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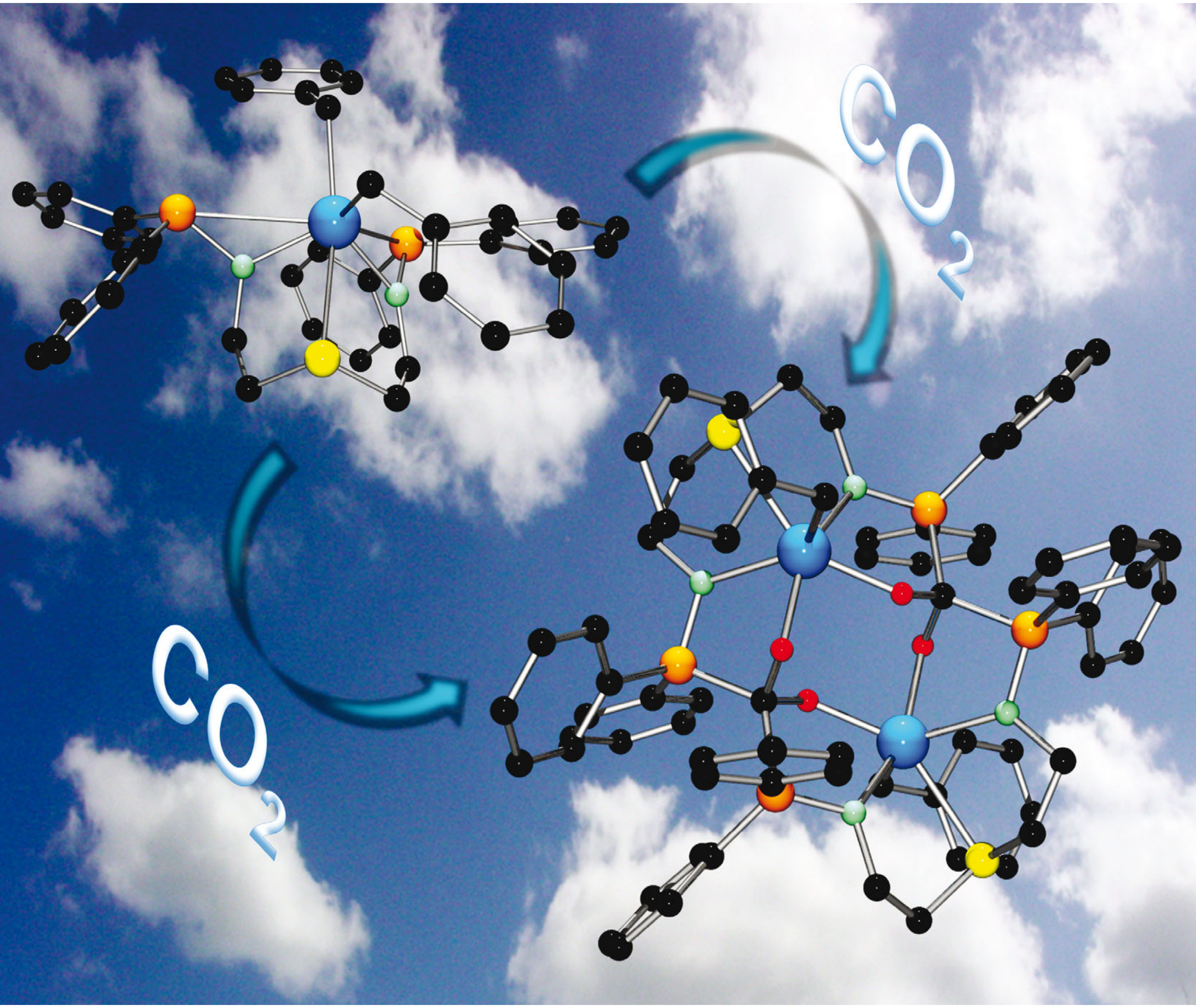

