Single Electron Transfer to Diazomethane–Borane Adducts Prompts C–H Bond Activations

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In memory of Nicholas C. Payne

Abstract: While \((\text{Ph}_2\text{CN})_2\text{B}(\text{C}_5\text{H}_5)_2\) is unstable, single electron transfer from \(\text{ Cp}^*\text{Co}\) affords the isolation of stable products \([\text{Cp}^*\text{Co}][\text{Ph}_2\text{CNNHB}(\text{C}_5\text{H}_5)_2]\) \(\text{I}\) and \([\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_3\text{CH}_2\text{B}-(\text{C}_5\text{F}_5)_2])\) \(\text{II}\). The analogous combination of \(\text{Ph}_2\text{CN}\) and \(\text{BPh}_3\) showed no evidence of adduct formation and yet single electron transfer from \(\text{Cp}^*\text{Co}\) affords the species \([\text{Cp}^*\text{Co]}\cdot\cdot\cdot\text{Ph}[(\text{C}_5\text{H}_4\text{NNBPh}_3)_2]\) \(\text{III}\) and \([\text{Cp}^*\text{Cr}][\text{Ph}_2\text{CNNBHPh}_3]\) \(\text{IV}\). Computations showed both reactions proceed via transient radical anions of the diphenyl diazomethane–borane adducts to effect C–H bond activations.

The activation of small molecules has been a major driver of organometallic chemistry over the last 60 years. Such efforts have spawned great interest and important developments. In recent years, such inquiries have begun to permeate main group chemistry. One avenue of main group chemistry exploited for the activation of small molecules has been the frustrated Lewis pair (FLP) chemistry.[1] While this initially emerged from the finding of the heterolytic activation of \(\text{H}_2\) by combinations of Lewis acids and bases,[2] subsequent efforts demonstrated reactivity of FLPs with a wide range of small molecules.[3] Noticeably absent from these investigations have been studies involving dinitrogen.

Or ganometallic chemists have studied metal–N\(_2\) systems since the seminal report of A. D. Allen[4] who described the first transition metal–dinitrogen complex. Over the past 50 years numerous advances have emerged from the luminaries of organometallic chemistry including Schrock,[5] Cummins,[6] Peters,[7] Fryzuk,[8] Evans,[9] Gambarotta,[10] Nishibashi,[11] Holland,[12] Chat\(\text{i}\),[13] and Liddle[14] among others.[15] Avenues to metal-mediated \(\text{N}_2\) chemistry have typically involved stoichiometric reductants.[16] More recently, in 2017 the Szymczak[16] and Simonneau[17] groups demonstrated the utility of a Lewis acidic borane in promoting reactivity of metal-bound \(\text{N}_2\) fragments, effecting protonation, borylation and silylation of \(\text{N}_2\) bound between the metal and boron.

Main group interactions with \(\text{N}_2\) have drawn much less attention. A number of computational studies have addressed the interactions of \(\text{N}_2\) with Lewis acids, while the species \((\text{N}_2)_2\text{BF}_2\) was spectroscopically characterized upon generation by supersonic expansion at 600 torr and 170 K.[18] The compound \(\text{Ph}_2\text{PNPPh}_3\)[19] although not derived from \(\text{N}_2\), was controversially described as \(\text{N}_2\) stabilized by two phosphine donors.[20] However, in a truly seminal finding, Braunschweig et al.[21] described the first metal-free capture of \(\text{N}_2\) using a \(\text{cAAC}\)-stabilized borylene (\(\text{cAAC}\): cyclic (alkyl)(amino) carbene).

In our own efforts towards main group–\(\text{N}_2\) chemistry, we initiated studies of diazomethanes which liberate \(\text{N}_2\). Such systems may provide insight for the design of main group–\(\text{N}_2\) systems.[22] In 2012, we reported the insertion of diazomethanes into B–C bonds of electrophilic boranes with the liberation of \(\text{N}_2\), (Scheme 1).[23] Such insertions were recently exploited in organic synthesis by Melen et al.[24] In recent work,[25] we showed that the stericly-encumbered diazomethane, \(\text{Ph}_2\text{CN}\), does not insert but rather forms a highly reactive, yet isolable borane-adduct, \((\text{Ph}_2\text{CN})_2\text{B}(\text{C}_5\text{F}_5)_2\). Moreover, we also showed weak Lewis acid–base adducts were stabilized by stoichiometric reduction.[26] This notion was also exploited by the Erker group in the isolation of Lewis acid stabilized radicals.[27] Herein, we probe the impact of reduction on the reactivity of the unstable \((\text{Ph}_2\text{CN})_2\text{B}(\text{C}_5\text{F}_5)_2\), demonstrating that single electron transfer to diazomethane-borane adducts stabilizes weak B–N interactions providing reactive transient radicals which effect C–H bond activation.

