

# Synthesis and characterization of metal (M = Al or Ga) 2-phosphino (phenolate/benzenethiolate) complexes and their electrochemical behavior in the presence of CO<sub>2</sub>

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**Abstract.** A series of Group 13 complexes MLX<sub>2</sub> (M = Al or Ga, L = SC<sub>6</sub>H<sub>4</sub>-2-P<sup>t</sup>Bu<sub>2</sub> or OC<sub>6</sub>H<sub>4</sub>-2-P<sup>t</sup>Bu<sub>2</sub>, X = Me or C<sub>6</sub>F<sub>5</sub>) have been synthesized and characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction. Reactions of Me<sub>3</sub>Al or Me<sub>3</sub>Ga with an equivalent of either 2-<sup>t</sup>Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)OH (**1**) or 2-<sup>t</sup>Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)SH (**5**) resulted in the formation of four new (**2,3,6**, and **7**), 4-coordinate dimethyl chelate (S,P or O,P) complexes via methane elimination. The dimethyl gallium complexes (**3** and **7**) underwent a further reaction with excess B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, and through ligand exchange (methyl/pentafluorophenyl), resulted in the disubstituted bis(pentafluorophenyl) analogs (**4** and **8**). Cyclic voltammetry (CV) experiments for all compounds in the presence of and the absence of (**1–8**) CO<sub>2</sub> were performed. For compounds showing cathodic reduction waves under CO<sub>2</sub> (**2,3,4**, and **6**), bulk electrolysis experiments were performed. Electrochemical studies indicate that, for several compounds, a transient CO<sub>2</sub> adduct is formed which undergoes a one-electron, irreversible (or partially irreversible) reduction to form an unstable radical anion.

Keywords: Carbon dioxide, main-group complex, cyclic voltammetry, X-ray crystallography, phosphinophenolate, phosphinobenzenethiolate, frustrated Lewis pair

## 1. Introduction

A mainstay of homogeneous catalysis is the activation of small molecules and their subsequent reactions to afford targeted chemical products, thereby using the small molecule as a building block. One of the most desirable small molecule synthons is CO<sub>2</sub>, as it is cheap, abundant, and can serve as a renewable source for higher-carbon feedstocks [1]. The activation of CO<sub>2</sub> at transition metal centers

has been thoroughly examined, which has resulted in a variety of metal-CO<sub>2</sub> adducts, most often with an electron-rich metal center interacting with the Lewis acidic carbon of CO<sub>2</sub> [2]. Far less examined is the activation of CO<sub>2</sub> by main-group metal complexes and to an even lesser extent, systems in which a secondary atom in the coordination sphere is involved in the activation of the CO<sub>2</sub> [3]. This is somewhat surprising as this is precisely how nature activates CO<sub>2</sub> during photosynthesis, a highly effective process for carbon fixation which results in an annual production of 10<sup>11</sup> tons of biomass [2c].

The coordination of CO<sub>2</sub> in an active site of the RuBisCO (Ribulose-1,5-bisphosphate carboxylase/oxygenase) enzyme consists of a dual Lewis acid-base pair. One pair consists of an O atom from CO<sub>2</sub> coordinating to a Mg<sup>2+</sup> Lewis acid metal center with a second pair between an  $\epsilon$ -NH<sub>2</sub> group in lysine and the C atom in CO<sub>2</sub> [4]. It is this evidence that initially inspired our research group to design and synthesize a variety of main-group (B, Ca, Ge, In, Mg, Pb, Sr and Sn) complexes containing accessible base sites in the ligand architecture, which has resulted in a number of successful dual Lewis acid-base adducts and insertion products upon reaction with CO<sub>2</sub> [5]. This synergistic behavior between a Lewis acid (main-group metal) and a Lewis base site (lone-pair base in ligand) towards CO<sub>2</sub> complexation has been detailed from the context of frustrated Lewis pairs (FLPs), [6] and there have been several reports of FLPs being used to activate CO<sub>2</sub> (See Fig. 1) [3, 7]. With the expansion of FLPs to include Lewis pairs which are not sterically encumbered, [8] one could certainly consider our previous main-group complexes to satisfy the criteria required for FLP status.

Once CO<sub>2</sub> is activated, the logical next step is to introduce a secondary reagent targeting chemistry at the C atom of the CO<sub>2</sub>, with hopes of releasing new, useful carbon-containing products and regenerating the main-group complex in a catalytic fashion. To this end, several of our previously reported main-group complexes were tested for their behavior in proton-coupled electron transfers (PCETs), where simple, single-carbon products such as CO, HCOOH, or CH<sub>3</sub>OH were desired [5n, 5o, 9]. Initially, we limited electrochemical experiments to include only complexes persistent enough to reveal crystallographic evidence of CO<sub>2</sub> adduct formation, but eventually extended these experiments to various Zn complexes which demonstrated more fleeting CO<sub>2</sub> interactions via FT-IR. One of these complexes [Zn(2-pyPPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> (py = pyridyl)] that exhibited a short-lived CO<sub>2</sub> interaction proved to be an effective and robust catalyst for the conversion of CO<sub>2</sub> to CO, [9] which is consistent with

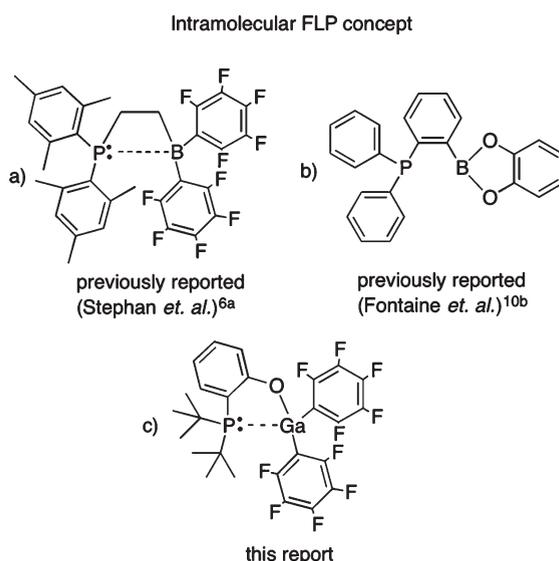


Fig. 1. a) An intramolecular FLP capable of small molecule (CO<sub>2</sub> & H<sub>2</sub>) activation, b) an effective FLP for catalytic conversion of CO<sub>2</sub> to CH<sub>3</sub>OH and c) compound **4** from this report.

