Notes

Mixed-Ligand Rhenium Tricarbonyl Complexes Anchored on a (κ^2-H,S) Trihydro(mercaptoimidazolyl)borate: A Missing Binding Motif for Soft Scorpionates

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*Summary: Complex fac-[Re{κ^3-H(μ-H)$_2$B(tim^{Me})}(CO)$_3$] (**1**) (tim^{Me} = 2-mercapto-1-methylimidazolyl) promptly reacts with the neutral substrates PPh$_3$, ^{t}BuNC and EtOOCCH$_2$NC yielding fac-[Re{κ^2-H$_2$(μ-H)B(tim^{Me})}(L)(CO)$_3$] (L = PPh$_3$(**2**), (^{t}BuNC) (**3**), (EtOOCCH$_2$NC) (**4**)). Complexes **2**−**4** have been fully characterized, including by variable-temperature NMR studies and X-ray diffraction analysis in the case of **2**. Unlike **1**, complexes **2**−**4** are fluxional in solution undergoing a dynamic process that accounts for the magnetic equivalence of all the B−H hydrogen atoms at room temperature. Compounds **1** and **2** were studied by DFT methods to explain the different solution behavior of the complexes anchored by (κ^2-H,S) and (κ^3-H,H′,S) soft scorpionates.*

Introduction

(Mercaptoimidazolyl)borates have been applied to enzyme modeling and more recently have been studied as ligands with Re and ^{99m}Tc due to the interest of these elements in the development of radiopharmaceuticals.[1–3] As part of our continuing interest in radiopharmaceutical sciences, we have explored the building blocks *fac*-[M{κ^3-R(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (M = Re, ^{99}Tc, ^{99m}Tc; R = H, Me, Ph), anchored on dihydrobis(mercaptoimidazolyl)borates, as platforms for designing target-specific radiopharmaceuticals, using different approaches.[4] However, for labeling low molecular weight biomolecules with high specific activity and retention of the biological activity and specificity, the development of small sized and stable metal fragments is an important issue.[5] To achieve such a goal we have recently described the first examples of trihydro(mercaptoimidazolyl)borates, which coordinate through two hydrides and one sulfur in scorpionate fashion (κ^3-H,H′,S) to the *fac*-[M(CO)$_3$]$^+$ moiety (M = Re, ^{99}Tc, ^{99m}Tc) in and from aqueous media.[6] It has been shown that such chelators, while providing a tridentate donor set (κ^3-H,H′,S) for binding to the metal, still retain the option of functionalization with targeting biomolecules, using the pendant or integrated approaches.[6] Taking into account that these unprecedented *fac*-[M{κ^3-R(μ-H)$_2$B(tim^{Me})}(CO)$_3$] complexes exhibit two B−H···M interactions, we wondered if it would be possible to break selectively only one of them with monodentate neutral substrates suitable to carry small biomolecules. Such a strategy, known as the [2 + 1] approach,[4,7] would allow a versatile and straightforward synthesis of a large number of biorganometallic complexes bearing different pharmacophores. In this paper, we report our efforts to validate this possibility, showing that in complex *fac*-[Re{κ^3-H(μ-H)$_2$B(tim^{Me})}Re(CO)$_3$] (**1**) only one B−H···M interaction can be disrupted by monodentate neutral substrates of the phosphine or isonitrile types leading to mixed-ligand complexes displaying the unprecedented (κ^2-H,S) binding motif. DFT studies, performed to rationalize the solution behavior of the mixed-ligand complexes and their precursor, are also presented.

Results and Discussion

As indicated in Scheme 1, complex **1** reacts with PPh$_3$, ^{t}BuNC or EtOOCCH$_2$NC, in toluene at room temperature, yielding quantitatively the complexes [Re{κ^2-H$_2$(μ-H)B(tim^{Me})}(L)(CO)$_3$] (L = PPh$_3$(**2**), ^{t}BuNC (**3**), EtOOCCH$_2$NC (**4**)). Independently of the amount of neutral substrates used, complexes **2**−**4** are the only species quantitatively formed, as indicated by ^{1}H and ^{11}B NMR spectroscopy. Compounds **2**−**4** were obtained as microcrystalline