A 1:1 combination of diphenyl diazomethane (\(\text{Ph}_2\text{CN}\)) with \(\text{B}(\text{C}_5\text{F}_5)_2\) in chlorobenzene was stirred at –35°C. Addition of an equal molar amount of \(\text{Cp}^*\text{Co}\) immediately gave a yellow solution. The crude \(1^\text{H}\) NMR spectrum showed two sets of resonances at –134.0, –163.9, and –167.3 ppm and –130.2, –161.9, –162.7 ppm, attributable to inequivalent \(\text{C}_5\text{F}_5\) rings. The \(1^\text{B}\) NMR spectrum showed two resonances at –7.6 and –13.0 ppm attributable to two tetra-coordinated boron species, \(\text{I}\) and \(\text{II}\), respectively. \(1^\text{B}\) NMR data showed resonances at 6.61 and 2.43 ppm attributable to NH and \(\text{CH}_2\) fragments. Fractional recrystallization permitted formulation of the two products \(\text{I}\) and \(\text{II}\) by X-ray crystallographic analysis. Compound \(\text{I}\) was found to be the salt \([\text{Cp}^*\text{Co}][\text{Ph}_2\text{CNNHB}(\text{C}_5\text{F}_5)_2]\) (Figure 1a). While the cation was unexceptional, the diazoborate anion was derived from the interaction of the hydrazide bound to borane. The \(\text{B}–\text{N}(\text{H})\) bond length in \(\text{I}\) is 1.539(7) Å, while the \(\text{N}–\text{N}\) and \(\text{C}–\text{C}\) bonds lengths is 1.342(5) Å.
and 1.303(7) Å, respectively. The B–N–N angle was determined to be 118.2(3)° while the C–N–N angle is 120.9(4)°. The second isolated product was confirmed to be 

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with am ethylene–boron B

\[ \text{co} \]

length of

and indendent combination of diazomethane with \( \text{[HB}(\text{C}_6\text{F}_5)_3]\) showed no reaction. This supports the view that compound 1 is formed through hydrogen atom abstraction from \( \text{Cp}^*\text{Co} \) by the transient diazomethane-borane adduct radical anion \( \text{[Ph}_2\text{CN} \text{B}(\text{C}_6\text{F}_5)_3]^- \) (Scheme 2), consistent with the overall reaction ratio of diazomethane: \( \text{Cp}^*\text{Co}: \text{B}(\text{C}_6\text{F}_5)_3 \) of 1:2:2.

Ph

\[ \text{CN} \]

was combined with \( \text{BPh}_3 \) in chlorobenzene at \(-35^\circ\text{C}\). Monitoring the solution by multinuclear NMR spectroscopy revealed no evidence of adduct formation. This is consistent with the poor Lewis basicity of the diazomethane and the weaker Lewis acidity of the \( \text{BPh}_3 \) in comparison to \( \text{B}(\text{C}_6\text{F}_5)_3 \), in line with the computed free energies (see Supporting Information). Addition of \( \text{Cp}^*\text{Cr} \) to a mixture of \( \text{BPh}_3 \) and diazomethane at \(-35^\circ\text{C}\) generated an orange solution. The \( ^{11}\text{B} \) NMR spectrum showed resonances at 23.0 and \(-3.5 \text{ ppm} \) consistent with the formation of two products, 3 and 4 which were isolated by fractional crystallization. An X-ray diffraction study revealed species 3 to be \( \text{[Cp}^*\text{Cr}]\text{[PhC}(\text{C}_6\text{H}_4)\text{NNBPh}_3] \) (Scheme 2, Figure 2a). While the cation was typical, the anion of 3 was shown to be a borate with a substituent derived from the cyclization of the \( \text{N}_2 \) fragment onto the \text{ortho} position of one of the aryl rings on the diazomethane carbon. The resulting five membered ring which is fused to the aryl ring is 1,3-disubstituted with a phenyl ring on carbon and \( \text{BPh}_3 \) bound to nitrogen. The resulting \( \text{N}–\text{B} \) bond is 1.566(6) Å, while the \( \text{N}–\text{N} \) and new \( \text{N}–\text{\text{\text{N}}_2} \) fragments.