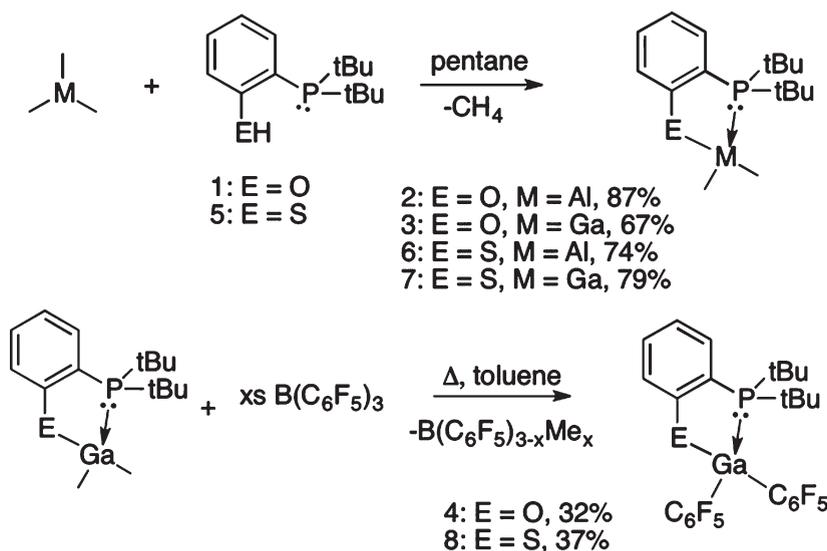
other reports that a weak interaction between the catalyst and CO<sub>2</sub> is actually a desirable attribute for catalytic CO<sub>2</sub> transformations [10]. For example, the compound seen in Fig. 1b (Fontaine et. al.) proved to be an excellent catalyst for the transformation of CO<sub>2</sub> to CH<sub>3</sub>OH despite the inability to obtain direct evidence of CO<sub>2</sub> interaction with the catalyst. Conversely, the compound seen in Fig. 1a forms a stable, isolable CO<sub>2</sub> adduct and no reports of its catalytic abilities have been offered.

Herein, we detail the synthesis and structural characterization of four new dimethyl Al or Ga compounds (**2**, **3**, **6**, and **7**) complexed by either the 2-(di-*tert*-butylphosphino)benzenethiolate or the 2-(di-*tert*-butylphosphino)phenolate ligand. The dimethyl Ga complexes were subsequently converted to their bis(pentafluorophenyl) analogs via ligand exchange affording two new complexes (**4** and **8**) (See Scheme 1). The design of compounds **4** and **8** was motivated by the previously reported intramolecular FLPs seen in Fig. 1. As with the compound seen in Fig. 1b, compounds **4** and **8**, offered no direct evidence of CO<sub>2</sub> adduct formation via NMR or FT-IR. As such, electrochemical experiments were performed to further probe any possible interactions. Several of the compounds (**2**, **3**, **4**, and **6**) revealed reduction waves in the presence of CO<sub>2</sub> while showing no reductions in inert gas environments in the absence of CO<sub>2</sub>. This direct evidence of a CE mechanism (chemical reaction followed by electron transfer) indicates that CO<sub>2</sub> is in fact interacting with the metal complexes, presumably on a timescale too short-lived for detection via NMR or FT-IR.

## 2. Experimental section

### 2.1. Reagents

The ligands 2-*t*Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)OH (**1**) and 2-*t*Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)SH (**5**) were prepared as previously reported [5j, 11]. Diethyl ether, pentane and toluene (Aldrich) were further dried using an LC Technology Solutions SP-105 purification system and stored over 4Å molecular sieves in the glovebox prior to use. The Me<sub>3</sub>Al, Me<sub>3</sub>Ga (Aldrich), and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (TCI) reagents were used as-received without further purification.



Scheme 1. Outline for reactions targeting compounds **2-4** & **6-8** and reaction yields.

## 2.2. General methods

Standard inert atmosphere and Schlenk techniques were used, as all reagents and products were presumed to be air and/or moisture-sensitive. Solution  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra were obtained on a Bruker Avance III 300 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR shifts were referenced to residual solvent peaks downfield of TMS.  $^{31}\text{P}\{^1\text{H}\}$  and  $^{19}\text{F}\{^1\text{H}\}$  spectra were referenced to external 85%  $\text{H}_3\text{PO}_4$ , and  $\text{CFCl}_3$  respectively. Repeated attempts were made to obtain bulk elemental analysis data, but even with added oxidant ( $\text{Ta}_2\text{O}_5$ ) carbon values were always lower than expected, consistent with incomplete combustion [12].

## 2.3. Electrochemical methods

Electrochemical measurements were carried out using an Autolab 302N potentiostat interfaced through Nova 2.0 software to a personal computer. Electrochemical measurements were performed using 0.1 M  $[\text{Bu}_4\text{NPF}_6]/\text{THF}$  electrolyte solutions from solvent that had been purified by passing through an alumina-based purification system. Diamond-polished glassy carbon electrodes of 3 mm diameter were employed for cyclic voltammetry (CV) scans. CV data were evaluated using standard diagnostic criteria for diffusion control and for chemical and electrochemical reversibility. The experimental reference electrode was a silver wire coated with anodically deposited silver chloride and separated from the working solution by a fine glass frit. The electrochemical potentials in this paper are referenced to ferrocene/ferrocenium couple, as recommended elsewhere [13]. The ferrocene potential was obtained by its addition to the analyte solution at an appropriate time in the experiment [14].

## 2.4. Crystallographic studies

The crystals (**3**, **4** & **6–8**) were coated with Paratone-N oil and were mounted on the nylon fiber of a CryoLoop™ that had been previously attached to a metallic pin using epoxy. The data were collected at the temperatures indicated in the tables using a Bruker X8 Apex II diffractometer using monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collection and processing were done using the APEX2 software suite [15]. The structures were solved using direct methods and refined with the full matrix least-squares method on F2 with SHELXTL [16]. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.5U equiv. of parent atom for methyl group hydrogens and 1.2U equiv. for all others. All final crystallographic figures shown in this document were generated by Diamond, v. 3.2i [17]. Crystallographic data are given in Table 2.