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Activation of CO_2 by phosphinoamide hafnium complexes†

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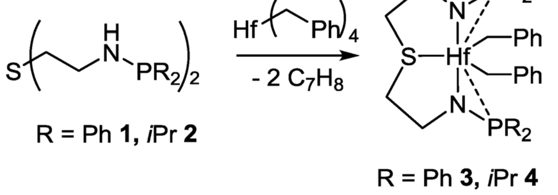
Hf–phosphinoamide cation complexes behave as metal-based frustrated Lewis pairs and bind one or two equivalent of CO_2 and in as well can activate CO_2 in a bimetallic fashion to give a pseudo-tetrahedral P_2CO_2 fragment linking two Hf centres.

Global warming and climate change are issues of considerable importance that are undeniably linked to the increase in the atmospheric concentration of CO_2.[1] It is this reason that has prompted the flourishing interest in the reactivity of CO_2, with extensive efforts on-going to develop strategies to effect its capture and storage. For example, materials such as zeolites, aluminas, activated carbons[2] and metal organic frameworks (MOFs)[3–5] have been explored in this regard. An alternative approach to address the increasing atmospheric CO_2 level is to employ CO_2 as a C_1 feedstock.[6–11] This latter approach has generated interest in the development of catalysts for the reduction of CO_2, with Ru,[10–14] Ir[15] and Fe[16,17] receiving particular attention.

As an alternative to the more conventional organometallic approach to the activation of small molecules, the past few years has seen the concept of "frustrated Lewis pairs" (FLPs) emerge as an effective strategy.[18–20] In the case of CO_2, since the initial report of CO_2 capture by FLPs, the chemistry has indeed been expended to effect reduction. In this context, Ashley *et al.*[21] demonstrated the conversion of CO_2 to MeOH under forcing conditions. Subsequently we reported the stoichiometric conversion of CO_2 to methanol[22] or CO[23] using Al/P based FLPs. In related work, Piers and coworkers described the catalytic deoxygenative hydrosilation of CO_2, generating methane.[24]

More recently, transition metal systems capable of FLP-like reactivity have been described.[25–28] Wass *et al.* have demonstrated the ability of metallocenium phosphinoaryloxide complexes to capture CO_2 in a FLP like fashion between the Lewis acidic metal center and the pendant phosphine.[26] In a related sense, the Sanford and Milstein groups have recently used ruthenium catalysts containing the tridentate ligands $(C_5H_3N)(CH_2PtBu_2)(C_5H_4N)$ and $(C_5H_3N)(CH_2PtBu_2)(CH_2NEt_2)$ for the catalytic reduction of CO_2 to MeOH,[12,13] exploiting systems capable of the cooperative activation of CO_2 by the ligand and the metal center.[29,30] Very recently we have been exploring complexes with phosphinoamine ligands,[31,32] and reported a tris–aminophosphine ruthenium complex that can trap CO_2 in an FLP-like fashion.[33] In this case, addition of boranes results in the catalytic reduction of CO_2 to $MeOBR_2$ and R_2BOBR_2. In seeking to extend the range of complexes capable of CO_2 capture, we were prompted to explore early metal phosphinoamide complexes. Herein we report the synthesis of Hf complexes of such ligands and demonstrate that the weakly interacting phosphine donors afford FLP-like reactivity to capture CO_2. Such derivatives are shown to either capture up to two equivalents of CO_2 or afford the unprecedented FLP-like double activation of CO_2 by metal-based Lewis acids and phosphine donors.

