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Short communication

Reduction of CO_2 to methanol using aluminum ester FLPs

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ABSTRACT

Herein we report the synthesis of Al-based esters containing halogenated benzene rings. These Lewis acids were paired with phosphines to form frustrated Lewis pairs (FLPs) which could subsequently bind CO_2. While these FLPs were not sufficiently water-stable to catalyze the reduction of CO_2 to MeOH using NH_3BH_3 as the reductant, we examine the effect of varying Lewis acid strength.

Frustrated Lewis pairs (FLPs) are combinations of Lewis acids and Lewis bases where the acid and base are either sterically or geometrically restricted from interacting as strongly as their electronic structures would allow. This effect leads to enhanced reactivity towards small molecules and, consequently, interest in their potential as metal-free catalysts [1–5]. To-date, the biggest success has been based around the ability of a myriad of systems to heterolytically cleave H_2 and perform catalytic hydrogenations [2,3].

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A variety of FLPs have been shown to bind CO_2, but relatively few FLPs support the conversion of CO_2 into useful reduction products such as MeOH [6,7] or CH_4 [8,9]. In particular, $PMes_3/AlCl_3$ and $PMes_3/AlBr_3$ react with CO_2 and ammonia borane (NH_3BH_3) to form MeOH upon quenching with H_2O [10]. However, the stability of the resulting Al–O bonds formed precludes catalytic reactivity. The pathway for this reaction is not clear, with computational results arguing for a stepwise mechanism [11], while further experimental results support the possibility of a more complicated pathway involving dissociation of components from the $PR_3(CO_2)(AlX_3)_2$ adduct [12]. More recently, using the concept of enhancing FLP reactivity through geometric constraint (preorganization) [13,14], a vicinal P–B was found to catalyze the formation of methoxyborates from CO_2 and various borane-based reducing agents [15,16]. As with $PMes/AlX_3$, MeOH is released upon quenching with H_2O, albeit with the formation of boric acid (a thermodynamic sink).

One of the limiting factors in this chemistry is the oxophilicity of B and Al. Not only does this cause an issue with concomitant H_2O formation during CO_2 conversion to MeOH (assuming hydrogenation as the model), but it also necessitates high temperatures if thermal extrusion of MeOH is attempted [6]. Our hypothesis at the outset of this work was that the use of B- and Al-esters [17] may decrease the H_2O-sensitivity of this class of complexes. While complexes of the type $A(OR)_3$ (A = B, Al, R = Me, *i*Pr, *t*Bu, Ph) are available commercially, they do not exhibit reactivity with CO_2 when paired with PCy_3 or PPh_3. With the exception of $Al(OPh)_3$ (Table 2), this is consistent with a relatively lower Lewis acidity of the esters. Thus we turned towards esters bearing more electron-withdrawing substituents.

$Al(OC_6F_5)_3$ (**F-5**) is a dimeric complex in the solid state ($[Al(OC_6F_5)_3]_2$) that can be synthesized by addition of $AlEt_3$ to a toluene solution of HOC_6F_5 [18,19]. Similar reaction conditions using HOC_6Cl_5 and HO-2,4,6-Cl_3Ph can be used to synthesize $[Al(OC_6Cl_5)_3]_2$ ((**Cl-5**)$_2$) and $[Al(O\text{-}C_6H_2Cl_3)_3]_2$ ((**Cl-3**)$_2$) respectively. (**Cl-5**)$_2$ is insoluble in toluene, and so precipitates from solution as a white solid during synthesis. In contrast, (**Cl3**)$_2$ is slightly soluble in toluene. While we did not obtain a solid-state structure of (**Cl-5**)$_2$, based upon (**F-5**)$_2$ and (**Cl-3**)$_2$ as well as other complexes such as $[Al(O\textit{t}Bu)_3]_2$ [20], $[Al(O\text{-}2,6\text{-}Me_2Ph)_3]_2$ [21], and $[Al(OCH(CF_3)_2)_3]_2$ [22], it is reasonable to believe that it also adopts a dimeric structure.