Collectively, the identification of 1 and 2 is consistent with two possible reaction mechanisms involving single electron transfer from a \( \text{Co}^3\) center to either \( \text{B}(\text{C}_6\text{F}_5)_3 \) or the diazomethane adduct of the borane, \( \text{[Ph}_2\text{CN}_2 \text{B}(\text{C}_6\text{F}_5)_3]^- \). It is noteworthy that although C–H activation by the radical \( \text{[B}(\text{C}_6\text{F}_5)_3]^- \) is expected to give the anion \( \text{[HB}(\text{C}_6\text{F}_5)_3]^- \), independent combination of diazomethane with \( \text{[HB}(\text{C}_6\text{F}_5)_3]^- \) showed no reaction. This supports the view that compound 1 is formed through hydrogen atom abstraction from \( \text{Cp}^*\text{Co} \) by the transient diazomethane-borane adduct radical anion \( \text{[Ph}_2\text{CN} \text{B}(\text{C}_6\text{F}_5)_3]^- \) (Scheme 2), consistent with the overall reaction ratio of diazomethane: \( \text{Cp}^*\text{Co}: \text{B}(\text{C}_6\text{F}_5)_3 \) of 1:2:2.

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C bond distances are determined to be 1.312(5) and 1.351-1.353(5) Å. The second product \(4\) was also characterized crystallographically revealing its formulation as \([\text{Cp}^*\text{Cr}][\text{Ph}_5\text{CNNHBPh}_3]\) (Scheme 2, Figure 2b). The B–N and N–N distances in the anion of \(4\) were determined to be 1.562(4) Å and 1.322(3) Å, respectively.

In contrast, the reaction of 9-diazofluorene \([(\text{C}_5\text{H}_4\text{N})\text{CN}_2]\) with \(\text{B}(\text{C}_6\text{F}_5)\), did not form an adduct but led to loss of \(\text{N}_2\) (Scheme 3) and the formation of the carboboration product \((\text{C}_5\text{H}_4\text{B}(\text{C}_5\text{F}_5)\text{CN}(\text{C}_5\text{F}_5))\) as confirmed spectroscopically and crystallographically (see Supporting Information). This is consistent with observations seen for less sterically encumbered diazomethanes.\(^{23,30}\) However, monitoring the reaction of \((\text{C}_5\text{H}_4\text{N})\text{CN}_2\) with \(\text{BPH}_3\) and \(\text{Cp}^*\text{Cr}\) by \(^1\text{H}\) NMR spectroscopy revealed the generation of three products as evidenced by the resonances at 26.2, 2.4, and 1.7 ppm. The peaks at 1.7 and 2.4 ppm were unambiguously assigned to \([\text{Cp}^*\text{Cr}][\text{C}_5\text{H}_4\text{N}][\text{CNH}](\text{BPH}_3)\) \(5\) and \([\text{Cp}^*\text{Cr}](\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{BP})\) \(6\) by NMR and crystallographic methods (Figure 3, see Supporting Information). The remaining resonance at 26.2 ppm, was attributed to the species \([\text{Cp}^*\text{Cr}][\text{C}_5\text{H}_4\text{N}][\text{CNH}](\text{BPH}_3)\) \(6\) by analogy to \(3\). These results suggest that the electron transfer to the weak adducts gives a transient radical \((\text{C}_5\text{H}_4\text{N}\text{CN}(\text{BPH}_3)\text{)N}^–\), which reacts further through competitive pathways involving either intramolecular cyclization or intermolecular H-atom abstraction.

The mechanism of these reactions were probed by density functional theory (DFT) calculations at the PW6B95-D3/def2-QZVP + COSMO-RS// TPSS-D3/def2-TZVP + COSMO level of theory in chlorobenzene solution.\(^{31}\) The reaction of \(\text{Ph}_5\text{CN}_2\) with \(\text{BPH}_3\) and \(\text{Cp}^*\text{Cr}\) is initiated by single electron transfer from \(\text{Cp}^*\text{Cr}\) to the unstable \(\text{Ph}_5\text{CN}_2\text{BPH}_3\) adduct (Figure 4) affording the radical anion \([\text{Ph}_5\text{CNNHBPH}_3]\text{N}^–\) \(\text{INT1}\) (spin on N next to B: 0.53e) is 4.3 kcal mol\(^{-1}\) endergonic. Alternative pathways involving electron transfers to separated \(\text{BPH}_3\) and \(\text{Ph}_5\text{CN}_2\) species (14.8 and 8.9 kcal mol\(^{-1}\)) are significantly less favorable. Similarly, further electron transfer to \(\text{INT1}\) is unlikely (12.2 kcal mol\(^{-1}\) endergonic). The N-centered radical \(\text{INT1}\) may then add intramolecularly to the \(\text{ortho}\) position of a phenyl ring (via transition structure \(\text{TS1}\)) to give \(\text{INT2}\) affording delocalization of the spin onto the ring. From here, a highly exergonic H-transfer to another \(\text{Ph}_5\text{CN}_2\) molecule (via \(\text{TS2}\)) gives the anion of \(3\) and the neutral N-radical \([\text{Ph}_5\text{CNNHBPH}_3]\text{Co}^+\) (spin on N next to H: 0.54e) with a moderate overall barrier of 23.5 kcal mol\(^{-1}\). The latter radical is readily reduced by \(\text{Cp}^*\text{Cr}\) through electron transfer and trapped by \(\text{BPH}_3\) giving the anion of \(4\) (–66.4 kcal mol\(^{-1}\))