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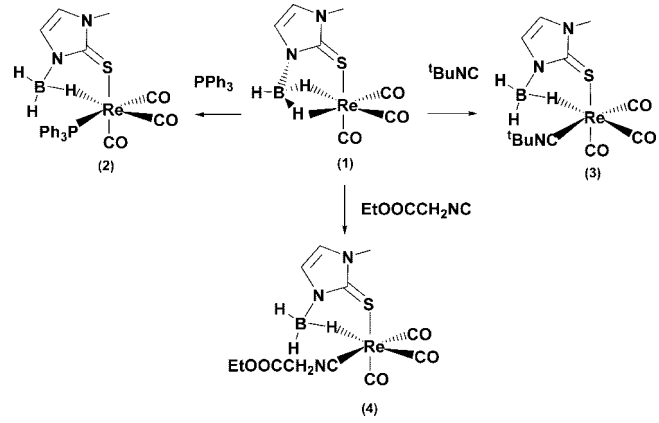
white solids, after removing the solvent (**3**) or after removing the solvent and purification by silica-gel flash chromatography (**2** and **4**). Unlike **2** and **3**, complex **4** was obtained with a relatively low isolated yield (37%), due most probably to partial decomposition in the column during the workup. Compounds **2**−**4** were characterized by ^{11}B, ^{13}C, and ^{1}H NMR, IR, elemental analysis, and, in the case of **2**, single-crystal X-ray diffraction.

The IR spectra of the compounds exhibit two (**2**) or three (**3**, **4**) very strong stretching bands in the 1896−2034 cm^{-1} range, assigned to the ν(CO) of the *fac*-[Re(CO)$_3$]$^+$ moiety.[8] For all the complexes the terminal ν(B−H) stretching bands, appearing in the range 2415−2442 cm^{-1}, could also be clearly identified. However, the bridging ν(B−H···Re) bands were only assigned in the IR spectra of **3** (2128 cm^{-1}) and **4** (2146 cm^{-1}). In the case of **2** this band occasionally overlaps with the two strong and broad ν(CO) stretching bands. The IR spectra of **2**, **3**, and **4** provide also additional evidence for the coordination of the neutral ligands, in particular for the isonitriles which display strong ν(C≡N) bands significantly shifted to high energies compared to the free ligands ($\Delta\nu$ = 57 cm^{-1}, **3**; $\Delta\nu$ = 71 cm^{-1}, **4**). The bidentate coordination mode of the trihydro(azolyl)borate in the mixed-ligand complexes **2**−**4** certainly justifies the significant high-field shift of the ^{11}B NMR signal of these complexes, relatively to the same resonance in complex **1** (11.9 ppm) ($\Delta\delta$ = 35.9 ppm, **2**; $\Delta\delta$ = 34.9 ppm, **3**; $\Delta\delta$ = 35.7 ppm, **4**). The ^{1}H NMR spectra of **2**−**4** present all the expected resonances for the mercaptoimidazolyl ring, as well as for the corresponding neutral substrates. At room temperature, the most striking difference between the ^{1}H NMR spectra of **2**−**4** and that of the precursor **1** is related to the chemical shift and splitting of the B−H resonances. For **1** two broad resonances appear at 6.20 (1H) and −5.48 (2H) ppm, which are due to the terminal and bridging B−H protons, respectively.[6] By contrast, the ^{1}H NMR spectra of **2**, **3**, and **4** present only one very broad resonance for the B−H protons at −0.47, −0.21, and −0.10 ppm, respectively. These data clearly indicate that the mixed-ligand complexes are fluxional in solution, exhibiting at room temperature a fast dynamic process in the NMR time scale, which accounts for the magnetic equivalence of the terminal and bridging B−H protons. The variable-temperature ^{1}H NMR studies performed for **2**−**4** have shown that by lowering the temperature the B−H resonances of **2**−**4** shift, collapse, and finally cause two broad resonances: one at high field between −6.33 and −7.01 ppm and another at lower field within the range 3.63–2.40 ppm. In the low-temperature spectra of **2**−**4** the pattern obtained for the terminal and bridging B−H protons compares well with the one found for **1** at room temperature.[6] All the other resonances in the spectra of **2**−**4** did not change with temperature, being only slightly shifted.

