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Frustrated Lewis Pairs

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Exchange chemistry of *t*Bu₃P(CO₂)B(C₆F₅)₂Cl⁺

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Halide exchange from the species $tBu_3P(CO_2)B(C_6F_5)_2Cl 1$ with Me₃SiOSO₂CF₃ gave $tBu_3P(CO_2)B(C_6F_5)_2(OSO_2CF_3) 2$. Similarly, Lewis acid exchange occurs in reactions of 1 with Al(C₆F₅)₃ and [Cp₂TiMe][B(C₆F₅)₄] affording the products, $tBu_3P(CO_2)Al(C_6F_5)_3 3$ and $[tBu_3P(CO_2)TiCp_2Cl][B(C_6F_5)_4] 4$.

The dramatic increase in atmospheric CO₂ levels has been shown to be a major contributing factor in global climate change.¹ Efforts to mitigate emissions have focused on reduced consumption, improved efficiencies and new technologies to capture the carbon products of combustion.² In our efforts we have been exploring fundamentally new reactivity of main group systems toward this end. In these efforts, we have uncovered the notion of "frustrated Lewis pairs" (FLPs) and have demonstrated that such systems react with a variety of small molecules.³⁻⁶ In particular, combinations of sterically demanding phosphines and boranes have been shown to reversibly bind CO₂.⁷ The O'Hare and Piers groups have since extended this chemistry to effect the reduction of CO2.8,9 We have also examined CO2 insertions into B-amidinates¹⁰ as well as explored bis-borane-containing systems. These latter systems demonstrate binding of both Oatoms of the CO₂ moiety to boron with phosphine binding to the central C-atom (Fig. 1).¹¹ Nonetheless, a common feature of these P/B CO₂ systems is their inherent thermal instability resulting in CO₂ loss and regeneration of the FLP thus, precluding further reactivity of the "activated" CO2 fragment. Recent efforts have also explored related Al-P FLP systems and demonstrated that the species $Mes_3PC(OAIX_3)_2$ (X = Cl, Br)¹² are readily formed and stable species capable of further reactivity of the CO₂ fragment. In this case, reduction employing ammonia borane with subsequent hydrolysis resulted in the stoichiometric reduction of CO₂ to methanol.¹² More recently, we reported that Mes₃PC(OAlX₃)₂ reacts further with CO₂ to liberate CO, Mes₃PC(OAlX₂)₂OAlX₃ and [Mes₃PX][AlX₄].¹³

Recent studies have probed the impact of substituent modification on the stability of boron- and phosphorus-based FLP-CO₂ and formate derivatives.¹⁴ In that work, the species $tBu_3P(CO_2)$ B(C₆F₅)₂Cl **1** was prepared. Herein, we explore the further reactivity of **1**, demonstrating that exchange of Cl for triflate is possible without loss of CO₂. The ability to perform such exchange

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Fig. 1 Examples of FLP-CO₂ derivatives.



Scheme 1 Synthesis of compounds 2–4.

chemistry is of interest as many of these CO_2 -complexes are thermally unstable and in extreme cases liberate CO_2 above -20 °C.⁷ Moreover, reactions of **1** with stronger Lewis acids provide facile pathways to access new main group- and transition metal- CO_2 derivatives.

Initial attempts to abstract chloride from $tBu_3P(CO_2)B$ (C₆F₅)₂Cl **1** *via* reaction with NaBPh₄ and Ag(OSO₂CF₃) resulted in no reaction. In contrast, stoichiometric reactions of **1** with K[B(C₆F₅)₄] or [Et₃Si][B(C₆F₅)₄] appeared to react, however the respective products could not be readily isolated. However, reaction of **1** with a stoichiometric equivalent of Me₃SiOSO₂CF₃ cleanly led to the facile and near quantative isolation of a new product **2** (Scheme 1). This product exhibited ³¹P {¹H} and ¹¹B{¹H} NMR signals at 48.88 and 3.76 ppm, respectively. These values are similar to those seen for **1**. The ¹H NMR

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Fig. 2 POV-Ray depiction of **2**, B: yellow-green, C: black, O: red, F: pink, P: orange, S: yellow, H-atoms are omitted for clarity.