The preparation of phosphinoamide complexes was undertaken *via* the reaction of the phosphinoamines $S(CH_2CH_2NHPR_2)_2$ (R = Ph **1**, *i*Pr **2**) with $Hf(CH_2Ph)_4$ in THF. This generated complexes $S(CH_2CH_2NPR_2)_2Hf(CH_2Ph)_2$ (R = Ph **3**, *i*Pr **4**) in 78% and 72% yield, respectively (Scheme 1). The $^{31}P\{^1H\}$ NMR spectra of these products display singlet resonances at 4.0 ppm and 11.8 ppm, respectively, and the *in situ* ^1H NMR spectra confirm the loss of the NH functionalities and the formation of toluene. In addition, triplet resonances were observed at 2.62 ppm (**3**) and 2.42 ppm (**4**) in the ^1H NMR spectra and these signals correlate with $^{13}C\{^1H\}$ resonances at 73.2 and 73.8 ppm, respectively. Interestingly these resonances exhibit coupling to ligand



Scheme 1 Synthesis of **3** and **4**.

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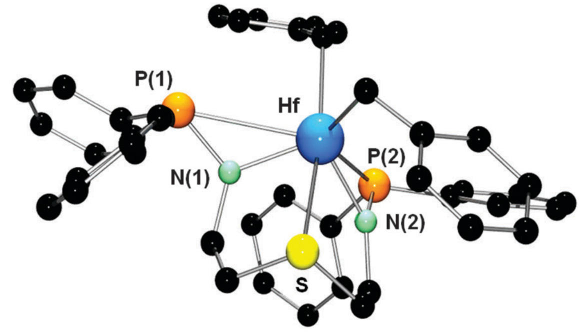


Fig. 1 POV-ray depiction the molecular structure of **3**. C: black, P: orange, N: aquamarine, S: yellow, Hf: slate blue; all H-atoms are omitted for clarity.

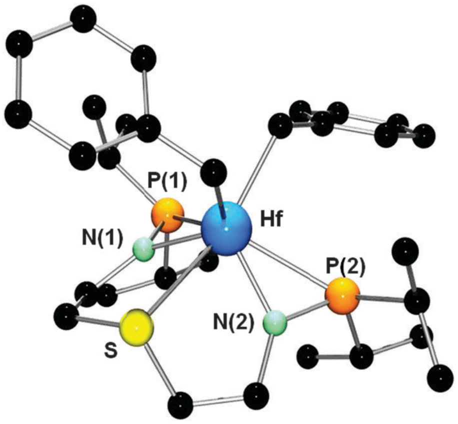


Fig. 2 POV-ray depiction of the molecular structure of **4**. C: black, P: orange, N: aquamarine, S: yellow, Hf: slate blue; all H-atoms are omitted for clarity.