Single crystals of **2** were grown by cooling saturated solutions of the compound in hexane. An ORTEP presentation of complex **2** is given in Figure 1. The structural analysis confirmed the presence of the chemically robust *fac*-[Re(CO)$_3$]$^+$ moiety. The Re(I) atom is six-coordinated, displaying a distorted octahedral coordination geometry. One face of the coordination polyhedron is defined by the three carbonyl ligands, while the three remaining positions are occupied by one hydrogen and a sulfur atom from the trihydro(mercaptoimidazolyl)borate and by the phosphorus from the neutral substrate. In **2**, the Re−CO 1.910(5)−1.932(5) Å bond distances are shorter than the average Re−CO (1.953(8) Å) bond distance in the precursor **1**.[6] The Re−H (1.96(10) Å) and the Re−B (2.7793(58) Å) bond

Scheme 1. Synthesis of Complexes 2−4



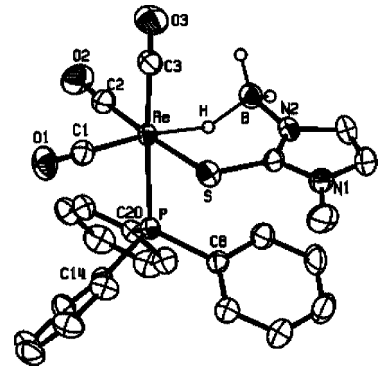


Figure 1. ORTEP view of *fac*-[Re{κ^2-(H)$_2$(μ-H)B(tim^{Me})}(PPh$_3$)(CO)$_3$] (**2**) with ellipsoids drawn at the 40% probability level. Selected bond distances (Å) and angles (deg): Re−C(1) 1.910(5), Re−C(2) 1.915(5), Re−C(3) 1.932(5), Re−H 1.91(5), Re−S 2.4913(14), Re−P 2.5063(12), Re−B 2.7793(58), C(1)−Re−C(2) 92.2(2), C(1)−Re−C(3) 90.2(2), C(1)−Re−S 90.79(15), C(2)−Re−S 176.70(15), C(1)−Re−P 92.15(15), C(2)−Re−P 94.86(15), C(3)−Re−P 176.55(15), S−Re−P 86.50(4), C(1)−Re−H 170.0(14), S−Re−H 91.7(14), P−Re−H 78.3(14).

distances in **2** are respectively, comparable and longer than the corresponding distances in **1** (av. Re−H, 1.91(5) Å; Re−B, 2.305(11) Å).[6] These differences can be explained by the different coordination mode of the azolyl borate in complexes **2** (κ^2-H,S) and **1** (κ^3-H,H′,S). The Re−S bond distance in **2** (2.4913(14) Å) is longer than the corresponding bond distance in **1** (2.470(2) Å) but is within the range found for the Re−S bond distances (2.462(6)−2.5190(11) Å) in previously reported *fac*-[M{κ^3-R(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (M = Tc, Re) complexes.[3,4,6]

DFT calculations[9] (G03/B3LYP[10]) were performed for complex **1** and a model of complex **2** (**2m**), where the phenyl groups of the phosphine were replaced by hydrogen atoms. The agreement between experimental and calculated structural parameters is good (see Table S1 in the Supporting Information), with maximum deviations below 0.1 Å, the largest one being associated with the Re−P bond, not so well modeled by PH$_3$. Calculations were also done to determine the ν(C≡O) and the terminal and bridging ν(B−H) vibrational modes for **1** and **2m.** The calculated values (Table S2, Supporting Information) are in good agreement with the experimental ones, considering that no scale factor was used. The frequencies of the ν(B−H) bridging vibration mode in **1** and **2m** lie below the high-intensity bands of the carbonyls, as suggested by the experimental data.

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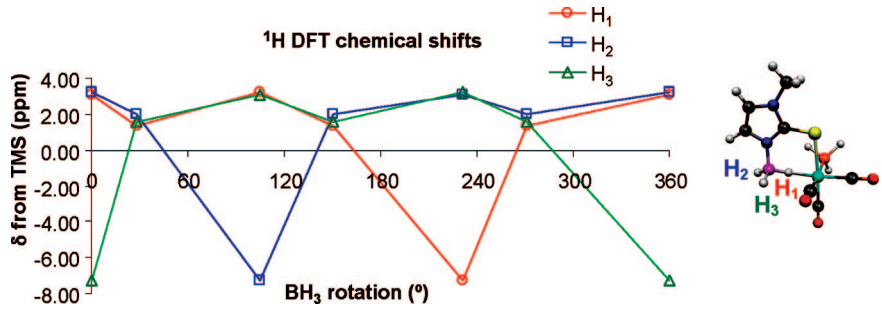

Figure 2. DFT calculated ^{1}H NMR chemical shifts for the H(B) protons in model complex **2m**, as the BH_3 rotates across the B−N bond.

