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Article

BN-Analogues of Vinylidene Transition Metal Complexes: The Borylnitrene Isomer

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Density functional computations using the BP86 functional within the resolution-of-identity approximation and polarized triple-ζ basis sets are employed for the study of the three isoelectronic $(CO)_4FeL$ (L = CCH_2 (**5**), BNH_2 (**6**), NBH_2 (**7**)) as well as $(CO)_4Fe(NBcat)$ (**9**) (cat = catecholato) complexes. In all complexes **5**–**7**, the ligand L prefers the equatorial position of a pseudo trigonal bipyramid. The borylnitrene complex **7** has a linear Fe–N–B arrangement; its Fe–L bond dissociation energy is similar to that of the vinylidene complex **5** and only slightly lower than that of **6**. Nonetheless, **7** is less stable thermodynamically than **6** by 40 kcal mol^{-1}. Complexes of type **7** are expected to be reactive on the basis of the following findings: the HOMO–LUMO energy gap is small, the rearrangement from **7** to **6** via an iminoborane intermediate involves barriers of 15 and 28 kcal mol^{-1}, and the dissociation of a CO molecule to give $(CO)_3FeNBH_2$ is only slightly endergonic (+7 kcal mol^{-1} at 298.15 K). The catecholate bridge in **9** results in significant changes: the bipyramidal complex is no longer a minimum, but an isocycanato complex is obtained instead computationally.

Introduction

Vinylidenes (**1**; Chart 1) are highly reactive molecules that, however, form stable transition metal complexes, $L_nM(CCR_2)$.[1–5] Isoelectronic substitution of the C_2 unit by BN yields the complexes of aminoborylene, BNR_2 (**2**). The isolobal relationship between the BNR_2 and CO ligands has been recognized,[6–8] and the chemistry of aminoborylene transition metal complexes has been developed and reviewed in detail during the last years.[9–13]

Chart 1. Ligands Discussed in This Work

1a **2a** **3a** **3b**

The other possible BN analogue of vinylidene, borylnitrene NBR_2 (**3**), has hardly received attention. The lowest energy state of NBH_2 **3a** is a singlet, but this does not correspond to a minimum on the potential energy surface: **3a** is unstable toward 1,2-hydrogen migration to yield iminoborane HB-NH.[14] We have obtained for the first time direct spectroscopic data for NBR_2 (R_2 = catecholate, **3b**) recently and have observed high thermal and photochemical reactivity in argon matrixes.[15] We are thus wondering if NBR_2 species can be used as ligands in transition metal complexes as this could provide a way for "taming" their reactivity.

Vinylidene **1a** and aminoborylene **2a** are typical two-electron σ-donor/π-acceptor ligands in transition metal complexes, while NBR_2 formally belongs to the group of imido (or nitrene) ligands $[NR]^{2-}$. The electron-rich and hard imido ligands, which have been the subject of numerous investigations and have been reviewed from various

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(1) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.
(2) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193–195*, 977.
(3) Werner, H. *Coord. Chem. Rev.* **2004**, *248*, 1693.
(4) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.* **2004**, *248*, 1703.
(5) Selegue, J. P. *Coord. Chem. Rev.* **2004**, *248*, 1543.
(6) Bickelhaupt, F. M.; Radius, U.; Ehlers, A. W.; Hoffmann, R.; Baerends, E. J. *New J. Chem.* **1998**, 1.
(7) Ehlers, A. W.; Baerends, E. J.; Bickelhaupt, F. M.; Radius, U. *Chem.—Eur. J.* **1998**, *4*, 210.
(8) Radius, U.; Bickelhaupt, F. M.; Ehlers, A. W.; Goldberg, N.; Hoffmann, R. *Inorg. Chem.* **1998**, *37*, 1080.
(9) Braunschweig, H. *Angew. Chem.* **1998**, *110*, 1882; *Angew. Chem., Int. Ed.* **1998**, *37*, 1786.
(10) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1.
(11) Braunschweig, H. *Adv. Organomet. Chem.* **2004**, *51*, 163.
(12) Wrackmeyer, B. *Angew. Chem.* **1999**, *111*, 817; *Angew. Chem., Int. Ed.* **1999**, *38*, 771.
(13) Braunschweig, H.; Colling, M. *Eur. J. Inorg. Chem.* **2003**, 393.
(14) Nguyen, M. T. *J. Chem. Soc., Chem. Commun.* **1987**, 342.
(15) Bettinger, H. F.; Bornemann, H. *J. Am. Chem. Soc.* **2006**, *128*, 11128.

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perspectives,[16−20] stabilize high formal oxidation states. Consequently the vast majority of the examples involve high-valent early transition metal centers, but recent research has demonstrated the stability of imido complexes of mid- and later transition elements.[21−25] Depending on the electronic structure of the complex, the imido ligand can be an inert "spectator" (e.g., in Schrock's[26] well-known metathesis catalysts) or can be transferred onto substrates.[20]

In line with the general properties of imido ligands, the very few examples of borylimido complexes involve early transition metals in high formal oxidation states. The first example, $[W(NBmes_2)_2Cl_2(PMe_3)_2]$ (**4**) (mes = mesityl) was obtained by Danopoulos et al. by oxidative addition of $(mes)_2BN_3$ to $WCl_2(PMe_3)_4$.[27] Following this route, Weber et al. synthesized two more borylimido complexes, $[W(NBmes_2)(Nmes)_2(PMe_3)_2]$ and $[V(NBmes_2)mes_3]$.[28]