## 2.5. Synthesis of $[\text{Me}_2\text{Al}\{(\text{OC}_6\text{H}_4-2\text{-}^t\text{Bu}_2)\text{-}\kappa^2\text{-O,P}\}]_2$ (**2**)

A solution of  $^t\text{Bu}_2\text{P}(\text{C}_6\text{H}_4)\text{OH}$  (0.730 g, 3.06 mmol) in ca. 15 mL of pentane is added dropwise over 10 min. to a stirring solution of  $\text{Me}_3\text{Al}$  (0.220 g, 3.06 mmol) in ca. 20 mL of pentane at  $-78 \text{ }^\circ\text{C}$ . After 30 min. of stirring at  $-78 \text{ }^\circ\text{C}$ , the solution is allowed to warm to room temperature overnight (15 h), resulting in a clear solution. The volatiles are removed *in vacuo* resulting in a white powder. The product was purified by recrystallization from  $\text{Et}_2\text{O}$  at  $-18 \text{ }^\circ\text{C}$ . Yield = 780 mg (87%). Colorless, single crystals were grown from  $\text{Et}_2\text{O}$  at  $-18 \text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$   $-0.56$  (s, br, 6 H,  $\text{Al}(\text{CH}_3)_2$ ), 1.34 (d,  $^3J_{\text{P-H}} = 14 \text{ Hz}$ , 18 H,  $\text{C}(\text{CH}_3)_3$ ), 6.77 (m, 1 H,  $\text{C}_6\text{H}_4$ ), 6.92 (m, 1 H,  $\text{C}_6\text{H}_4$ ), 7.32 (m, 1 H,  $\text{C}_6\text{H}_4$ ), 7.43 (m, 1 H,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$   $-6.81$  (s, br,  $\text{Al}(\text{CH}_3)_2$ ), 29.8

(d,  $^2J_{P-C} = 6.2$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 33.6 (d,  $^1J_{P-C} = 9.7$  Hz, C(CH<sub>3</sub>), aromatic carbons 118.1, 119.7, 123.3, 133.1.  $^{31}P\{^1H\}$  (C<sub>6</sub>D<sub>6</sub>, 121 MHz):  $\delta$  1.09 ppm.

### 2.6. Synthesis of $Me_2Ga\{(OC_6H_4-2-P^tBu_2)-\kappa^2-O,P\}$ (3)

A solution of  $^tBu_2P(C_6H_4)OH$  (0.983 g, 4.13 mmol) in ca. 20 mL of pentane is added dropwise over 10 min. to a stirring solution of  $Me_3Ga$  (0.474 g, 4.13 mmol) in ca. 25 mL of pentane at  $-78$  °C. After 30 min. of stirring at  $-78$  °C, the solution is allowed to warm to room temperature overnight (15 h), resulting in a clear solution. The volatiles are removed *in vacuo* resulting in a white powder. The product was purified by recrystallization from Et<sub>2</sub>O at  $-18$  °C. Yield = 932 mg (67%). Colorless, single crystals were grown from Et<sub>2</sub>O at  $-18$  °C.  $^1H$  NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$   $-0.08$  (d,  $^3J_{P-H} = 3.3$  Hz, 6H, Ga(CH<sub>3</sub>)<sub>2</sub>), 1.37 (d,  $^3J_{P-H} = 14$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.67 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.92 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.30 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.41 (m, 1H, C<sub>6</sub>H<sub>4</sub>).  $^{13}C\{^1H\}$  (CDCl<sub>3</sub>, 75 MHz):  $\delta$   $-3.50$  (d,  $^2J_{P-C} = 19$  Hz, Ga(CH<sub>3</sub>)<sub>2</sub>), 29.7 (d,  $^2J_{P-C} = 4.7$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 34.4 (d,  $^1J_{P-C} = 15$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), aromatic carbons 115.8, 120.8, 132.6, 133.6, 171.1.  $^{31}P\{^1H\}$  (C<sub>6</sub>D<sub>6</sub>, 121 MHz):  $\delta$  9.23 ppm.

### 2.7. Synthesis of $(C_6F_5)_2Ga\{(OC_6H_4-2-P^tBu_2)-\kappa^2-S,P\}$ (4)

A solution of  $Me_2Ga\{(OC_6H_4-2-P^tBu_2)-\kappa^2-O,P\}$  (0.441 g, 1.31 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1.005 g, 1.96 mmol) in ca. 35 mL of toluene is heated to reflux under an Ar atmosphere for 48 h, resulting in a faint gold-colored translucent solution. The volatiles are removed *in vacuo* resulting in a sticky, gold-colored solid. The sample is purified by recrystallization from pentane at  $-18$  °C, resulting in colorless, crystalline product. Yield = 264 mg (32%).  $^1H$  NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  1.34 (d,  $^3J_{P-H} = 16$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.82 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.14 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.43 (m, 2H, C<sub>6</sub>H<sub>4</sub>).  $^{13}C\{^1H\}$  (CDCl<sub>3</sub>, 75 MHz):  $\delta$  29.2 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.6 (d,  $^1J_{P-C} = 19$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), aromatic carbons 117.6, 120.9, 132.4, 134.  $^{19}F\{^1H\}$  (C<sub>6</sub>D<sub>6</sub>, 282 MHz):  $\delta$   $-160.5$  (m, *o*-C<sub>6</sub>F<sub>5</sub>),  $-151.8$  (t,  $^3J_{F-F} = 20$  Hz, *p*-C<sub>6</sub>F<sub>5</sub>),  $-120.8$  (d,  $^3J_{F-F} = 20$  Hz, *m*-C<sub>6</sub>F<sub>5</sub>).  $^{31}P\{^1H\}$  (C<sub>6</sub>D<sub>6</sub>, 121 MHz):  $\delta$  24.8 ppm.

