Stoichiometric Reduction of CO₂ to CO by Phosphine/AIX₃-Based **Frustrated Lewis Pairs**

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S Supporting Information

ABSTRACT: The reactions of the bulky phosphines Mes_3P or $(otol)_3P$ with AlX_3 (X = I, Br, Cl) and CO_2 are probed and shown to give complexes of the form $Mes_3PC(OAIX_3)_2$ (X = I (3), Br (4), Cl (5)) and $(otol)_3PC(OAII_3)_2$ (6). The former compounds under CO₂ are further transformed to Mes₃PC(OAIX₂)₂OAIX₃ (X = I (8), Br (10)) and $[Mes_3PX][AIX_4] (X = I (9), Br (11))$. These latter reactions are thought to proceed via dissociation of alane, as evidenced by the generation of $(otol)_3 PC(OAl(C_6F_5)_3)$ from $(otol)_3 PC(OAl(C_6F_5)_3)_2$ (7) and the isolation of $(otol)_3 PC(O)OAl(OC(CF_3)_3)_3$ (15). Subsequent insertion of CO₂ into the Al-X bond is evidenced by the characterization of $[(C_6F_5)C(O)OAl(C_6F_5)_2]_2$ (14) from the reaction of Al(C_6F_5)₃ and CO₂. The isolation of Al(C_6F_5)₃·2-



 (C_6H_5Br) (16) also suggests dissociation of Al $(C_6F_5)_3$ from 7 may be facilitated by interactions with solvent. Kinetics of the formation of 8/9 from 3 show the reaction is first order in 3 and CO_2 and the rate-determining step involves an associative process. A mechanism involving dissociation of alane and subsequent insertion of CO₂ into the Al-X bond is proposed.

INTRODUCTION

Rapidly increasing levels of greenhouse gases in the atmosphere, especially levels of CO₂, require urgent action to mitigate emissions.¹ While the direct use of CO₂ as a C₁ feedstock for chemical transformation is attractive, $2^{2,3}$ the reduction of CO_2 could be far more useful. This C_1 feedstock⁴ can be used in large-scale processes including the Cativa (formerly Monsanto) process to produce acetic acid,⁵ Fischer-Tropsch chemistry to produce liquid hydrocarbons,^{6,7} or hydroformylation reactions to produce aldehydes.⁸ Because of the scale of these industries, a process where CO_2 is recycled and used to generate CO could help to mitigate greenhouse gas emissions; however, reduction of the strong C=O bonds (532 kJ/mol)⁹ presents a significant kinetic barrier.²

The enzyme carbon monoxide dehydrogenase (CODH) is Nature's approach to reducing CO_2 to CO and H_2O .¹⁰ Heterogeneous systems have been developed to effect similar reductions via photochemical¹¹⁻¹⁵ or electrochemical^{16,17} methods. Alternatively, chemical reduction remains under intense investigation.^{9,18-28} More recently, main group mediated routes for CO₂ reduction have also been reported.²⁹⁻³⁸ In this vein, we have previously reported the reversible capture of CO2 by phosphine/borane combinations.³⁹ Modification of these so-called "frustrated Lewis pairs" (FLP) to combinations of phosphine and alane allows for capture of CO₂ and further reaction with ammonia borane to afford methanol in a stoichiometric fashion.³³ Alternatively, we

have also reported the further reaction of these systems with CO_2 to give CO^{32} . In this full report, we focus our attention on the latter reactions, probing related systems and aspects of the mechanism of CO₂ reduction.

RESULTS AND DISCUSSION

Combinations of the bulky phosphines Mes_3P or $(otol)_3P$ with AlI₃ affords the isolation of the adducts $(R_3P)AlI_3$ (R = Mes, 1; otol, 2).³² Interestingly, while both displayed broad ${}^{31}P{}^{1}H{}$ NMR resonances due to coupling to the quadrupolar (I = 5/2)²⁷Al nucleus, the spectrum for 1 displayed a second broad resonance centered at -35 ppm, indicative of free Mes₃P. This is consistent with an equilibrium involving dissociation of the adduct. Variable-temperature NMR spectroscopy was used to extract the thermodynamic parameters of this equilibrium: ΔG = 8.2 kJ/mol, ΔH = 42(1) kJ/mol, and ΔS 113(3) J/(K·mol) with a K_{eq} of 0.0372 at 25 °C. NMR spectra show that such dissociation is significantly less for the analogous AlCl₃ and AlBr₃ adducts.³³ The adduct **2** shows no ³¹P NMR resonance attributable to free $(otol)_3P$ over the same temperature range, consistent with stronger Al-P binding as a result of the diminished steric congestion.