In view of the very limited knowledge on NBR_2 complexes, we wish to present here a comparative analysis of the electronic and geometric properties of isoelectronic CCH_2, BNH_2, and NBH_2 complexes bound to the zerovalent $Fe(CO)_4$ fragment. The choice of $Fe(CO)_4$ was motivated by previous computational investigations of the complexes $(CO)_4FeCCH_2$ (**5**) and $(CO)_4FeBNH_2$ (**6**) by Frenking's group.[29,30] Note that low-valent nitrene complexes like $(CO)_4Fe{=}NR$[31] or $(CO)_5W{=}NPh$,[32−34] which are related to the borylnitrene system $(CO)_4Fe(NBR_2)$ (**7**) investigated here, are either unknown or only transient intermediates. Using computational chemistry techniques, the following questions are addressed in this work:

(i) Is NBH_2 stable toward hydrogen migration in the coordination sphere of a low-valent transition metal complex?

(ii) If so, what is the electronic and geometric structure of $(CO)_4Fe(NBH_2)$ (**7**) compared to **5**, **6**, and the low-valent nitrene complex $(CO)_4Fe(NH)$ (**8**)?

(iii) What is the influence of electron donor substituents, as exemplified by catecholato, o-$C_6H_4O_2$ (cat), in $(CO)_4Fe(NBcat)$ (**9**), on the electronic properties of the low-valent complexes?

Theoretical Details

This work employed the Turbomole[35] program (Version 5.8) and its resolution of the identity (RI) approximation for the fast evaluation of Coulomb integrals in density functional theory.[36] Becke's[37] 1988 exchange functional and the correlation functional of Perdew[38] (BP86) were used in conjunction with the TZVP basis set.[39] This basis sets uses the following contraction schemes: Fe (17s11p6d)/[6s4p3d]; B, C, N, O (11s6p1d)/[5s3p1d]; H (5s1p)/[3s1p]. Geometries were fully optimized, and harmonic vibrational frequencies were obtained from analytic second derivatives[40] at the RI-BP86/TZVP level of theory. As comparison of the obtained structural parameters with previous B3LYP computations on $(CO)_4Fe(CCH_2)$ and $CO_4Fe(BNH_2)$ by Chen and Frenking[29,30] and with the X-ray data[27] for $W[NB(mes)_2]_2Cl_2(PMe_3)_2$ shows good agreement, the RI-BP86/TZVP appears adequate for the purpose of this study. The bonding in the complexes was investigated using the natural bond orbital (NBO)[41] analysis at the BP86/TZVP level using the Gaussian 03[42] program. Molecular orbitals were plotted using Molden.[43]

Results and Discussion

Geometries and Energies. In agreement with previous results,[29,30] **1a** and **2a** prefer the equatorial position in $(CO)_4Fe(CCH_2)$ (**5**) and $(CO)_4Fe(BNH_2)$ (**6**), while the axial CO ligands bend toward **1a** and **2a**, respectively (Table 1).[29] The second derivative computations give one imaginary vibrational frequency for the axial isomers $\mathbf{5}_{ax}$ and $\mathbf{6}_{ax}$. The energy difference between these two forms, $\mathbf{5}_{eq}$ and $\mathbf{5}_{ax}$ and $\mathbf{6}_{eq}$ and $\mathbf{6}_{ax}$, are 4.5 and 1.3 kcal mol^{-1} at the RI-BP86/TZVP level of theory. These energy differences, which correspond to the barriers for Berry pseudorotation, compare well to

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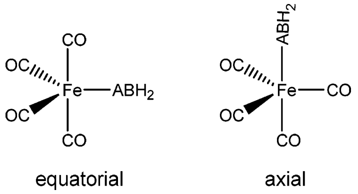
(16) Dehnicke, K.; Strähle, J. *Angew. Chem.* **1981**, *93*, 451; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413.
(17) Dehnicke, K.; Strähle, J. *Angew. Chem.* **1992**, *104*, 978; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955.
(18) Dehnicke, K.; Strähle, J. *Chem. Rev.* **1993**, *93*, 981.
(19) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.
(20) Zarubin, D. N.; Ustynyuk, N. A. *Russ. Chem. Rev.* **2006**, *75*, 671.
(21) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623.
(22) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322.
(23) Brown, S. D.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 1913.
(24) Mehn, M. P.; Peters, J. C. *J. Inorg. Biochem.* **2006**, *100*, 634.
(25) Badiei, Y. M.; Krishnaswamy, A.; Melzer, M. M.; Warren, T. H. *J. Am. Chem. Soc.* **2006**, *128*, 15056.
(26) Schrock, R. R. *Angew. Chem.* **2006**, *118*, 3832; *Angew. Chem., Int. Ed.* **2006**, *45*, 3748.
(27) Danopoulos, A. A.; Redshaw, C.; Vaniche, A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, *12*, 1061.
(28) Weber, K.; Korn, K.; Schorm, A.; Kipke, J.; Lemke, M.; Khvorost, A.; Harms, K.; Sundermeyer, J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 744.
(29) Chen, Y.; Frenking, G. *J. Chem. Soc., Dalton Trans.* **2001**, 434.
(30) Chen, Y.; Hartmann, M.; Frenking, G. *Z. Anorg. Allg. Chem.* **2001**, *627*, 985.
(31) Dekker, M.; Knox, G. R. *Chem. Commun.* **1967**, 1243.
(32) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007.
(33) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871.
(34) McGowan, P. C.; Massey, S. T.; Abboud, K. A.; McElwee-White, L. *J. Am. Chem. Soc.* **1994**, *116*, 7419.
(35) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.
(36) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652.
(37) Becke, A. D. *Phys. Rev. B* **1988**, *38*, 3098.
(38) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(39) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
(40) Deglmann, P.; Furche, F.; Ahlrichs, R. *Chem. Phys. Lett.* **2002**, *362*, 511.
(41) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(42) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. J. A.; 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.; 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 B.4; Gaussian: Pittsburgh, PA, 2003.
(43) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123.