### 2.8. Synthesis of $Me_2Al\{(SC_6H_4-2-P^tBu_2)-\kappa^2-S,P\}$ (6)

A solution of  $^tBu_2P(C_6H_4)SH$  (0.553 g, 2.17 mmol) in ca. 15 mL of pentane is added dropwise over 10 min. to a stirring solution of  $Me_3Al$  (0.157 g, 2.17 mmol) in ca. 20 mL of pentane at  $-78$  °C. After 30 min. of stirring at  $-78$  °C, the solution is allowed to warm to room temperature over 1.5 h, resulting in a clear solution. The volatiles are removed *in vacuo* resulting in a oily white solid. The crude product is dissolved in a minimal amount of Et<sub>2</sub>O, filtered through Celite® – filter aid, and recrystallized at  $-18$  °C to give a colorless crystalline product which contained X-ray quality single crystals as well. Yield = 502 mg (74%).  $^1H$  NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$   $-0.07$  (d,  $^3J_{P-H} = 2.7$  Hz, 6H, Al(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d,  $^3J_{P-H} = 14$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.71 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.89 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.13 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.81 (m, 1H, C<sub>6</sub>H<sub>4</sub>).  $^{13}C\{^1H\}$  (CDCl<sub>3</sub>, 75 MHz):  $\delta$   $-5.80$  (s, br, Al(CH<sub>3</sub>)<sub>2</sub>), 29.2 (d,  $^2J_{P-C} = 4.4$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 34.8 (d,  $^1J_{P-C} = 13$  Hz, C(CH<sub>3</sub>), aromatic carbons 122.4, 131.3, 133.5, 134.0, 154.6.  $^{31}P\{^1H\}$  (C<sub>6</sub>D<sub>6</sub>, 121 MHz):  $\delta$  21.9 ppm.

### 2.9. Synthesis of $Me_2Ga\{(SC_6H_4-2-P^tBu_2)-\kappa^2-S,P\}$ (7)

A solution of  $^tBu_2P(C_6H_4)SH$  (0.420 g, 1.65 mmol) in ca. 15 mL of pentane is added dropwise over 10 min. to a stirring solution of  $Me_3Ga$  (0.190 g, 1.65 mmol) in ca. 20 mL of pentane at  $-78$  °C. After 30 min. of stirring at  $-78$  °C, the solution is allowed to warm to room temperature over 1.5 h, resulting in a clear solution. The volatiles are removed *in vacuo* resulting in a white solid. Yield = 458 mg

(79%). Colorless, single crystals were grown from Et<sub>2</sub>O at -18 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 0.28 (d, <sup>3</sup>J<sub>P-H</sub> = 3.6 Hz, 6 H, Ga(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, <sup>3</sup>J<sub>P-H</sub> = 14 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.69 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.89 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.18 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.84 (m, 1H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>, 75 MHz): δ -2.91 (s, br, Ga(CH<sub>3</sub>)<sub>2</sub>), 28.6 (d, <sup>2</sup>J<sub>P-C</sub> = 4.2 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 34.7 (d, <sup>1</sup>J<sub>P-C</sub> = 14 Hz, C(CH<sub>3</sub>), aromatic carbons 120.8, 130.5, 132.8, 133.2. <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 121 MHz): δ 32.4 ppm.

### 2.10. Synthesis of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ga{(SC<sub>6</sub>H<sub>4</sub>-2-*P*<sup>t</sup>Bu<sub>2</sub>)-κ<sup>2</sup>-S,P} (8)

A solution of **3** (0.302 g, 0.86 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.657 g, 1.28 mmol) in ca. 40 mL of toluene is heated to reflux under an argon atmosphere for 48 h, resulting in a faint gold-colored translucent solution. The volatiles are removed *in vacuo* resulting in a sticky, gold-colored solid. The sample is purified by recrystallization from pentane at -18 °C, resulting in colorless, crystalline product. Yield = 207 mg (37%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 0.94 (d, <sup>3</sup>J<sub>P-H</sub> = 15 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.69 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.90 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.07 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.77 (m, 1H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>, 75 MHz): δ 29.0 (s, C(CH<sub>3</sub>)<sub>3</sub>), 36.6 (d, <sup>1</sup>J<sub>P-C</sub> = 15 Hz, C(CH<sub>3</sub>)<sub>3</sub>), aromatic carbons 123.5, 123.7, 132.2, 133.5. <sup>19</sup>F{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 282 MHz): δ -160.7 (m, *m*-C<sub>6</sub>F<sub>5</sub>), -152.3 (t, <sup>3</sup>J<sub>F-F</sub> = 20 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), -118.7 (d, <sup>3</sup>J<sub>F-F</sub> = 20 Hz, *o*-C<sub>6</sub>F<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 121 MHz): δ 32.5 ppm.

## 3. Results and discussion

### 3.1. Preparation and characterization

The 2-<sup>t</sup>Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)OH (**1**) and 2-<sup>t</sup>Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)SH(**5**) proligands were synthesized according to literature methods, [5], [11] and were diluted in pentane before addition to solutions of either Me<sub>3</sub>Ga or Me<sub>3</sub>Al, which were also diluted in pentane. Furthermore, prior to addition the reaction flasks were cooled to -78 °C in an <sup>i</sup>PrOH slurry cooled by N<sub>2(l)</sub>. These precautions were taken in attempts to avoid the disubstitution of the metal center and to maximize production of the monoligated products Me<sub>2</sub>ML (compounds **2**, **3**, **6**, and **7**). After warming to room temperature (15 h), the solvent was removed *in vacuo* and products were then purified via recrystallization from saturated Et<sub>2</sub>O solutions at -18 °C, resulting in colorless crystalline material in respectable yields (>65%) in each instance. It should also be noted that for these four compounds, X-ray quality crystals were also obtained from concentrated Et<sub>2</sub>O solutions at -18 °C (Table 1).