Addition of PPh_3 to (**Cl-3**)$_2$ allowed for the isolation of (PPh_3)**Cl-3** from toluene and its structural determination (Fig. 1). The Al–P bond length is 2.438 [4] Å. To the best of our knowledge PPh_3 adducts of aryl Al esters of this type have not been previously structurally characterized. A few PPh_3-Al adducts are available in the Cambridge Structural Database for comparison. The Al–P bond lengths of $(PPh_3)AlEt_3$ [23] and $(PPh_3)AlMe_3$ [24] are 2.5413 [4] Å and 2.535 [1] Å respectively. For $(PPh_3)AlCl_3$ [25] and $(PPh_3)Al(OC(CF_3)_3)_3$ [26], this distance is 2.4296 [15] Å and 2.447 [2] Å. The longest Al–P bond lengths being in the alkyl aluminum complexes is consistent with the concept that they are the most electron rich and thus least Lewis acidic (see Table 2). It is also reasonable that PPh_3-$AlCl_3$ would exhibit a shorter Al–P distance. The increased Al–P distance within $(PPh_3)Al(OC(CF_3)_3)_3$ [27] does not follow this trend, but it could be due to more favorable hydrogen

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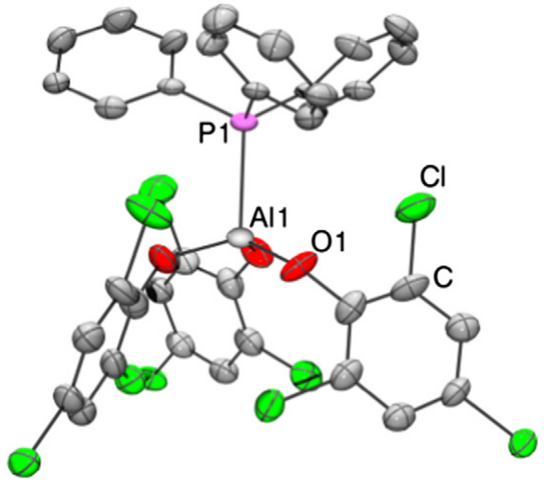

Fig. 1. X-ray crystal structure of PPh_3-(**Cl-3**) with hydrogen atoms omitted and 50% thermal ellipsoids.

bonding interactions [25]. Attempts to quantify the Lewis Acidity trend via the [31]P NMR shift of $OPEt_3$ were ambiguous due lack of clear 1:1 $OPEt_3$-$AlOR_3$ adduct formation.

Density functional theory (B3LYP/DZVP2) [28–30] and G3MP2 [31] electronic structure calculations of the bond dissociation free energies of AlX_3/PR_3 (X = H,F,Cl,Br,CH_3; R = H, CH_3) adducts (Table 1) are not consistent with a clear trend along the halogens (which agrees with the varied rankings available in the literature), but it is clear that more electron-rich phosphines bind more tightly (PH_3 vs. PMe_3) and that more electron-rich alanes bind more loosely (AlH_3 vs. $AlMe_3$ vs. AlX_3, X = F, Cl, Br).

The negativity of the fluoride affinity (FA = ΔH(298) for the reaction $A + F^- \rightarrow AF^-$) of a compound has been shown to be a good measure of its Lewis acidity [34,35]. The fluoride affinities of the types of AlR_3 compounds being discussed have been calculated at the density functional theory B3LYP/DZVP2++//B3LYP/DZVP2 (for Br and I, the aug-cc-pVDZ-PP basis sets were used) level with the values for AlR_3, R = H, F, Cl, Br, I, benchmarked at the CCSD(T) FPD level (Table 2). The computational details are given in the Supporting Information. The CCSD(T) FPD results show that the DFT B3LYP results are semi-quantitative. The aluminum esters have FA's that range from moderately strong ~90 kcal/mol (O-tBu, O-i-Pr) to very strong ~120–130 kcal/mol (O-C_6Cl_5, O–$C(CF_3)_3$). The latter are stronger Lewis acids than SbF_5 [34]. The calculations were done with the Gaussian and MOLPRO program systems [36,37],

Similar to PPh3-Al(OC(CF3))3 [26], we did not observe splitting of H2 with PPh3-**F-5**, but the PPh3 adduct did bind CO_2. However, these early experiments displayed indications of aryl C–H activation and so further work was conducted using PCy3 despite the expected higher binding energy (more electron-rich phosphine). PCy3-(**Cl-3**) shows slow C–H activation of CH_2Cl_2, with the appearance of [HPCy3] + in the 31P NMR spectrum. This was verified using CD_2Cl_2 (see supporting information).