It is interesting to note that mixtures of Mes₃P/AlX₃ yield deep purple solutions in bromobenzene ($\lambda_{max} = 384, 572$ nm;

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see the Supporting Information). This color is attributable to the generation of the $[Mes_3P]^{\bullet+}$ radical cation via electron transfer to the alane.⁴⁰ Indeed, monitoring solutions of $Mes_3P/$ AlX₃ (X = Br, I) by X-band EPR spectroscopy revealed the presence of a doublet (g = 2.0056, $a_p = 239$ G) consistent with literature reports of the $Mes_3P^{\bullet+}$ radical (Figure 1).^{41–43} The



Figure 1. X-band EPR spectrum of $Mes_3P/2$ AlBr₃ in bromobenzene (experimental: blue, simulation: red). Analogous signals are observed when using AlI₃. Simulation was done using PIP4Win v. 1.2.⁴⁶

corresponding Al-based radical anion does not generate an EPR signal. While this may be due to signal broadening due to the quadrupole of Al, an electron transfer equilibrium is suggested by the presence of both ³¹P/²⁷Al NMR and EPR spectra for these solutions. While the nature of the anion in this case remains unknown, Norton has characterized the corresponding B-radical anion $[B(C_6F_5)_3]^{\bullet-.44}$ In this regard it is notweworthy that the diamagnetic dimer $[X_3Ga-GaX_3]^{2-}$ is known.⁴⁵ Interestingly, solutions of AlX₃ (X = Br, I) with $(otol)_3P$ are EPR inactive, consistent with the higher oxidation potential of this phosphine.⁴¹

We previously reported that initial exposure of the FLPs derived from Mes_3P and AlX_3 to CO_2 leads to the rapid formation of the complexes $Mes_3PC(OAlX_3)_2$ (X = I (3), Br (4), Cl (5)), which can be isolated in high yields (Scheme 1).^{32,33}

Scheme 1. Reaction of Mes₃P and AlX₃ with CO₂



The synthesis of the related compound $(otol)_3PC(OAII_3)_2$ (6)³² required heating of the $(otol)_3P/AII_3$ solution to 80 °C for 1 h under an atmosphere of CO₂. Single crystals of 6 suitable for X-ray diffraction (Figure 2) reveal that the structure is largely analogous to 3 with the P–CO₂ bond length in 6 being shorter (1.877(4) Å) than that in 3 (1.903(8) Å).³³ The O–C–O angle in 6 is also slightly larger (127.4(4)°) than in 3 (125.0(8)°).³³ Both these metric parameters reflect the reduced steric bulk around $(otol)_3P$ vs Mes₃P, as reflected in the differing Tolman cone angles of 196° and 212°, respectively.⁴⁷

On prolonged exposure of Mes_3P/AlX_3 solutions to a CO_2 atm, the compounds $Mes_3PC(OAlX_2)_2OAlX_3$ (X = I (8), Br



Figure 2. POV-Ray depiction of the molecular structure of 6. C: black; P: orange; Al: teal; I: pink; O: red. H atoms are omitted.

(10)) and [Mes₃PX][AlX₄] (X = I (9), Br (11)) were formed with the concurrent liberation of CO (Scheme 1).³² These reactions took ca. 16 h (X = I) and 48 h (X = Br), respectively. While similar reactivity seemed to occur with AlCl₃, the reaction was significantly slower, precluding product isolation. This trend parallels the reactivity of AlX₃ (I > Br \gg Cl).⁴⁸ Reaction times also varied with solvent with completion after ca. 4 days in fluorobenzene and <12 h in iodobenzene. This observation suggests solvent-induced dissociation of AlX₃ from 3 or 4 may be necessary to initiate the reduction of CO₂ to CO (*vide infra*).⁴⁹ In further support for this dissociative pathway, [Mes₃PMe][AlI₄] (12) was found to enhance the rate of reaction, yielding 8 and 9 under CO₂.³² This is thought to act by promoting dissociation of AlI₃ from 3, generating the halidebridged species [I₃Al(μ -I)AlI₃]⁻.

Further evidence of dissociation of alane is derived from the analogous species $(otol)_3$ PC(OAl(C₆F₅)₃)₂ (7).⁵⁰ This species does not react under CO₂ (1 atm) at 25 °C, consistent with the relatively high computed Lewis acidity of Al(C₆F₅)₃.⁵¹ However, heating a sample of 7 to 90 °C under CO₂ in bromobenzene for 48 h led to the gradual consumption of 7 and the appearance of the new species 13 and 14 (Scheme 2).





The product **13** exhibits doublets in the ³¹P{¹H} and ¹³C NMR spectra at 12 and 160 ppm (¹ $J_{P-C} = 121$ Hz) when [¹³C]-7 is used. Similar resonances in the ³¹P{¹H}, ¹³C, and ¹⁹F NMR spectra were observed when a 1:1 solution of $(otol)_3P/Al(C_6F_5)_3$ was exposed to an atmosphere of ¹³CO₂, suggesting that **13** is the 1:1 species $(otol)_3PC(O)OAl(C_6F_5)_3$ (Scheme 2). While this is thought to be similar to the previously

reported species $tBu_3PC(O)OB(C_6F_5)_3$,³⁹ attempts to isolate **13** were unsuccessful. Nonetheless, the closely related species $(otol)_3PC(O)OAl(OC(CF_3)_3)_3$ (**15**) was prepared by exposing a 1:1 solution of $(otol)_3P$ and the sterically encumbered $Al(OC(CF_3)_3)_3^{52}$ to CO_2 (Scheme 2). The formulation of **15** was confirmed both spectroscopically and by an X-ray diffraction study (Figure 3). The metric parameters for **15** were similar to the previously reported P/B³⁹ and P/Al₂ species.^{32,33}



Figure 3. POV-Ray depiction of the molecular structure of 15. H atoms are omitted. C: black; P: orange; Al; teal; F: pink; O: red.