Table 1. Selected Bond Lengths (in Å) and Bond Angles (in deg) in Free Ligands L [ABH_2 (**1a**−**3a**)] and $(CO)_4Fe{-}L$ Complexes and Fe−L Bond Dissociation Energies D_e and D_0 (without and with Zero Point Vibrational Energy Correction, Respectively, in kcal mol^{-1}) As Computed at the RI-BP86/TZVP Level of Theory



species[a]	L	***d*(AB)**	***d*(FeA)**	∠C_{ax}−Fe−A	∠C_{eq}−Fe−A	D_e (D_0)[b]
1a		1.300				
2a		1.387				
3a[c]		1.307				
$\mathbf{5}_{eq}$	CCH_2	1.309	1.790	82.7	127.2	79.7 (75.4)
$\mathbf{5}_{ax}$[c]	CCH_2	1.305	1.792	173.0	84.5, 90.9	74.8 (70.9)
$\mathbf{6}_{eq}$	BNH_2	1.377	1.818	78.1	126.3	87.4 (83.5)
$\mathbf{6}_{ax}$[c]	BNH_2	1.375	1.827	174.7	82.2, 87.7	85.6 (82.2)
$\mathbf{7}_{eq}$	NBH_2	1.344	1.785	82.9	129.8	80.9 (76.5)
$\mathbf{7}_{ax}$[c]	NBH_2	1.336	1.790	170.1	83.1, 93.3	71.8 (68.1)
$\mathbf{8}_{eq}$	NH[d]		1.809	79.8, 83.0	131.8	63.7 (59.5)[e]
$\mathbf{9}_{eq}$[f]	NBcat	1.394	1.771	78.4	132.3	67.2 (65.5)[e]
$\mathbf{9}_{ax}$[f]	NBcat	1.424	1.787	164.2	75.4, 97.1	56.7 (55.1)[e]

[a] All equatorial complexes have C_{2v} and all axial complexes have C_s symmetry, with the exception of C_s symmetric $\mathbf{8}_{eq}$. [b] With respect to formation of $(CO)_4Fe(^1A_1)$ + L. [c] Number of imaginary vibrational frequencies (NIMAG): 1. [d] ∠Fe−N−H = 115.4°. [e] L in triplet ground state. [f] NIMAG = 2.

those reported by Chen and Frenking (6.2 and 2.7 kcal mol^{-1}, respectively) using the B3LYP functional.[30]

The $(CO)_4Fe(NBH_2)$ complex **7** has geometric features which are generally similar to those of its constitutional isomer **6**: the equatorial position of the borylnitrene ligand **3a** results in a minimum $\mathbf{7}_{eq}$, while the axial isomer $\mathbf{7}_{ax}$ is a saddle point. The energy difference between $\mathbf{7}_{eq}$ and $\mathbf{7}_{ax}$ is 8.4 kcal mol^{-1}. The stronger preference for the equatorial position reflects the better π-acceptor properties of NBH_2 compared to the BNH_2 ligand (vide infra). As in **6**, the axial CO ligands in $\mathbf{7}_{eq}$ are bent toward the **3a** ligand.

The following discussion is limited to the equatorial complexes. The Fe−L distance, 1.790 Å in **5**, increases upon isoelectronic BN substitution to 1.818 Å in **6**. In **7**, it decreases slightly to 1.785 Å. This distance is significantly shorter than in C_s-symmetric $(CO)_4Fe(NH)$ (**8**): here the Fe−N bond length is 1.809 Å, while the Fe−N−H unit is nonlinear, ∠Fe−N−H = 115°. Compared to the free ligands, **2a** and **3a**, the BN distance shortens by 0.010 Å in the aminoborylene complex **6** but lengthens by 0.037 Å in the borylnitrene complex **7**. Vinylidene, on the other hand, increases the CC distance by only 0.009 Å upon complexation to $Fe(CO)_4$.

The bond dissociation energies of $(CO)_4Fe{-}L$ were previously found to be largely insensitive to the level of theory for L = BNH_2 (CCSD(T) vs B3LYP or BP86).[29] For the purpose of a comparative analysis of ligands presented here, it thus not necessary to go beyond our standard RI-BP86/TZVP level. The Fe−L bond dissociation energies with respect to the $^1A_1$ state of C_{2v}-symmetric $Fe(CO)_4$ at this level of theory (Table 1) are 79.7 kcal mol^{-1} for **5** (74.8 and 88.3 kcal mol^{-1} at B3LYP and CCSD(T)//B3LYP)[30] and 87.4 kcal mol^{-1} for **6** (83.0 kcal mol^{-1} at B3LYP),[29] again in good agreement with the literature data. As the dissociation to the triplet ground state of $Fe(CO)_4$[44−46] is spin-forbidden, the singlet state of $Fe(CO)_4$ is considered here, as done previously.[7]

The Fe−L bond dissociation energy of **7**, 80.9 kcal mol^{-1}, is very similar to that in **5** and only slightly lower than that in isomeric **6**. However, bond dissociation energies (BDEs) take into account the stability of the fragments by definition, and large BDEs can result if formation of high-energy fragments is involved. Free ligand **3a**, in its lowest energy singlet state, is 34 kcal mol^{-1} higher in energy (without ZPVE correction) than **2a**. This preference for BNH_2 over NBH_2 arrangement is even more pronounced in the $(CO)_4Fe{-}L$ complexes, where **6** is more favorable than **7** by 40 kcal mol^{-1} (37 kcal mol^{-1} with ZPVE correction).