Table 1
B3LYP/GZVP2 and G3MP2 gas-phase dissociation energies (kcal/mol) of AlX_3/PR_3 adducts[a].a

Lewis acid–base adduct	B3LYP (ΔG(298 K))	G3MP2 (ΔG(298 K))
AlH_3PH_3	−0.2	4.8[a]
AlH_3PMe_3	7.1	17.3
$AlMe_3PH_3$	−4.8	−0.1
$AlMe_3PMe_3$	1.2	10.6
AlF_3PH_3	11.6	9.8
AlF_3PMe_3	26.7	25.5
$AlCl_3PH_3$	6.2	8.8
$AlCl_3PMe_3$	21.0	27.0
$AlBr_3PH_3$	4.5	8.8
$AlBr_3PMe_3$	18.7	27.8

[a] A highly accurate calculated value [32] for ΔH_{298} obtained at the Feller–Peterson–Dixon (FPD) level [33] is 14.7 kcal/mol as compared to the G3MP2 value of 13.2 kcal/mol and the B3LYP value of 10.8 kcal/mol.

Table 2
Negative of the fluoride affinity of AlR_3 calculated at the density functional theory level. FPD benchmark values in parentheses.

R	FA (kcal/mol)	R	FA (kcal/mol)
H	84.8 (90.3)	O–$C(CF_3)_3$	129.5
F	112.0 (113.9)	O-C_6Cl_5	121.4
Cl	116.3 (118.8)	O-$C_6H_2Cl_3$	114.2
Br	110.4 (119.4)	O-C_6H_5	111.4
I	110.7 (120.6)	O-i-C_3H_7	91.3
CH_3	79.5	O-t-C_4H_9	87.8
C_2H_5	81.5	O-Et	90.7
O–Me	89.4	O-C6F5	128.7

Testing for CO_2 reactivity was accomplished by exposing a degassed solution or mixture of PCy3 and Lewis acid to ca. 1 atm. of $^{13}CO_2$ and then examining the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. In contrast to $Al(OiPr)_3$, $Al(OtBu)_3$, and $Al(OPh)_3$, **F-5**, **Cl-3**, and **Cl-5** all bind CO_2 with diagnostic ^{31}P–^{13}C coupling when paired with PCy_3 (see Fig. 2 as an example).

The Al systems structurally characterized by Stephen et al. show a 2:1:1 Al:CO_2:P ratio [10,12]. In contrast, reports of known B-based Lewis acid FLP-CO_2 complexes predominantly have a 1:1:1 B:CO_2:P ratio [1]. This difference likely arises from the decreased Lewis acidity and oxophilicity of B relative to Al. This would also be consistent with known pre-organized P-Al complexes lacking electron-withdrawing groups binding CO_2 through only one aluminum center. While we were unable to obtain a solid-state structure of a CO_2 adduct, the solution $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of our Al:CO_2:P adducts are consistent with a mixture consisting of mostly the 1:1:1 complex when $^{13}CO_2$ is added to a 1:2 PCy_3:**Cl-3** mixture (Est. 5–9% *bis*). It would be expected that the CO_2 carbon atom would have less electron density when two Lewis acids are coordinated to the CO_2 moiety rather than one. This is consistent with the observed shift in the NMR spectra where the carbon atom is effectively deshielded. Taking this view, this Al ester is more akin to Lewis acids such as $B(C_6F_5)_3$ than AlX_3 in terms of FLP reactivity. As the aryl substituent is adjusted going to **Cl-5** (Est. ca. 1:1 *bis*:*mono*) and then **F5** (Est. 23–26% *mono*), this balance changes and the mixture becomes more biased towards bis coordination. This is a trend that tracks with what one may predict based on trends in substituent electron-withdrawing ability. The stronger the Lewis acid, the greater the average number of acids there are per CO_2.