Table 1  
Select bond lengths, angles, chemical shifts and J coupling constants

	M <sup>a</sup> -P (Å)	M-E <sup>b</sup> (Å)	∠E-M-P (deg.)	δ <sup>31</sup> P <sup>c</sup>	δ <sup>13</sup> C ( <sup>1</sup> J <sub>P-C</sub> ) <sup>d</sup> C(CH <sub>3</sub> ) <sub>3</sub>	δ <sup>13</sup> C ( <sup>2</sup> J <sub>P-C</sub> ) <sup>d</sup> C(CH <sub>3</sub> ) <sub>3</sub>	δ <sup>13</sup> C <sup>d</sup> M(CH <sub>3</sub> ) <sub>2</sub>	δ <sup>1</sup> H <sup>d</sup> M(CH <sub>3</sub> ) <sub>2</sub>
<b>2</b>	–	–	–	1.09	33.6 (9.7)	29.8 (6.2)	-6.81	-0.56
<b>3</b>	2.4427(3)	1.9119(9)	85.22(3)	9.23	34.4 (15)	29.7 (4.7)	-3.50	-0.08
<b>4</b>	2.3939(10)	1.868(2)	86.79(8)	24.9	35.6 (19)	29.2 (-) <sup>e</sup>	–	–
<b>6</b>	2.4825(8)	2.2865(8)	87.60(3)	21.9	34.8 (13)	29.2 (4.4)	-5.80	-0.07
<b>7</b>	2.4509(6)	2.3203(7)	87.83(2)	32.4	34.7 (14)	28.6 (4.2)	-2.91	0.28
<b>8</b>	2.4080(7)	2.2736(7)	90.04(2)	32.5	36.6 (15)	29.0 (-) <sup>e</sup>	–	–

<sup>a</sup>M = Al (**2** & **6**), Ga (**3**, **4**, **7** & **8**), <sup>b</sup>E = O (**2–4**), S (**6–8**), <sup>c</sup>All <sup>31</sup>P performed in C<sub>6</sub>D<sub>6</sub> shifts reported in ppm, <sup>d</sup>All <sup>13</sup>C and <sup>1</sup>H performed in CDCl<sub>3</sub>, all shifts reported in ppm and J coupling constants reported in Hz, <sup>e</sup>These signals were slightly broad and the <sup>2</sup>J<sub>P-C</sub> coupling constants could not be resolved.

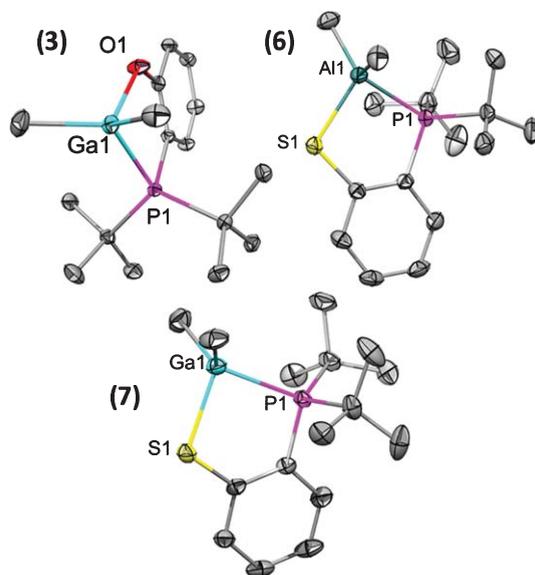


Fig. 2. Molecular structures of **3**, **6**, and **7** (50% ellipsoids). Hydrogens have been omitted for clarity and carbon atoms are shown in grey. Select bond lengths and angles can be seen in Table 1.

The transformation of the dimethyl Ga complexes **3** and **7** to their bis(pentafluorophenyl) analogs was then targeted and was achieved by heating **3** and **7** in refluxing toluene overnight with an excess of  $\text{B}(\text{C}_6\text{F}_5)_3$ . The concept of  $\text{Me}/\text{C}_6\text{F}_5$  ligand exchange was first introduced by Klosin et al. where it was shown that the reaction of  $\text{B}(\text{C}_6\text{F}_5)_3$  with  $\text{Me}_3\text{Al}$  produced  $\text{Al}(\text{C}_6\text{F}_5)_3$  and  $\text{Me}_3\text{B}$  when reacted in non-coordinating solvents [18]. When adopting this methodology, initial attempts were performed adding enough  $\text{B}(\text{C}_6\text{F}_5)_3$  such that the methyl and pentafluorophenyl groups were in a 1 : 1 stoichiometric ratio, or 0.66 equivalents of  $\text{B}(\text{C}_6\text{F}_5)_3$  per metal center. This resulted in an incomplete exchange as evidence by isolated crystals of a monosubstituted complex  $\text{LGaMe}(\text{C}_6\text{F}_5)$  (where  $\text{L} = \text{SC}_6\text{H}_4\text{-2-}P^t\text{Bu}_2$ ). When the amount of  $\text{B}(\text{C}_6\text{F}_5)_3$  was increased to 1.5 equivalents per metal center, the bis(pentafluorophenyl) analogs **4** and **8** were successfully produced along with non-volatile  $\text{B}(\text{C}_6\text{F}_5)_{3-x}\text{Me}_x$  byproducts. The crude mixture of products after solvent removal was a sticky solid, but the pure products could be isolated via recrystallization from pentane at  $-18^\circ$ , albeit in lowered yields ( $\sim 30\%$ ).

Multinuclear NMR spectra were collected for species **2–4** and **6–8**, resulting in singlets in the  $^{31}\text{P}$  experiments for all compounds with chemical shifts ranging from  $\sim 1\text{--}33$  ppm (see Table 1) when measured in  $\text{C}_6\text{D}_6$ . These results indicate that the ligand, at least at room temperature, is not exhibiting any hemilability towards the metal center. We have reported previously an instance when the  $2\text{-}^t\text{Bu}_2\text{P-C}_6\text{H}_4\text{S}^-$  ligand does exhibit room temperature hemilabile behavior in a  $\text{Sn}^{\text{IV}}$  complex [5j]. The presence of two signals in the  $^{31}\text{P}$  NMR spectrum which have temperature-dependent relative integration ratios, along with Sn-P coupling constant data, clearly reveal the hemilabile behavior. The lack of hemilabile behavior in the compounds reported here is not completely surprising due to the lack of ring strain in the resulting 5-membered chelate rings and with the strong Lewis acid nature of  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  metal centers. When comparing the chemical shifts of compound **2** to those in compound **3** as well as **6** to **7**, the only difference is the identity of the metal center. In both pairs of comparisons, it is clear by looking at chemical shifts from  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra of atoms directly bound to the metal center (P and C), that the Ga center is deshielding its nearest neighbors noticeably more than the Al analogs. For example, the  $^{31}\text{P}$  signal is 1.09 ppm for **2** while compound **3** is further downfield at 9.23 ppm. This trend is also seen when looking at the  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR of the metal-bound methyl groups (see