Electronic Structure. The changes of the electronic structure of vinylidene resulting from BN substitution can be considered in terms of molecular orbital theory.[47] For a comparative discussion of the electronic structures of the CO, BNH_2, and CCH_2 and the implications for bonding to metal centers, the reader is referred to the work of Bickelhaupt et al.[6] Briefly, the smaller and larger electronegativities of B and N with respect to C result in an upshift of the HOMO (sp-type lone pair on boron, $5a_1$) and the LUMO (p_y on boron, $2b_2$) for **2a** and a stronger localization on the terminal boron atom compared to **1a** (Figure 1).[6] The overall similarity of CCH_2 and BNH_2 was predicted to result in similar coordination properties,[6] in agreement with the quantitative analysis

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(44) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W. *J. Chem. Phys.* **1991**, *94*, 2031.
(45) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.
(46) Tsuchiya, T.; Roos, B. O. *Mol. Phys.* **2006**, *104*, 1123.
(47) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985.

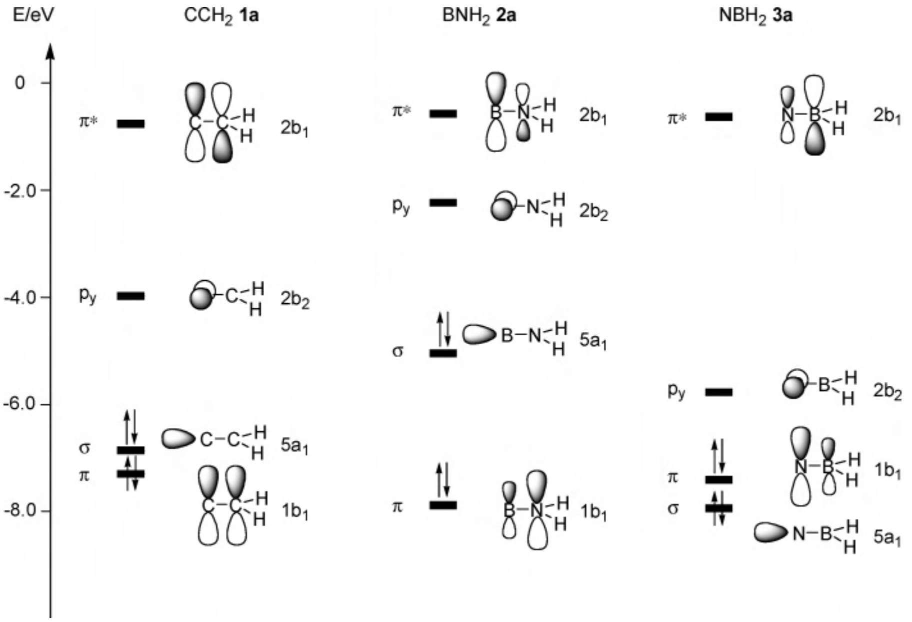

Figure 1. Schematic MOs and energy level diagrams for **1a**−**3a** as obtained at the RI-BP86/TZVP level of theory.

of Chen et al.,[29,30] which shows that both ligands are stronger π acceptors than CO.

In the case of **3a**, the energetic changes of frontier orbitals are more pronounced: the LUMO (p_y on nitrogen) shifts strongly to lower energies, while the N(sp) even shifts below the π orbital of the BN bond, which becomes the HOMO of **3a**. Due to the higher electronegativity of N, the $5a_1$ orbital is more compact in **3a** than in **2a**. Consequently, **3a** should be a poorer σ-donor but a better π-acceptor ligand than **2a**. The π^* orbital ($2b_1$), which is not important for bonding to the $Fe(CO)_4$ fragment, remains energetically similar in **1a**−**3a**.

These changes in energies and shapes of the ligand MOs also are reflected in the MO levels of the complexes $(CO)_4FeL$ (Figure 2). In the reference $Fe(CO)_4(CCH_2)$ (**5**), the HOMO is the metal-centered $d_{x^2-y^2}$ orbital having an antibonding interaction with the C(sp) fragment orbital. In **6** this Fe−L antibonding orbital is slightly shifted upward in energy as expected due to the electronegativity perturbation and the resulting enhanced σ donation. The HOMO of **7** differs: it is largely the bonding π orbital of the BN bond. Considering the LUMOs, it is seen for **5** and **7** that they are similar to the LUMOs of the ligands, i.e., largely the p_y orbital, but a pronounced shift to lower energy by about 1 eV is recognized for **7**. In contrast, in **6** the B(p_y) orbital is shifted upward on the energy scale beyond the π^* of the BN bond, which is the LUMO of **6**.