data were consistent with the presence of tBu moieties while the ¹⁹F NMR spectrum showed resonances at -78.59 and -134.40, -157.34 and -164.94 ppm attributable to the presence of triflate and chemically equivalent fluoroarene rings on B. The IR spectrum exhibited a C=O stretch at 1706 cm^{-1} further supporting the retention of the CO₂ moiety. Repetition of the reaction employing 1-13C showed P-C coupling of 93 Hz, reaffirming the presence of the P-CO₂ bond. These data led to the formulation of 2 as the product of Cl-triflate metathesis $tBu_3P(CO_2)B$ $(C_6F_5)_2(OSO_2CF_3)$. Crystals suitable for X-ray diffraction were grown from a layered solution of CH₂Cl₂ and hexanes and the crystal structure confirmed the proposed formulation (Fig. 2).‡ The geometry about B is pseudo-tetrahedral with a B-O bond distances of 1.498(2) Å and 1.545(2) Å to the CO₂ and triflate fragments, respectively. The corresponding C-O bond distance in the CO₂ moiety is 1.318(2) Å while the B-O-C angle is 118.7(1)°. The terminal C=O bond distance was found to be 1.199(2) Å. The P-C bond distance to the CO₂-carbon was found to be 1.892(1) Å. While this latter metric parameter is similar to that seen in $tBu_3P(CO_2)B(C_6F_5)_3$ (P–C: 1.893(1) Å, B-O: 1.547(2) Å)⁷ and $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2(CO_2)$ (P-C: 1.900(3) Å, B-O: 1.550(4) Å),⁷ the B-O bond distance in 2 is significantly shorter, consistent with the stronger Lewis acidity of $B(C_6F_5)_2(OSO_2CF_3)$ versus $B(C_6F_5)_3$. The P-C bond of **2** is also longer than that reported for $Me_2C = C(BCl_2)_2(CO_2)$ PtBu₃ (P-C: 1.874(3) Å, B-O: 1.577(4) Å, 1.585(3) Å)¹⁴ and slightly shorter than that in Me₂C= $C(B(C_6F_5)_2)_2(CO_2)PtBu_3$ (P-C: 1.896(2) Å, B-O: 1.647(3) Å, 1.672(3) Å). It should be noted, that the B-O distance in 2 is significantly shorter than those seen in these bisborane compounds.

Compound **1** was also observed to react with an equivalent of (0.5tol)·Al(C₆F₅)₃ at room temperature to give a faintly yellow solution which following manipulation yielded a white solid **3** in 65% isolated yield (Scheme 1). This species gave rise to a ³¹P {¹H} signal at 46.65 ppm, however no ²⁷Al NMR signal was discernible at room temperature. The ¹⁹F data consisted of signals at -123.12, -155.83 and -163.39 ppm supporting the inclusion of the Al(C₆F₅)₃ moiety. An infrared absorption at



Fig. 3 POV-Ray depiction of 3, C: black, O: red, F: pink, Al: bluegrey, P: orange. H-atoms are omitted for clarity.

band at 1686 cm^{-1} was consistent with the retention of CO₂ in 3. Reaction of $1^{-13}C$ with 0.5tol·Al(C₆F₅)₃ yielded $3^{-13}C$ which displayed a resonance in the ${}^{31}P{}^{1}H$ NMR at 47.72 ppm with a P-C coupling constant of 89 Hz, corresponding to a one bond phosphorous-carbon coupling. Previously reported activation of CO₂ by aluminum-based FLPs involved the Lewis acid in a 2 : 1 ratio relative to the Lewis base. However, in the exchange chemistry of 1 with a single equivalent of 0.5tol·Al(C₆F₅)₃, there proved to be complete conversion to 4 with no evidence of unreacted 1 thereby confirming the presence of a 1:1 Lewis base to Lewis acid CO₂ activation product. Collectively, the spectroscopic data in addition to elemental analysis were consistent with the formulation of **3** as $tBu_3P(CO_2)Al(C_6F_5)_3$. This was subsequently confirmed crystallographically (Fig. 3).‡ There are two molecules in the asymmetric unit where both phosphines are bound to the C of CO₂ with P–C distances of 1.884(2) Å and 1.885(2) Å, respectively. A single oxygen atom of the CO_2 fragment was found to be bound to Al with a O-Al distance averaging 1.828(2) Å. The terminal C=O bond distances were found to be 1.208(2) Å and 1.211(2) Å.

To probe the exchange capabilities with a transition metalbased Lewis acid, compound 1 was reacted with a solution in which the Ti-cationic salt $[Cp_2TiMe][B(C_6F_5)_4]$ was preformed via the reaction of Cp_2TiMe_2 and $[Ph_3C][B(C_6F_5)_4]$. The deep red-brown solution of the Ti cation progressively and quickly lightened in colour to a vibrant red. After stirring for an hour, manipulation afforded an orange solid 4 in 96% yield (Scheme 1). The ${}^{31}P{}^{1}H$ NMR spectrum of 4- ${}^{13}C$ revealed the P-C coupling of 86 Hz, inferring that the phosphine-CO₂ fragment was successfully exchanged between the Lewis acid centers. This was further supported by the observation of the infrared absorption at 1670 cm⁻¹, assignable to the carbonyl stretching frequency. ¹¹B{¹H} and ¹⁹F NMR spectra confirmed that the $[B(C_6F_5)_4]$ anion was a component of 4 with no evidence of residual $ClB(C_6F_5)_2$. The ¹H NMR spectrum showed a resonance at 6.65 ppm attributable to the cyclopentadienyl rings on Ti as well as a signal at 1.66 ppm attributable to the tert-butyl