NMR studies (see above) clearly suggest that the dynamic process responsible for the magnetic equivalence of the B−H protons in **2**−**4** involves only these atoms, the most probable mechanism being their scrambling.[11] This hypothesis was checked by DFT calculations (GIAO method[12]), allowing the BH_3 group to rotate across the N−B bond for complexes **1** and **2m**. A potential energy surface was obtained in each case with a 3-fold repetition pattern. The maxima were optimized as transition states and the same energy was obtained for the three in each molecule. The imaginary frequency mode corresponded to the rotation of the BH_3 group. The rotation barriers could thus be calculated as 8.6 and 20.1 kcal mol^{-1} for **2m** and **1,** respectively. The difference between these values explains the fluxional and static behavior found at room temperature for **2** and **1,** respectively.

The chemical shift of the B−H protons for each point along the pathway was also estimated. For **1**, as rotation proceeds the chemical shifts of the three B−H protons vary between the extreme values −5.16 and 4.20 ppm, which correspond to the bridging and terminal (B)−H protons, respectively. These values are in good agreement with the experimental chemical shifts found for **1** (B−H···Re, −5.48 ppm, 2H; B−H_{term}, 6.20 ppm, 1H). For complex **2m**, the calculated chemical shifts for the bridging and terminal B−H protons were respectively –7.29 and 3.10 ppm, intermediate values being expected during the rotation (Figure 2). These results are also in good agreement with the experimental chemical shifts found for those protons at low temperature (B−H···Re, –7.01 ppm, 1H; B−$H_{term.}$, 2.40 ppm, 2H).

In conclusion, we have shown that in complex **1** only one B−H···Re interaction can be disrupted by monodentate substrates of the phosphine and isonitrile types, independently of the reaction conditions. The mixed-ligand tricarbonyl complexes formed in these reactions, *fac*-[Re{κ^2-H_2(μ-H)B(tim^{Me})}(L)(CO)$_3$] (**2**−**4**), are the first organometallic complexes anchored on a trihydro(mercaptoazolyl)borate coordinating through one hydride and one sulfur in a (κ^2-H,S) fashion. ^{1}H NMR spectra at room temperature have shown that complex **1** presents a static behavior, while **2**−**4** are fluxional, certainly due to scrambling between the three B−H protons. DFT calculations carried out for **1** and for a model complex of **2** (**2m**) have shown that the rotation barrier of the B−H_3 group is higher in **1** (20.1 kcal mol^{-1}) than in **2m** (8.6 kcal mol^{-1}), justifying therefore the different solution behavior found for these complexes at room temperature.

Experimental Section

General Procedures. All chemicals and solvents were of reagent grade and were used without purification unless stated otherwise. The syntheses of the complexes were carried out under a N_2 atmosphere, using solvents which have been dried and distilled prior to use, according to described procedures. *fac*-[Re{κ^2-H(μ-H)$_2$B(tim^{Me})}(CO)$_3$] (**1**) was prepared as described previously.[6] ^{1}H, ^{11}C, ^{11}B, and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^{1}H and ^{11}C chemical shifts (ppm) were referenced with the residual solvent resonances relative to tetramethylsilane. The ^{11}B and ^{31}P NMR spectra were recorded in ppm relative to $BF_3 \cdot Et_2O$ and H_3PO_4 external references, respectively. IR spectra were recorded on a Perkin-Elmer 577 spectrometer as KBr pellets. Carbon, hydrogen, and nitrogen analyses were performed on a EA110 CE Instruments automatic analyzer.

