M.; Merlino, S. *Chem. Commun.* **1976**, 300–301. (b) Dell'Amico, G.; Marchetti, F.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1982**, 2197–2202. (c) Männig, D.; Nöth, H.; Schwartz, M.; Weber, S.; Wietelmann, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 998–999. (d) Binger, P.; Sandmeyer, F.; Krüger, C. *Organometallics* **1995**, *14*, 2969–2976. (e) Fryzuk, M. D.; MacKay, B. A.; Johnson, S. A.; Patrick, B. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3709–3712. (f) Hillier, A. C.; Fox, T.; Schmalle, H. W.; Berke, H. *J. Organomet. Chem.* **2003**, *669*, 14–24. (g) MacKay, B. A.; Johnson, S. A.; Patrick, B. O.; Fryzuk, M. D. *Can. J. Chem.* **2005**, *83*, 315–323.

(11) Zimmerman, P. M.; Paul, A.; Zhang, Z.; Musgrave, C. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 2201–2205.

(12) (a) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802–803. (b) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326–328. (c) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629–1637. (d) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289–1291. (e) Conroy-Lewis, F. M.; Mole, L.; Redhouse, A. D.; Litster, S. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1601–1603. (f) Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653–2662. (g) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 1602–1612. (h) Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984–11994.

(13) (a) Hughes, E. W. *J. Am. Chem. Soc.* **1956**, *78*, 502–503. (b) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337–6343. (c) Bowden, M. E.; Gainsford, G. J.; Robinson, W. T. *Aust. J. Chem.* **2007**, *60*, 149–153.

(14) van Nes, G. J. H.; Vos, A. *Acta Crystallogr.* **1978**, *34B*, 1947–1956.

(15) (a) Smith, J.; Seshadri, K. S.; White, D. *J. Mol. Spectrosc.* **1973**, *45*, 327–337. (b) Hess, N. J.; Bowden, M. E.; Parvanov, V. M.; Mundy, C.; Kathmann, S. M.; Schenter, G. K.; Autrey, T. *J. Chem. Phys.* **2008**, *128*, 034508.

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