The bonding in **5**−**7** can further be analyzed by NBO analysis. Our data (Table 2) for **6** are in good agreement with the results of Chen and Frenking.[29] Both the out-of-plane (0.18 e) and, much more pronounced, the in-plane (0.47 e) boron orbitals receive significant charge upon complexation, resulting in a pp occupation for the ligand in the complex, $p_\pi(L)$, of 0.90. Considering the difference in occupation of the boron π orbitals (of b_1 and b_2 symmetry) in the complex and the free ligand to be due to π back-donation $\Delta q_\pi(L)$ (−0.65 e), as done by Chen and Frenking,[29] the σ donation $\Delta q_\pi(L)$ (+0.92 e) is obtained as the difference between charge on the ligand $q(L)$ (+0.28 e) and π back-donation. The analogoues analysis for **3a** and **7** gives a very different picture of bonding. The in-plane π orbital on nitrogen also receives significant charge upon complexation (0.68 e) in agreement with expections expressed above, and the overall π back-donation (−0.79 e) is larger than in the case of **6**. At the same time the σ donation is much smaller, only +0.36 e, again as expected on the basis of the orbital energies of the free ligands. In summary, the NBO analysis reveals that the borylnitrene ligand is a much stronger π acceptor than a σ donor.

Table 2. Results of the NBO Analysis of $(CO)_4FeL$ Complexes **6** and **7** As Computed at the BP86/TZVP Level of Theory

L	$q(L)$	$p_\pi(L)$	$\Delta q_\pi(L)$[a]	$\Delta q_\sigma(L)$[b]	b:d[c]
BNH_2 (**6**)	+0.28	0.90	−0.65	+0.92	0.71
NBH_2 (**7**)	−0.44	2.64	−0.79	+0.36	2.19

[a] Difference between the π population at the boron atom in the complex and in the free ligand. [b] Difference between $q(L)$ and $\Delta q_\pi(L)$. [c] Ratio $|\Delta q_\pi(L)|/|\Delta q_\sigma(L)|$.

Finally, a comparison of the borylnitrene complex **7** with a prototypical zerovalent nitrene complex $(CO)_4Fe{=}NH$ (**8**) is instructive. Considering NH as a neutral two-electron donor, **8** has 18 valence electrons and is isoelectronic in the valence shell to $(CO)_5W{=}NH$, whose electronic structure has been studied as a model for transient nitrene complexes.[33] The bending at nitrogen in such complexes reduces unfavorable four-electron−four-orbital interactions, as discussed by Arndtsen et al.[33] in detail for $(CO)_5W{=}NH$ and in a broader context by Trinquier and Bertrand.[48] The topological similarity of the frontier orbitals in **7** and the nitrene complex **8** is obvious, but the energies of frontier orbitals differ: the HOMO in **7** is lower in energy than in **8** by 0.4 eV, while the LUMO is slightly higher. In **7** the

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(48) Trinquier, G.; Bertrand, G. *Inorg. Chem.* **1985**, *24*, 3842.

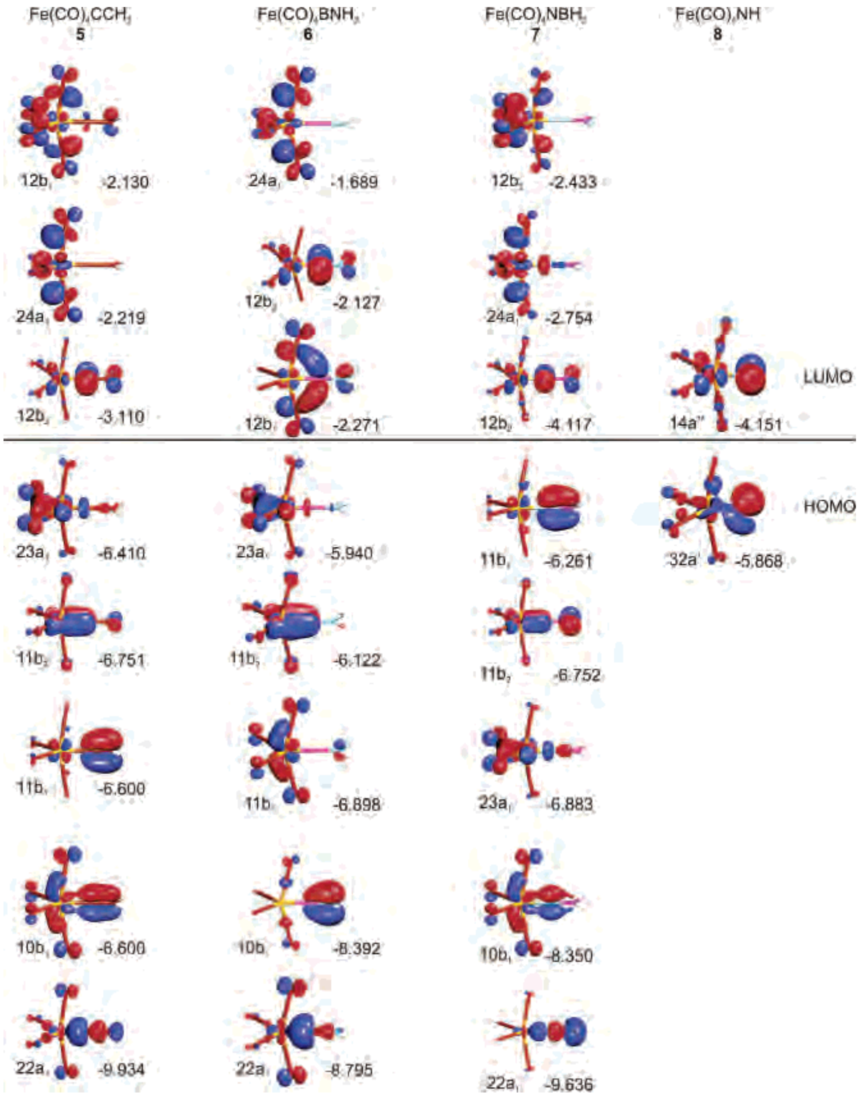

Figure 2. Frontier molecular orbitals and energies (in eV) computed (RI-BP86/TZVP) for **5**−**8**.