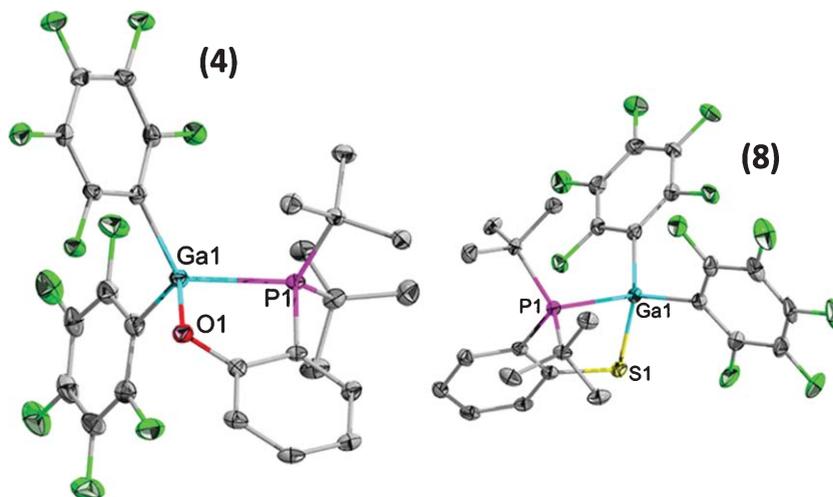


Fig. 3. Molecular structures of **4** and **8** (50% ellipsoids). Hydrogens have been omitted for clarity, carbon atoms are shown in grey, and fluorine atoms in green. Select bond lengths and angles can be seen in Table 1.

Table 1). In another set of comparisons, the effect that the chalcogenide identity (E) has on chemical shifts can be scrutinized by comparing pairs of compounds **2** to **6** and **3** to **7**. In both instances, the S containing compounds (**6** & **7**) revealed a downfield shift in the metal-bound atoms relative to their phenolate analogs (**2** & **3**) (see Table 1). For example, the  $^{31}\text{P}$  signal in compound **3** is at 9.23 ppm while in compound **7** it is at 32.4 ppm.

Crystal structures were collected for compounds **3**, **4**, **6**, **7**, and **8** revealing distorted tetrahedral metal center geometries for all compounds (see Figs. 2 and 3). Crystallographic data and parameters for these compounds has been compiled in Table 2. Exhaustive attempts were made to obtain a high quality solution for X-ray data collected for compound **2**, but these were not successful. However, although we obtained poor data, it was clear from our efforts to solve the crystal structure of **2** that it dimerizes in the solid state resulting in a 5-coordinate distorted trigonal bipyramidal coordination environment around the Al. The dimerization occurs through adduct formation between an O lone pair from the phenolate coordinating to a neighboring Al. The equatorial positions in **2** are occupied by two methyl groups and the covalently bound O atom from the  $2\text{-}^t\text{Bu}_2\text{P-C}_6\text{H}_4\text{O}^-$  ligand while the axial positions are occupied by the P atom from the same  $2\text{-}^t\text{Bu}_2\text{P-C}_6\text{H}_4\text{O}^-$  ligand and the O atom from a neighboring molecule. Aside from the dimerization of compound **2**, there are no remarkable or unexpected crystallographic features found in the structures seen in Figs. 2 and 3. For the bis(pentafluorophenyl) compounds **4** and **8**, the expectation is that the strong electron withdrawing nature of the perfluorinated substituents will shorten the Ga-P and Ga-E (E=O or S) bonds relative to their dimethyl counterparts. This expectation holds true as the Ga-P bond lengths and Ga-E bond lengths for compounds **4** and **8** are  $\sim 0.05$  Å shorter than of those found in compounds **3** and **7** (see Table 1).

### 3.2. $\text{CO}_2$ reactivity studies

Upon successful isolation and characterization of compounds **2**, **3**, **4**, **6**, **7**, and **8**, focus was then turned to probing the reactivity of these compounds with  $\text{CO}_2$ . Initial experiments looked for evidence of  $\text{CO}_2$ -complex interactions via FT-IR and NMR after bubbling  $\text{CO}_2$  through solutions of the aforementioned compounds. If stable adducts were to form, there would be clear evidence of this in both the NMR and FT-IR spectra when compared to the complexes before exposure to  $\text{CO}_2$ . For example, in one of our

Table 2  
Crystallographic Data and Parameters for Compounds **3**, **4**, & **6–8**

	<b>3</b>	<b>4</b>	<b>6</b>	<b>7</b>	<b>8</b>
empirical formula	C <sub>16</sub> H <sub>28</sub> GaOP	C <sub>26</sub> H <sub>22</sub> F <sub>10</sub> GaOP	C <sub>16</sub> H <sub>28</sub> AlPS	C <sub>16</sub> H <sub>28</sub> GaPS	C <sub>26</sub> H <sub>22</sub> F <sub>10</sub> GaPS
FW	337.07	641.13	310.39	353.13	659.20
<i>T</i> , K	173(2)	173(2)	173(2)	173(2)	173(2)
cryst size (mm)	0.50×0.50×0.19	0.34×0.26×0.12	0.58×0.30×0.22	0.46×0.34×0.30	0.37×0.34×0.34
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	P2(1)/c	P2(1)/n	Pbca	Pbca	P2(1)/n
<i>a</i> , Å	13.9275(14)	9.9121(4)	14.0758(5)	14.0468(6)	8.6475(2)
<i>b</i> , Å	9.6095(9)	11.3953(4)	15.4382(6)	15.4442(6)	25.4338(7)
<i>c</i> , Å	12.9652(13)	23.0044(9)	16.5577(6)	16.5316(7)	12.4720(3)
α, deg	90.00	90.00	90.00	90.00	90.00
β, deg	96.635(4)	95.846(2)	90.00	90.00	91.6240(10)
γ, deg	90.00	90.00	90.00	90.00	90.00
vol, Å <sup>3</sup>	1723.6(3)	2584.86(17)	3598.1(2)	3586.4(3)	2741.97(12)
<i>Z</i>	4	4	8	8	4
calcd density (g/cm <sup>3</sup> )	1.299	1.647	1.146	1.308	1.597
μ, mm <sup>-1</sup>	1.681	1.218	0.305	1.727	1.221
R1 [I>2σ( <i>I</i> )] <sup>a</sup>	0.0204	0.0395	0.0351	0.0285	0.0333
wR2[I>2σ( <i>I</i> )] <sup>b</sup>	0.0558	0.0999	0.0981	0.0896	0.0901