Synthesis of Compounds 2–4. *fac*-[Re{κ^2-H$_2$(μ-H)B(tim^{Me})}(CO)$_3$(PPh$_3$)] (2). To a solution of *fac*-[Re(CO)$_3${κ^3-H(μ-H)$_2$B(tim^{Me})}] (**1**) (40 mg, 0.101 mmol) in dry toluene was added a solution of PPh_3 (40 mg, 0.151 mmol) in the same solvent. The mixture was stirred for 45 min at room temperature. The solvent was evaporated and compound **2** was purified by silica-gel flash chromatography, using CH_2Cl_2/*n*-hexane (65/35) as eluent. After removal of the solvent from the collected fractions, complex **2** was obtained as a microcrystalline white solid. Yield: 65% (43 mg, 65.2 μmol). Anal. Calcd (found) for $C_{25}H_{23}N_2SO_3BPRe$: C, 45.53 (44.82); H, 3.52 (3.68); N, 4.25 (4.22). IR (KBr, ν/cm^{-1}): 2415 (ν(B−H)), 2027, 1919 (ν(CO)). ^{1}H NMR ($CDCl_3$) (293K) δ (ppm): −0.47 (3H, br, BH_3), 3.17 (3H, s, CH_3), 6.50 (1H, d, 1.8 Hz, C−H), 6.43 (1H, d, 1.8 Hz, C−H), 7.44–7.31 (15H, m, Ph). ^{13}C NMR ($CDCl_3$) (293 K): 33.9 (N−Me), 121.9 (CH), 121.0 (CH), 133.7 (Ph), 132.1 (Ph), 130.1 (Ph), 127.9 (Ph), 160.8 (C═S), 191.2 (CO), 191.6 (CO), 192.9 (CO). ^{11}B NMR ($CDCl_3$) (293 K) (ppm): −24.01 (br). ^{31}P NMR ($CDCl_3$) (293 K) δ (ppm): 11.1. ^{1}H NMR ($CDCl_3$) (213 K) δ (ppm): −7.01 (1H, br, BH···Re), 2.40 (2H, br, B−H_{term}), 3.12 (3H, s, CH_3), 6.47 (1H, d, 1.8 Hz, C−H), 6.38 (d, 1.8 Hz, C−H), 7.42–7.28 (15H, m, Ph).

***fac*-[Re{κ^2-H$_2$(μ-H)B(tim^{Me})}(CO)$_3$(^{t}BuNC)] (3).** To a solution of *fac*-[Re(CO)$_3${κ^3-H(μ-H)$_2$B(tim^{Me})}] (**1**) (40 mg, 0.101 mmol)

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in dry toluene was added a slight excess of ^{t}BuNC (10.6 mg, 0.127 mmol), and the mixture was stirred for 1 h at room temperature. Compound **3** was recovered as a white solid, after removal of the solvent under vacuum. Yield: 99% (48 mg, 0.1 mmol). Anal. Calcd (found) for $C_{12}H_{17}N_3SO_3BRe$: C, 30.00 (30.85); H, 3.57 (3.08); N, 8.75 (8.51). IR (KBr, ν/cm^{-1}): 2442, 2398 ν(B−H), 2193 (ν(C≡N)), 2128 (ν(B−H···Re)), 2026, 1941, 1896 (ν(CO)). ^{1}H NMR (C_7D_8) (293 K) δ (ppm): 6.35 (1H, d, 1.8 Hz, C−H), 5.69 (1H, d, 1.8 Hz, C−H), 2.67 (s, CH_3), 0.74 (9H, s, $(CH_3)_3C$), −0.21 (3H, br, BH_3). ^{13}C NMR (C_6D_6) (293 K) δ (ppm): 29.55 ($\underline{C}-Me_3$), 33.46 ($C-(\underline{C}H_3)_3$), 57.08 ($N-CH_3$), 121.09 (CH), 122.30 (CH), 139.2 (CN), 162.48 (C═S), 189.33 (CO), 190.80 (CO), 191.10 (CO). ^{11}B NMR (C_6D_6) (293K) δ (ppm): −23.05 (br). ^{1}H NMR (C_7D_8) (193 K) δ (ppm): −6.33 (1H, br, BH···Re), 0.54 (9H, s, $(CH_3)_3C$), 2.37 (3H, s, $N-CH_3$), 3.63 (2H, br, $B-H_{term}$), 5.31 (1H, d, 1.8 Hz, C−H), 6.33 (d, 1.8 Hz, C−H).