electron deficient boron center acts as a stabilizing Lewis acid, which lowers the energy of the HOMO. This interaction is most favorable for a linear Fe−N−B arrangement. A well-known and closely related phenomenon in main group chemistry is the planarity of the $N(SiR_3)_3$ molecule compared to the pyramidal shape of organic amines.[47] Counting the electrons in $(CO)_4FeL$ using the commonly adopted neutrality of the ligands **1a** and **2a**, we arrive at 18 valence electrons. The isoelectronic ligand **3a** also contributes two electrons in this scheme. But its linear coordination geometry is akin to imido complexes rather than to low-valent nitrene complexes like **8**.

The low energy of the LUMO of **7** compared to **5** is a direct consequence of the electronic structure of the free ligand **3a**. As a result of the electronegativity difference between boron, nitrogen, and carbon, the HOMO−LUMO gap is increased in **6** (3.7 eV) and decreased in **7** (2.1 eV) compared to **5** (3.3 eV). The small HOMO−LUMO gap in **7**, though still larger than in **8** (1.7 eV), is expected to result in a high kinetic reactivity toward nucleophiles, but by introduction of bulky substituents on the boron atom derivates of **7** can experience kinetic stabilization.

Intramolecular Rearrangements. While bulky substituents can provide kinetic stabilization in bimolecular reactions, they might not block low-energy *intramolecular* pathways, which could limit the stability and thus hamper the experimental realization of low-valent complexes of type **7**. We here consider two possible intramolecular rearrangement reactions, (i) isomerization of **7** to **6** and (ii) formation of an isocyanate η^2-C,N complex.

The possible interconversion of **6** and **7** is involving an κ^2-B,N-coordinated iminoborane (**10**) intermediate.[49−51] This is 22 kcal mol^{-1} lower in energy than **7**, and hence the formation of **6** from **7** is expected to be thermodynamically feasible. The barriers for rearrangement are only moderately high: 15 kcal mol^{-1} for interconversion of **7** to **10** ($\mathbf{TS}_{7-10}$)

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(49) Bulak, E.; Herberich, G. E.; Manners, I.; Mayer, H.; Paetzold, P. *Angew. Chem.* **1988**, *100*, 964; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 958.

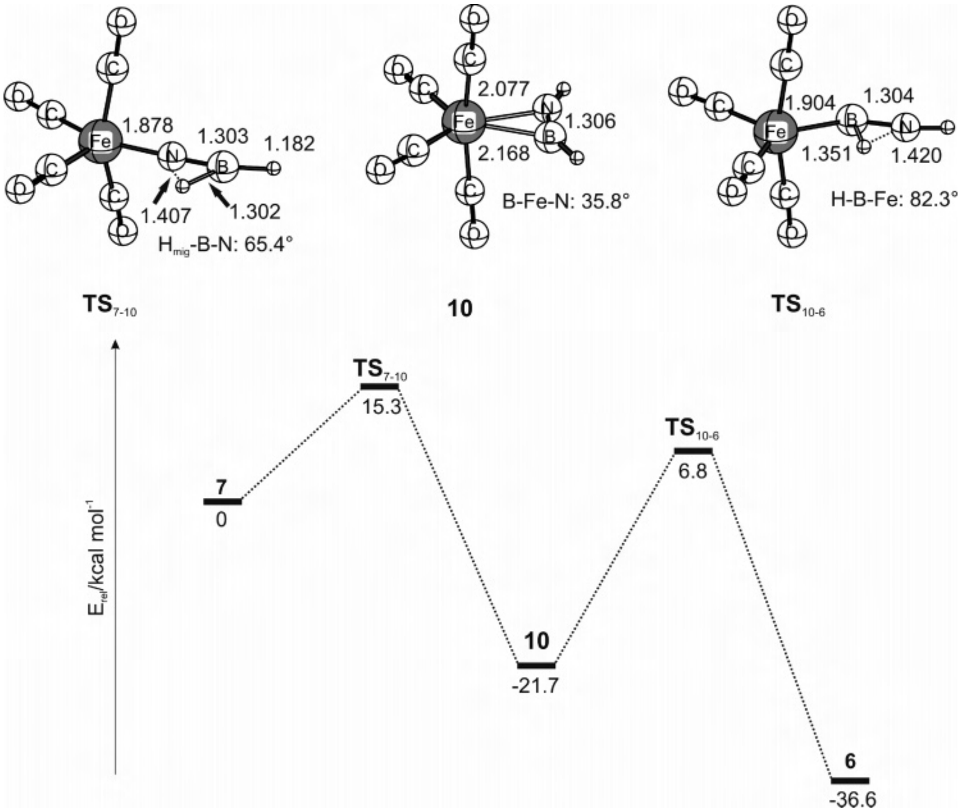

Figure 3. Geometries of transition states ($\mathbf{TS}_{7-10}$ and $\mathbf{TS}_{10-6}$) and the iminoborane intermediate (**10**) for the interconversion of **6** and **7** as computed at the RI-BP86/TZVP level of theory. Important geometry parameters are given in Å and deg.