$${}^a\text{R1} = \sum F_o - |F_c| / \sum |F_o|, \quad {}^b\text{wR2} = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

previous studies, a P,P-chelated stannylene [(<sup>i</sup>Pr<sub>2</sub>P)<sub>2</sub>N]<sub>2</sub>Sn formed an isolable CO<sub>2</sub> dual Lewis acid-base adduct upon insertion of CO<sub>2</sub> into one of the Sn-P bonds [5c]. Evidence for CO<sub>2</sub> incorporation was clearly demonstrated by both FT-IR and NMR as a strong C=O absorbance at 1629 cm<sup>-1</sup> was seen and the chemical resonance of the P atom directly bound to the C in CO<sub>2</sub> could be observed.

In another example, [9] our group synthesized a Zn complex ([Ph<sub>2</sub>Ppy]<sub>2</sub>ZnCl<sub>2</sub>, py = 2-pyridyl) which showed no evidence of CO<sub>2</sub> interaction via NMR, even when experiments were performed at 100 psig CO<sub>2</sub> and at -48 °C. However, a short-lived (~10 minutes) C=O stretch could be observed at 1726 cm<sup>-1</sup> in the solid state FT-IR spectrum. The higher wavenumber seen in the Zn complex is consistent with a weaker, more transient CO<sub>2</sub>-complex interaction, and is consistent with the inability to isolate a stable adduct or observe any change in the NMR spectra upon CO<sub>2</sub> exposure. The Zn complex did however prove to be a robust electrocatalyst for the reduction of CO<sub>2</sub> to CO, whereas the Sn-CO<sub>2</sub> complex was not, suggesting that perhaps a weaker interaction between CO<sub>2</sub> and the complex is desirable for catalytic transformations of the CO<sub>2</sub>.

After exposing compounds **2**, **3**, **4**, **6**, **7**, and **8** to CO<sub>2</sub>, no evidence of an adduct could be observed via NMR or FT-IR even when elevated pressures (10 atm) and extended exposure durations (15 h) were employed. This lack of evidence, however, did not deter further examination of these compounds for their ability to activate CO<sub>2</sub> as we have stated that other reports have revealed that a complex (See Fig. 1b) that lacks evidence of CO<sub>2</sub> interaction via NMR and FT-IR is still capable of performing as a catalyst for CO<sub>2</sub> transformations [10b]. In this study, it was revealed that CO<sub>2</sub> was only susceptible to chemical reduction in the presence of catalyst providing indirect evidence of CO<sub>2</sub> activation. In contrast to this report, we aim to use electrochemical reduction to provide direct evidence of CO<sub>2</sub> activation by the Al and Ga complexes **2**, **3**, **4**, **6**, **7**, and **8**. Evidence for a CE mechanism, which in this case establishes CO<sub>2</sub> activation, can be clearly demonstrated if the reduction onset potential of the complex in the presence of CO<sub>2</sub> is lowered relative to the onset potential of the complexes in an inert gas environment.

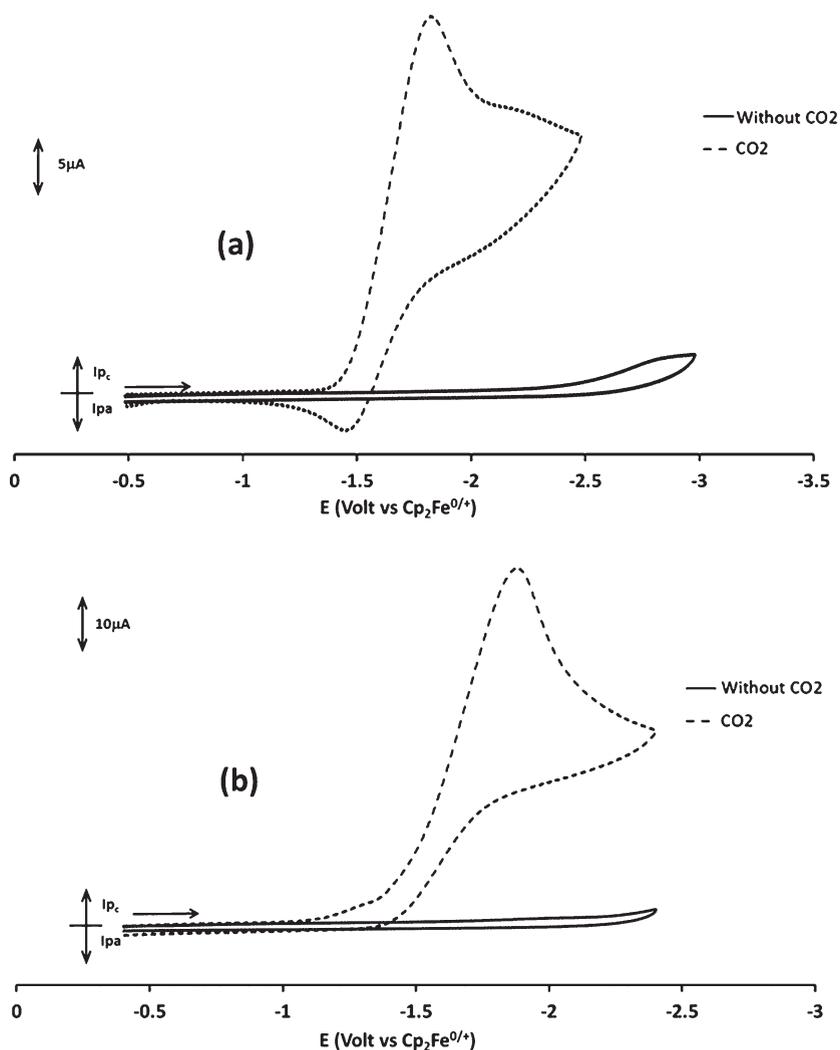


Fig. 4. Cyclic Voltammetry scans of (a) 1 mM **3** and (b) 1 mM **4** both in THF/0.1 M [NBU<sub>4</sub>][PF<sub>6</sub>] at 3 mm glassy carbon electrodes, and both with scan rates of 0.2 V s<sup>-1</sup>.