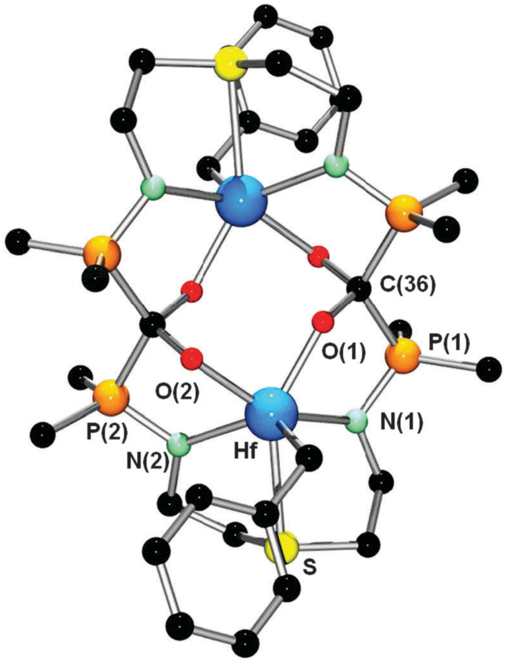


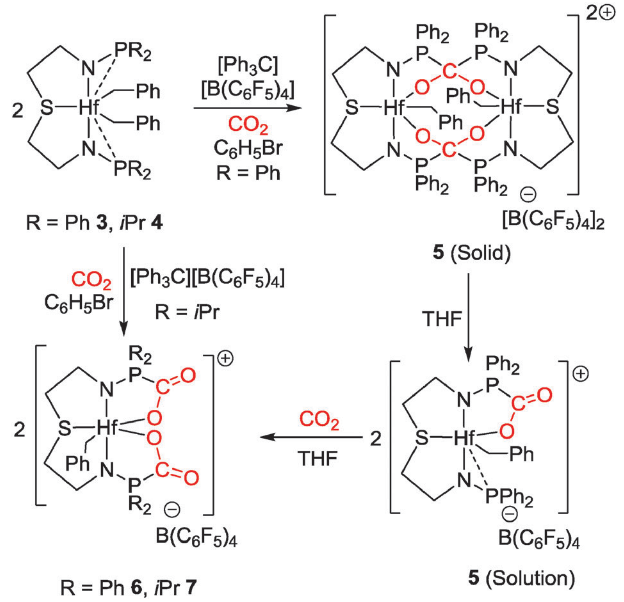
Fig. 3 POV-ray depiction of the cation of the molecular structure of **5**. C: black, P: orange, N: aquamarine, O: red, S: yellow, Hf: slate blue; phenyl carbon from PPh_2 except C_{ipso} omitted for clarity. All H-atoms are omitted for clarity.

phosphorus atoms ($^3J_{HP}$ = 5 Hz, $^2J_{CP}$ = 7 Hz). In each case, these signals were attributed to the methylene groups of two remaining benzyl groups on Hf. Single crystal X-ray diffraction studies of **3** and **4** reveal unique coordination geometries about Hf (Fig. 1 and 2) in which the metal is coordinated to the N_2S donors of the phosphinoamide ligand and two benzyl carbons. The Hf–N and Hf–S distances were found to be 2.052(2), 2.071(2) and 2.8939(8) Å, respectively. The latter distance reflects the soft nature of the thioether S donor. In addition, the P atoms also interact with the Hf center to some degree. For **3**, the Hf–P distances are 2.6897(8) and 3.0743(8) Å, while for **4**, the two Hf–P distances were found to be 2.7212(14) and 2.8244(11) Å. The longer Hf–P distance in **3** suggests a very weak interaction consistent with lower basicity of the PPh_2 fragment in comparison to the P*i*Pr2 units in **4**. The shorter distances in **4** are consistent with the greater basicity of the P centers. Previously reported Hf–P bonds in phosphine adducts of $HfCl_4$ range from 2.808(2) to 2.825(5) Å (ref. 34) while Wass *et al.* reported a P–Hf distance of 2.8209(6) Å in the cation $[Cp_2HfOC_6H_4PtBu_2]^+$.[25] The differences in the N–Hf–P angles in **3** of 31.05(7) and 38.13(6)° parallel the Hf–P distances and may arise from the steric congestion about the metal. In the case of **4** the N–Hf–P angles are 35.83(9) and 37.3(1)°.

Addition of $[Ph_3C][B(C_6F_5)_4]$ to **3** or **4** in C_6D_5Br generates the corresponding cationic species by benzyl abstraction. In the case of the reaction of **3**, further slow addition of an atmosphere of CO_2 over 12 h, results in the subsequent isolation of colorless plates of **5** in 62% yield. An X-ray diffraction study of **5** revealed the capture of two equivalents of CO_2 by two Hf complexes yielding the twofold symmetric bimetallic species $[S(CH_2CH_2NPPh_2)_2Hf(CH_2Ph)(CO_2)]_2[B(C_6F_5)_4]_2$ (Scheme 2). Two pendant phosphines from the two complexes bind to each of the C atoms of the two CO_2 molecules while the oxygen atoms are bound to the two Hf centers (Fig. 3). The P–C bond lengths of 1.878(2) and 1.880(2) Å are similar to those observed for the Zr–FLP system $[Cp_2Zr(OC_6H_4PtBu_2CO_2)]^+$ described by Wass and coworkers (1.892(4) Å). The C–O bonds of 1.383(3) and 1.369(3) Å are both significantly longer than those previously described in B/P and Al/P-based FLP–CO_2 complexes consistent with the strong Lewis acidity of the Hf centers. Although Cummins and coworkers[35] have reported a bimetallic species in which Ta centers are linked by a OCH_2O^{2-} fragment derived from CO_2 insertion in the corresponding Ta-hydride species, to the best of our knowledge, **5** represents the only example in which CO_2 is doubly activated by phosphine donors that has been crystallographically characterized. In this regard, Fontaine and coworkers have described the species $(Me_2PCH_2AlMe_2)_2(CO_2)$ in which two P–C bonds are also formulated.[36]