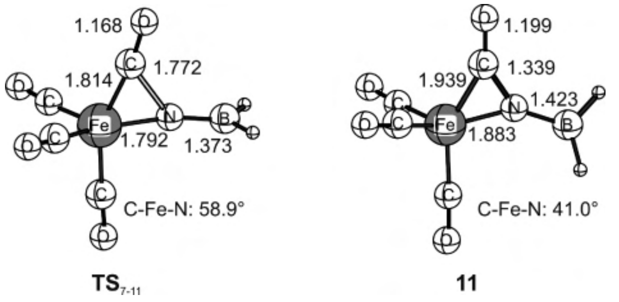

Figure 4. Geometries of the transition state ($\mathbf{TS}_{7-11}$) for formation of the η^2-*C*,*N*-isocyanate complex **11** as computed at the RI-BP86/TZVP level of theory. Important geometry parameters are given in Å and deg. The energies relative to **7** are +4.3 kcal mol^{-1} for $\mathbf{TS}_{7-11}$ and −2.9 kcal mol^{-1} for **11**.

and 28 kcal mol^{-1} for rearrangement from **10** and **6** ($\mathbf{TS}_{10-6}$). The geometries of these stationary points are given in Figure 3.

The stability of **7** could also be limited by the formation of the η^2-*C*,*N*-isocyanate complex $(CO)_3Fe(OCNBH_2)$ (**11**). This reaction is only slightly exothermic (−3 kcal mol^{-1}) but has a barrier ($\mathbf{TS}_{7-11}$; see Figure 4) of only 4 kcal mol^{-1}. Thus, our computations suggest that the stability of complex **7** is severly limited by the existence of a very low energy intramolecular reaction channel. The aminoborylene complex **6** does not appear to suffer from this low-energy rearrangement channel, and this is possibly due to the high energy of the required $(CO)_3Fe(OCBNH_2)$ product.

Donor-Functionalized R_2BN Ligands. The boryl substituent favors a linear arrangement in the nitrene complex **7** by stabilizing the nitrogen lone pair. If the Lewis acidity of the boron center is reduced by donor substituents, it can be reasoned that the interaction with the nitrogen lone pair is reduced. Such a boryl nitrene is the catechole derivative, which has been obtained from the corresponding azide under the conditions of matrix isolation at 10 K.[15] The catecholato (cat) substituent is not "innocent" electronically. The oxygen donor atoms reduce the Lewis acidity of boron, disfavor the electronic singlet state, and consequently turn the borylnitrene into a ground triplet state species.[15] This modified electronic structure of the ligand NB(cat) (**3b**) is also expected to bear ramifications in the singlet $(CO)_4$FeNB(cat) (**9**) complex.

Complex **9** with NB(cat) in an equatorial position is not a minimum but rather a second-order stationary point (i59 and i22 cm^{-1}) on the potential energy surface. The Fe−N distance in **9** is reduced by 0.014 Å to 1.771 Å (see Figure 5), while the B−N distance is lengthened by 0.050 Å compared to the corresponding values in **7**. These changes in geometry are in agreement with the expected reduced B−N interaction. At the same time, the Fe−L bond strength also is *decreased* markedly to only 83% of its value in **7**. Clearly, the increased π electron density at the nitrogen atom results in an increase of unfavorable two-orbital−four-electron interactions with the corresponding metal fragment. This interaction is evidenced by an upshift of the HOMO by 1.11 eV in energy and a downshift of the LUMO by 0.51 eV. The resulting small HOMO−LUMO gap of only 0.52 eV is indicative of

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(50) Männig, D.; Nöth, H.; Schwartz, M.; Weber, S.; Wietelmann, U. *Angew. Chem.* **1985**, *97*, 979; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 998.

(51) Bulak, E.; Paetzold, P. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1277.

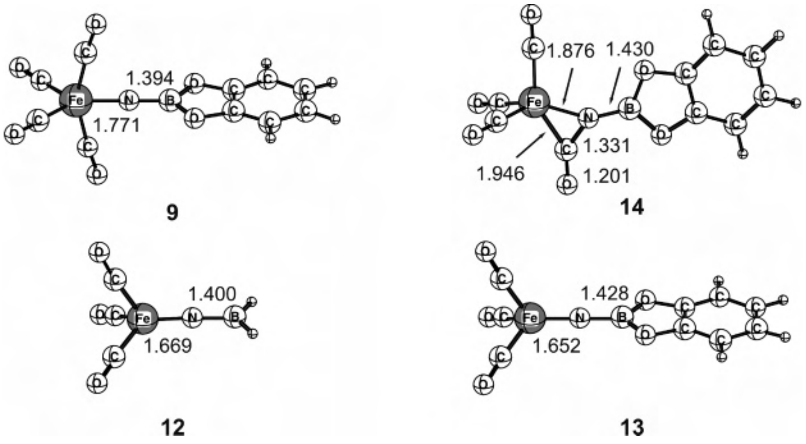

Figure 5. Geometries of **9** and **12**−**14** as computed at the RI-BP86/TZVP level of theory. Selected bond lengths are given in Å.