Fig. 4 POV-Ray depiction of the cation of **4**, C: black, O: red, P: orange, Cl: green, Ti: grey. H-atoms and the $B(C_6F_5)_4$ counter anion are omitted for clarity.

groups, however no resonance was assignable to a methyl group bound to Ti. These data did not allow an unambiguous formulation of 4, however the nature of the compound was determined via X-ray diffraction employing crystals grown from a solution of CH₂Cl₂ layered with hexanes (Fig. 4).[‡] The X-ray data confirmed 4 as the salt, $[tBu_3P(CO_2)TiCp_2Cl][B(C_6F_5)_4]$. In this case, following liberation of the Lewis acid $ClB(C_6F_5)_2$, there was Cl-Me exchange between the free Lewis acid and titanocene fragment. The coordination sphere of the cation was shown to involve coordination of tBu₃PCO₂ to [Cp₂TiCl] with a Ti-O bond distance of 2.016(2) Å. The titanocene fragment is as expected with a Ti-Cl bond length of 2.3171(9) Å. The O-C and C=O bond distances to the carbon of CO₂ were determined to be 1.270(3) and 1.220(3) Å, while the P-C bond length was found to be 1.896(3) Å. The Ti-O-C and O-C-O angles were determined to be 135.8(2)° and 128.2(3)° while the O-C-P angles were found to 116.3(2)° and 115.5(2)°, respectively.

The derivatives **3** and **4** are thought to form by transient interaction of the incoming Lewis acid with the terminal C=O oxygen atom, affording a purported intermediate analogous to $Mes_3PC(OAIX_3)_2$.¹² The congestion in the present cases, results in the steric ejection of the borane, $CIB(C_6F_5)_2$. This strategy of Lewis acid exchange from FLP derivatives has previously found utility in the preparation of Zn–N₂O derivatives from the FLP-N₂O complex *t*Bu₃PN₂OB(*p*-C₆H₄F).¹⁵

Conclusions

The FLP-CO₂ species $tBu_3P(CO_2)B(C_6F_5)_2Cl 1$ can be derivatized *via* exchange of the halide for triflate to give **2**. Alternatively, the borane is readily exchanged for the alane Al(C₆F₅)₃ or the Ti-cation [Cp₂TiCl] affording compounds **3** and **4** respectively. The further reactivity of FLP systems with CO_2 and the subsequent chemistry of such species are the subject of ongoing efforts in our laboratory.

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Notes and references

‡2: C₂₆H₂₇BF₁₃O₅PS MW = 740.32, Space group: triclinic, $P\bar{1}$, *a* = 9.7343(4) Å, *b* = 10.7665(4) Å, *c* = 14.9487(6) Å, *α* = 98.123(1)°, *β* = 97.127(2)°, *γ* = 106.658(1)°, *V* = 1463.3(1) Å³, *Z* = 2, *μ* = 0.287, *T* = 150(2) K. Total data: 24 536, *R*_{int} = 0.0226, Unique Data = 6690, Variables = 444, *R*(>2σ) = 0.0303, *R*(all) = 0.0835, GOF = 1.043.3: C₃₁H₂₇AlF₁₅O₂P, MW = 774.48, Space group: monoclinic, *P*2₁/*n*, *a* = 18.2162(8) Å, *b* = 15.2634(7) Å, *c* = 24.776(1) Å, *β* = 108.346(2)°, *V* = 6538.7(5) Å³, *Z* = 8, *μ* = 0.226, *T* = 150(2) K. Total data: 59519, *R*_{int} = 0.0472, Unique Data = 15499, Variables = 919, *R*(>2σ) = 0.0464, *R*(all) = 0.1219, GOF = 1.018.4: C₄₇H₃₇BClF₂₀O₂PTi, MW = 1138.90, Space group: triclinic, *P*I, *a* = 10.7349(9) Å, *b* = 14.415(1) Å, *c* = 15.088(1) Å, *α* = 85.942(4)°, *β* = 88.205(4)°, *γ* = 81.850(5)°, *V* = 2304.8(3) Å³, *Z* = 2, *μ* = 0.400, *T* = 150(2) K. Total data: 35 285, *R*_{int} = 0.0578, Unique Data = 10 393, Variables = 707, *R*(>2σ) = 0.0483, *R*(all) = 0.1080, GOF = 1.011.

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