For the reaction of \(\text{Ph}_5\text{CN}_2\) with the stronger Lewis acid \(\text{B}(\text{C}_6\text{F}_5)\), the more reductive \(\text{Cp}^*\text{Co}\)\(^{32}\) electron transfer from \(\text{Cp}^*\text{Co}\) to the reversible adduct \([\text{Ph}_5\text{CNNHBPH}_3]\text{B}(\text{C}_6\text{F}_5)\text{Co}\) is –15.3 kcal mol\(^{-1}\) exergonic affording the radical anion \([\text{Ph}_5\text{CNNHB}(\text{C}_6\text{F}_5)\text{Co}\text{N}]^–\). This intermediate is computed to effect H-atom from one methyl group of \(\text{Cp}^*\text{Co}\) over a barrier of 16.6 kcal mol\(^{-1}\) to form the stable anion of \(1\) (see Supporting Information). The alternative intramolecular pathway, analogous to that above encounters a higher overall barrier of 23.3 kcal mol\(^{-1}\) (see Supporting Information).

To garner further support for the computed mechanism, efforts to observe the transient radical adducts in the reactions were undertaken, but were unsuccessful. However, monitoring the reaction of \((\text{C}_5\text{H}_4\text{N})\text{CN}_2, \text{Cp}^*\text{Fe}\) and \(\text{Al}(\text{C}_6\text{F}_5)\) in \(\text{C}_5\text{H}_4\text{Cl}\) at room temperature by EPR spectroscopy revealed a pentet resonance at g(iso) = 2.0039, with \(^{13}\text{N}\) hyperfine couplings of 3.70 G and 3.58 G. This signal was similar to the related \(\text{N}\)-based radicals\(^{33}\) and was attributed to the radical species \([\text{Ph}_5\text{CN}_2\text{Al}(\text{C}_6\text{F}_5)\text{N}]^–\). This signal slowly degrades at room temperature over 5 h, leaving a broad resonance attributed to an organic radical (see Supporting Information). Subsequent addition of \(\text{Ph}_5\text{SnH}\) generated a mixture of products, from which \([\text{Cp}^*\text{Fe}]\)\([\text{C}_5\text{H}_4\text{N}][\text{CNH(Ph}_5\text{BPH}_3)\text{)Co}]\) \(7\) was identified by NMR spectroscopy while single crystals of \([\text{Cp}^*\text{Fe}]\)\([\text{C}_5\text{H}_4\text{N}][\text{CNH(Ph}_5\text{BPH}_3)\text{)Co}]\) \(9\) were obtained from the reaction mixture (Figure 5). Com-

Figure 4. DFT-computed free energy profile (kcal mol\(^{-1}\), at 298 K and 1 mol L\(^{-1}\) reference concentration) for the formation of anion of \(3\) and \(4\). Selected bond lengths are given in angstroms while selected C: grey, H: white, N: blue, and B: pink.

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Figure 5. POV-Ray depiction of the anion of a) 8 and b) 9. The cation and hydrogen atoms (except the NH and the Al-bound CH) are omitted for clarity. C: black, N: blue, Al: cyan, and F: pink.

Scheme 4. Reactions of (C3H3)3CN-Al(Cp3)3− and [(C3H3)CHAl(Cp3)3]− (Scheme 4).

In conclusion, we have demonstrated that single electron transfer to unstable diazomethane-borane adducts, accesses reactive radical anions that effect H-atom abstraction from C–H bonds. The resulting anionic species are significantly more stable than the corresponding neutral adducts, suggesting that in situ reductions may be a useful strategy to infer the presence of weakly bound adducts. We suggest that this strategy could be exploited in developing main group-N2 chemistry. At the same time, the potential utility of main group radical anions in C–H bond homolysis offers an interesting prospect for C–H functionalization.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: borane · DFT · diazomethane · one-electron reduction · radical anions

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