Table 3. Heats of Reaction at 0 K and Gibbs Free Energies of Reaction at 298.15 K for Eq 1 As Computed at the RI-BP86/TZVP Level of Theory (kcal mol^{-1})

L	$\Delta_R H$(0 K)	$\Delta_R G$(298.15 K)
CCH_2 (**1a**)	+49.7	+39.4
BNH_2 (**2a**)	+46.7	+36.3
NBH_2 (**3a**)	+18.7	+6.6
NBcat (**3b**)	+1.0	−11.8

the instability of complex **9**. Nonetheless, it is computed to favor the singlet over a triplet state ($\Delta E_{ST} = 7$ kcal mol^{-1}). From a technical perspective, it is worth mentioning that the spin-restricted description of **9** at the RI-BP86/TZVP level of theory does not show a triplet instability in spite of the small ΔE_{ST}.[52]

Compared with the NBH_2 ligand **3a**, NB(cat) (**3b**) thus has a higher tendency to act as a four-electron-donating imido ligand. Consequently, it is expected that NB(cat) better binds to a 14 valence electron metal fragment than NBH_2 does.[48] This is indeed observed for the $(CO)_3Fe-L$ complexes. Both $(CO)_3FeL$ borylnitrene complexes **12** (L = **3a**) and **13** (L = **3b**) are minima on the potential energy surface (see Figure 5 for geometries). The iron atom is in an approximate tetrahedral environment, although the ∠C−Fe−C angles are rather small (93 and 100°) while the ∠C−Fe−N angles are large (120 and 122°). The HOMO−LUMO gap in **12** (2.4 eV) is significantly larger than that in **9** (0.5 eV) and even in **7** (2.1 eV), hinting to an enhanced kinetic stability of **12**. The Fe−L bond dissociation energy is 108 kcal mol^{-1} for **12**, and this is increased by 5% to 113 kcal mol^{-1} in **13** (L = **3b**). The possible formation of the borylimido complexes (**12** and **13**) from their corresponding nitrene complexes (**7** and **9**) according to eq 1 is mildly endothermic for **3a** but thermoneutral for **3b** at 0 K (Table 3):

$$(CO)_4Fe-L \rightarrow (CO)_3Fe-L + CO \qquad (1)$$

For comparison, this reaction is highly endothermic for L = **1a** (+50 kcal mol^{-1}) and L = **2a** (+47 kcal mol^{-1}), but the corresponding $(CO)_3FeL$ species do not correspond to minima (L = **1a**, i202 cm^{-1}; L = **2a**, i92 cm^{-1}). Note that the pseudotetrahedral arrangement of the low-spin Fe(II) center in **12** and **13** is not without precedence in imido chemistry: Brown and Peters have structurally characterized the d^6 iron imide L_3FeNR (L = $[PhB(CH_2P^iPr_2)_3]^-$, R = 1-adamantyl) recently.[23] Earlier, Trinquier and Bertrand have concluded that a d^8 $Fe(CO)_3$ fragment would bind most strongly to phosphinidenes.[48]

Considering the entropic favor of reaction 1 at nonzero temperature, it could be expected that attempts at synthesizing complex **9** might actually result in complex **13**. However, reaction of **3b** with CO in the ligand sphere of the iron complex is more likely. As mentioned above, **9** is not a minimum on the potential energy surface, and reduction of symmetry to C_1 followed by relaxation of the geometry gives an isocyanato complex **14** bound in η^2-C,N fashion to a Fe(CO)$_3$ fragment (Figure 5). The structure of **14**, converged to C_s symmetry after optimization, is akin to that of the η^2-C,N isocycanato complex $Co(PhNCO)(PMe_3)_3$ determined by Klein et al.[53] using X-ray crystallography: the iron is roughly in a tetrahedral environment. The Fe−N and Fe−C distances (1.88 and 1.95 Å) in **14** are related to the Co−N and Co−C distances (1.95 and 1.88 Å). The distance between Fe and the midpoint M of the C−N bond computed to be 1.791 Å is almost identical with the experimental value (1.790 Å) determined for the Co−M distance.[53] In **14**, the CO molecule is now much more strongly bound (24.6 kcal mol^{-1}) toward formation of **13** + CO than in **9**. As the catBNCO ligand, on the other hand, is even more strongly bound (30.6 kcal mol^{-1}), CO loss cannot be excluded at elevated temperatures. However, due to the high reactivity of isocyanates, in particular in the presence of metals,[53] a more complex chemistry than that outlined here is not unlikely.

Conclusions

On the basis of the computational analyses of the borylnitrene complexes, it is concluded that an isostructural relationship with complexes **5** and **6** exists only for **7** but not for **9**, which carries the electron-donating chatecholate substituent.

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(52) Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047.

(53) Klein, H.-F.; Helwig, M.; Karnop, M.; König, H.; Hammerschmitt, B.; Cordier, G.; Flörke, U.; Haupt, H.-J. *Z. Naturforsch., B* **1993**, *48*, 785.

Rather unusual for nitrene complexes is the linear M−N−B arrangement found in **7**. However, on the basis of the low energy of the LUMO and the resulting rather small HOMO−LUMO gap, the small barrier for CO and hydrogen shifts to give the isocyanate and imino complexes, respectively, and the thermodynamic lability toward CO elimination, we conclude that complexes of type **7** should be highly reactive and labile. The catecholato group has pronounced influence on the structure of the complex: the typical trigonal bipyramidal arrangment around the iron atom does not correspond to a minimum on the potential energy surface; rather a tetrahedral isocyanate complex is obtained upon geometry optimization.

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Supporting Information Available: Cartesian coordinates and absolute energies of all stationary points discussed in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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