### 3.3. Electrochemical studies

The electrochemical properties of all metal complexes were investigated using CV experiments, and four of the six compounds demonstrated cathodic waves consistent with a CE mechanism when exposed to CO<sub>2</sub>. Compounds **7** and **8** showed a complex series of reduction in absence of CO<sub>2</sub>. No difference in their cathodic behavior was observed when the compounds were exposed to CO<sub>2</sub>, and as such will not be discussed further in this section. Complexes **2**, **3**, **4**, and **6**, however, display very similar cathodic behaviors. In the absence of CO<sub>2</sub>, none of the compounds showed any reduction waves within the limits of the solvent window. However, when CO<sub>2</sub> was passed through the electrochemical cell, a diffusion-controlled *electrochemically*-reversible but *chemically*-partially reversible cathodic reduction was observed at the potentials collected in Table 3 for **2**, **3**, **4**, and **6**. Overlaid CV scans of these four compounds in the presence of and in the absence of CO<sub>2</sub> is shown in Fig. 4 for compounds **3** and **4**, and in the supporting information (Figure S3) for **2** and **6**. Compound **4** was the only species that displayed a diffusion-controlled both *electrochemically* and *chemically*-irreversible cathodic reduction [19]. Voltammetry at higher sweeping rates (up to 250,000 V.s<sup>-1</sup>) and at low temperature (-50°C) did

Table 3  
Electrochemical half-wave reduction potentials  
for compounds showing cathodic reduction  
in the presence of CO<sub>2</sub>

Compound	Reduction
<b>2</b>	$E_{p1/2} = -1.65 \text{ V}$
<b>3</b>	$E_{p1/2} = -1.65 \text{ V}$
<b>4</b>	$E_{p1/2} = -1.88 \text{ V}$
<b>6</b>	$E_{p1/2} = -1.70 \text{ V}$

not allow the observation of any *chemical*-reversibility for **4**. The  $E_p - E_{p/2}$  value of **4** is 240 mV at  $\nu = 0.2 \text{ V s}^{-1}$ , diagnostic of a slow charge transfer process with a transfer coefficient ( $\alpha$ ) of 0.20 [20]. For all of the compounds, no peak was observed in the oxidative region.

For compounds **2**, **3**, **4**, and **6**, bulk coulometries were carried out at a controlled potential 150 mV more negative than the potential of the cathodic wave observed by CV. Both coulometries in the absence of or in the presence of CO<sub>2</sub> reached completion after the passage of 1F per mol of compound through the solution. This confirms therefore the cathodic event is a one-electron process and that no electrocatalytic reduction is taking place. Unfortunately, in both cases, the mono-electronically reduced product undergoes a rapid follow-up chemical reaction which did not allow identification of its structure. The fact that the complexes display a cathodic reduction only in presence of CO<sub>2</sub>, due to the reduction of a CO<sub>2</sub> adduct with the complexes, is a very promising starting point for the development of a new family of CO<sub>2</sub> electrocatalysts. Further investigations will be carried out using ultrafast voltammetry combined with spectroelectrochemistry in order to shed light on the mechanism of reduction and identify the structure of the intermediates.

#### 4. Conclusions

The ability to use CO<sub>2</sub> as a C1 synthon for the production of useful chemicals is a longstanding goal of the chemical community. This endeavor still has much room for improvement both in the development of suitable catalysts, but also in the fundamental understanding of how to best activate CO<sub>2</sub>. A handful of reports are now reporting successful catalytic transformations of CO<sub>2</sub> using catalysts that have weak interactions with CO<sub>2</sub>, which will surely lead to further investigations into this concept. Herein we report the synthesis and characterization of several new Al and Ga phosphinobenzenethiolates and phosphinophenolates, which were shown to have these weak interactions with CO<sub>2</sub>. This was exhibited by both the lack of stable adduct formation seen in NMR and FT-IR experiments, along with the cathodic waves observed in CV experiments upon exposure to CO<sub>2</sub>. Although none of the electrochemical experiments afforded catalytic transformations of the CO<sub>2</sub>, we were able to show that many of our catalyst designs were capable of activating CO<sub>2</sub>.

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ated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the United States Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The electrochemical analyses were supported by Nazarbayev University (ORAU grant for Medicinal Electrochemistry) and the Ministry of Education and Science of Kazakhstan. (KL) A partial structure solution for compound **2**, the crystal structure for the untargeted complex LGaMe(C<sub>6</sub>F<sub>5</sub>) (where L = SC<sub>6</sub>H<sub>4</sub>-2-P<sup>t</sup>Bu<sub>2</sub>), all NMR spectra, and CV scans for compounds **2** and **6** can be made available by request to the corresponding author. (BB) CCDC 1546738–1546742 and 1563648 contain the supplementary crystallographic data for complexes **3**, **4**, **6–8** and the untargeted complex. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving/html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: E-mail: deposit@ccdc.cam.ac.uk.

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- [19] In practical terms, electrochemical reversibility (also termed Nernstian behavior) refers to the speed of charge-transfer in a redox reaction, whereas chemical reversibility refers to follow-up reactions that accompany the charge-transfer process. For an introductory discussion of these terms, see A.J. Bard and L.N. Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York, 2001, 2nd Ed., pp 35–38 and pp 44–49).
- [20] See ref. 18, page 236.