***fac*-[Re{κ^2-H$_2$(μ-H)B(tim^{Me})}(CO)$_3$(EtOOCCH$_2$NC)] (4).** A solution of $CNCH_2COOEt$ (12.3 mg, 109 μmol) in dry toluene was added to a solution of *fac*-[$Re(CO)_3\{\kappa^3$-H(μ-H)$_2$B(tim^{Me})}] (**1**) (31 mg, 78 μmol) in the same solvent. The mixture was stirred for 1 h at room temperature and then the solvent was evaporated. Compound **4** was purified by silica-gel flash chromatography, using CH_2Cl_2/*n*-hexane (70:30) as eluent. Yield: η = 37% (20 mg, 40 μmol). Anal. Calcd (found) for $C_{12}H_{15}N_3SO_5BRe$: C, 28.24 (28.89); H, 2.96 (2.88); N, 8.23 (8.13). IR (ν/cm^{-1}): 2428 (ν(B−H)); 2207 (ν(B−H···Re)); 2146 (ν(C≡N)); 2034, 1958, 1912 (ν(CO)). ^{1}H NMR (C_7D_8) (293K) δ (ppm): −0.10 (3H, br, BH_3), 0.85 (3H, t, $CH_2C\underline{H}_3$), 2.75 (3H, s, $N-CH_3$), 2.82 (2H, s, $N-CH_2$), 3.64 (2H, q, $C\underline{H}_2CH_3$), 5.78 (1H, d, d, J_{H-H} = 1.8 Hz, CH), 6.42 (1H, d, J_{H-H} = 1.8 Hz, CH). ^{13}C NMR (C_7D_8) (293 K) δ (ppm): 13.66 ($CH_2\underline{C}H_3$), 33.46 ($N-CH_3$), 44.11 ($\underline{C}H_2CH_3$), 62.32 ($CN\underline{C}H_2$), 121.39 (CH), 122.28 (CH), 144.98 (CN), 162.46 (C═S), 162.73 ($\underline{C}OOEt$), 188.85 (CO), 190.43 (CO), 190.60 (CO). ^{11}B NMR (C_7D_8) δ (ppm): –23.80 (br). ^{1}H NMR (C_7D_8) (190 K) δ (ppm): –6.66 (1H, br, BH···Re), 0.77 (3H, br, $CH_2C\underline{H}_3$), 2.13 (2H, s, $N-CH_2$); 2.48 (3H, s, $N-CH_3$), 3.49 (2H, br,$C\underline{H}_2CH_3$; 2H, br, $B-H_{term}$), 5.46 (1H, d, d, J_{H-H} = 1.8 Hz, CH), 6.41 (1H, d, J_{H-H} = 1.8 Hz, CH).

X-ray Crystal Structure Determination of 2. A yellow crystal of **2** was mounted in a thin-wall glass capillary. The X-ray intensity data for **2** were collected at room temperature on an Enraf Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects as well as for absorption (numerical). Structures were solved with direct methods using SIR97[13] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[14] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms linked to the boron atoms were located in the difference Fourier map and refined isotropically. The remaining hydrogen atoms were placed in calculated positions. Crystal data for **2**: $C_{25}H_{23}BN_2O_3SPRe$, fw 659.49, triclinic $P\bar{1}$, a = 8.486(2) Å, b = 10.7559(19) Å, c = 15.5117(15) Å, α = 94.743(11)°, β = 103.313(12)°, γ = 109.504(17)°, V = 1278.9(4) Å^3, Z = 2, R_1= 0.0287 and wR_2 = 0.0626 ($I > 2\sigma$), R_1 = 0.0384 and wR_2 = 0.0648 (all data).

DFT Calculations. [9]DFT calculations were performed by using the Gaussian03[10a] program with the B3LYP hybrid functional, which includes a mixture of Hartree–Fock exchange with DFT exchange-correlation given by Becke's three-parameter hybrid functional with Lee, Yang, and Parr's gradient-corrected correlation functional. [10b,c] The basis set for Re consisted of the standard SDD basis set[15] augmented with an f polarization function in all calculations, [16] while the 6-311G** basis set[17] was used on all remaining atoms. The starting geometries of **1** and of **2m** were based on their single-crystal X-ray structures and were optimized without any symmetry constraints. Frequency calculations were performed at the same level of theory to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by irc calculations. NMR chemical shifts were calculated by using the GIAO algorithm,[12] with TMS (tetramethylsilane) as reference for ^{1}H and ^{13}C and $BF_3\cdot Et_2O$ for ^{11}B.

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Supporting Information Available: CIF files for **2** and DFT calculated bond lengths and angles, as well as carbonyl and B−H vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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