Complex **5** exhibited poor solubility in most organic solvents, but NMR data were obtained in d_8-THF. Employing $^{13}CO_2$, a doublet at 168.1 ppm with a $^1J_{CP}$ of 138.9 Hz is observed in the $^{13}C\{^1H\}$ NMR spectrum. The corresponding $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 36.3 ppm ($^1J_{PC}$ 138.9 Hz) and a singlet at 2.5 ppm. These data infer that **5** is monomeric in THF solution. Variable temperature NMR studies to −80 °C showed no evidence of dimer formation.

Subjecting a solution of **5** in THF to 1 atm of CO_2 prompted quantitative formation of a new product, **6**, as evidenced by



Scheme 2 Synthesis of **5–7**.

NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **6** reveals one singlet at 31.9 ppm, and the ^1H and $^{13}C\{^1H\}$ resonances attributable to the methylene groups of the ligand backbone are consistent with a symmetric molecule. Employing $^{13}CO_2$, the signal in the $^{31}P\{^1H\}$ NMR spectrum became a doublet with $^1J_{CP}$ of 133.1 Hz while the $^{13}C\{^1H\}$ NMR spectrum displays the corresponding doublet at 166.5 ppm. These data are consistent with the uptake of a second equivalent of CO_2 to give $[S(CH_2CH_2NPPh_2(CO_2))_2Hf(CH_2Ph)][B(C_6F_5)_4]$ **6**. Removal of the CO_2 atmosphere or when a solution of **6** is subjected to vacuum, loss of one equivalent of CO_2 occurs and **5** is reformed.

The corresponding treatment of **4** with $[Ph_3C][B(C_6F_5)_4]$ and 1 atm of CO_2 in C_6D_5Br yielded the product **7**. This species exhibits a singlet at 67.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum, that is a doublet with $^1J_{CP}$ of 122.5 Hz when $^{13}CO_2$ is used. The corresponding $^{13}C\{^1H\}$ NMR spectrum shows a doublet at 166.4 ppm while the IR spectrum shows an absorption at 1644 cm^{-1}, consistent with activated CO_2.[37,38] These data indicate that **7** is a symmetric structure consistent with the formulation as $[S(CH_2CH_2NPiPr_2(CO_2))_2Hf(CH_2Ph)][B(C_6F_5)_4]$ (Scheme 2). Unlike **6**, **7** is stable in the absence of CO_2 and can be isolated in 77% yield. The greater stability of **7** over **6** is attributed to the enhanced basicity of the P centers.

In conclusion, phosphinoamines have been shown to bind to Hf *via* the N-atom, providing weak interaction with P. Generation of cationic Hf centers provides a combination of a Lewis acidic metal center with a pendant donor-phosphine that can act in concert to bind one or two equivalents of CO_2. The basicity of the phosphine center determines the stability the resulting complex. In addition, we have also confirmed activation of a CO_2 fragment by two phosphine donors affording tetrahedral P_2CO_2 links between two Hf centers. We are continuing to exploit phosphinoamine–amide ligand complexes in probing metal-based chemistry that emulates FLPs with a view to effecting the activation of other small molecules and developing new approaches to catalysis.

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