Regardless of the ratio, addition of NH_3BH_3 to $PCy_3/CO_2/Al(OR)_3$ (**F-5**, **Cl-5**, **Cl-3**) systems resulted in complete conversion of PCy_3 to $[HPCy_3]^+$ as determined by $^{31}P\{^1H\}$ and ^{31}P NMR spectra. $^{13}C\{^1H\}$ NMR spectra show a methoxy group (presumably coordinated to $Al(OR)_3$) along with formate in the case of **F-5** and **Cl-3**. Addition of H_2O to these mixtures releases MeOH, but also results in the decomposition of the aluminum esters.

Aluminum esters derived from halogenated aromatic alcohols were synthesized and tested as Lewis acids for the FLP-mediated reduction of CO_2 using NH_3BH_3. While **F-5**, **Cl-5**, and **Cl-3** were competent in this regard when paired with PCy_3, the reaction could not be made catalytic due to the need to quench the resulting complex with H_2O in order to release MeOH. It may be possible to use stoichiometric quantities of H_2O to preserve these esters [26], however, the FLP would still need to be regenerated from the resulting H_2O adduct. These results reinforce the need to develop systems that can release MeOH under mild thermolysis rather than form Al (and B) oxides and hydroxides which require much more energy to regenerate into usable FLPs. This is a limitation that even catalytic FLP-mediated CO_2 reduction to MeOH suffers

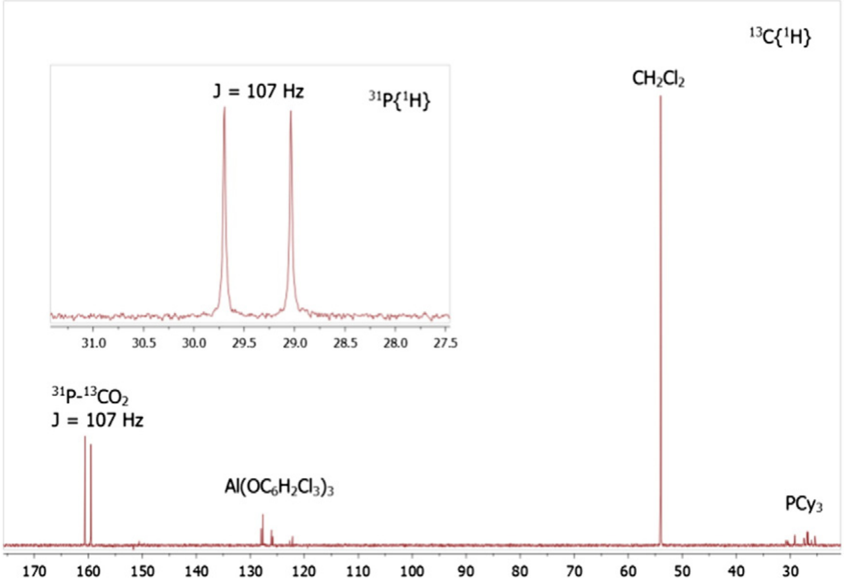

Fig. 2. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (inset) of $^{13}CO_2$ addition to a 1:1 mixture of PCy_3:$Al(OC_6H_2Cl_3)_3$ in CH_2Cl_2 showing ^{31}P–^{13}C coupling.

[15]. We have also examined the effect of tuning Lewis acid strength within an analogous class of complexes.

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Appendix A. Supplementary data

Experimental procedures, spectroscopic data, X-ray crystallographic data in the CIF format and computational details with full references. Crystal structure data has also been deposited with the CCDC (http://www.ccdc.cam.ac.uk). **(Cl-3)$_2$**: 1,047,472, PPh_3-**Cl-3**: 1,047,471. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.inoche.2015.10.009

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