In addition to 13, heating 7 under CO_2 also yielded a second product, 14. This species exhibited six resonances in the ¹⁹F NMR spectrum: two sets of three peaks integrating in a 2:1 ratio. This species was independently prepared by the reaction of CO_2 and $Al(C_6F_5)_3$, yielding the symmetric dimeric species $[(C_6F_5)C(O)OAl(C_6F_5)_2]_2$ (14). This species showed a singlet at 168 ppm in the ¹³C NMR spectrum attributable to the CO_2 moiety. The solid-state structure of 14 (Figure 4) revealed two



Figure 4. POV-Ray depiction of the molecular structure of 14. C: black; Al; teal; F: pink; O: red.

 CO_2 moieties, bound in an inequivalent fashion to the Al centers with C_1-O_1 and C_2-O_2 bond lengths of 1.257(2) and 1.262(2) Å. The corresponding O–Al bond lengths are slightly different, at 1.773(1) and 1.814(1) Å, respectively. The Al–O–C bond angles also differ, being 135.1(1)° and 160.4(1)°, respectively.

The dissociation of $Al(C_6F_5)_3$ from 7 may also be facilitated by interactions with solvent. This is evidenced in the crystallization of $Al(C_6F_5)_3$ from bromobenzene, which afforded crystals of $Al(C_6F_5)_3$. (16) (Figure 5).



Figure 5. POV-Ray depiction of the molecular structure of 16. H atoms are omitted. C: black; Al; teal; F: pink; Br: scarlet.

While the geometry about Al remains trigonal planar as expected, the bromine atoms of two bromobenzene molecules occupy positions above and below the trigonal plane with Al…Br distances of 2.80 and 3.12 Å. Such an interaction may mimic solvation, although, π -stacking between the electron-rich arene bromobenzene ring and the electron-deficient fluoroarene ring may stabilize the interactions observed in the solid state. It is noteworthy that computational studies by Kwon et al.⁴⁹ further suggested that such solvation of the Lewis acid by the solvent bromobenzene favors the dissociation of the (Mes₃P)AlCl₃ adduct.³³

Mechanistic Insights. While solutions of Mes₃P/AlX₃ generate some adduct and some radical cation, addition of CO₂ results in loss of color and disappearance of any EPR signal. This infers that the formation of the adduct 3 precludes an open-shell mechanism for the subsequent reduction of CO_2 to 8 and 9. To further examine the generation of CO from 3, solutions of 3 were prepared and exposed to a 50-fold excess of CO_2 . This was done using 5.0 atm of CO_2 pressure and using a known volume of solvent. The concentration of CO₂ in solution was estimated to be 0.4 M, based on Raoult's law and the known mole fraction of 0.0079 for CO₂ in bromobenzene at 1.0 atm.⁵⁴ Under these conditions, the reaction of 3 to 8 and 9 proceeds under pseudo-first-order conditions. Monitoring the reaction by ${}^{31}P{}^{1}H$ NMR spectroscopy experiments over a 30 K range (303-333 K) showed a first-order dependence on 3 with the activation parameters $\Delta H^{\ddagger} = 85(5)$ kJ/mol and $\Delta S^{\ddagger} =$ -45(15) J/(mol·K) (Figure 6).

Similarly reduction of CO_2 pressure was also consistent with a first-order dependence of the reaction rate with CO_2 . This, together with a negative activation entropy, suggests that the rate-determining step in the reduction of CO_2 to CO and the formation of 8/9 involves an associative process.

A kinetic study of the conversion of 3 to 8/9 at 50 °C in the presence of 0.5 or 1.0 equiv of cyclohexene revealed an inverse first-order dependence on the concentration of cyclohexene. This suggests competitive binding of the olefin to AlX₃. ¹H NMR spectra for these solutions do exhibit a shifted olefini resonance consistent with coordination to Al. This view is also supported by computational studies. Using the OG2R3(SCRF) approach, the olefin adduct (η^2 -C₆H₁₀)AlI₃ is computed to be 34 kJ/mol more stable than the (η^1 -CO₂)AlI₃ adduct in bromobenzene solvent. It is noteworthy that we have previously characterized the cyclohexene adduct Al-(C₆F₅)₃(μ^2 -C₆H₁₀).⁵¹

The consumption of 3 in the reduction of CO_2 suggests that species 3 is the initial kinetic product. Conversion of 3 to 8 and 9 requires some free phosphine and alane. Dissociation of AlX₃



Figure 6. Top: Stacked plot of ${}^{31}P{}^{1}H$ NMR spectra at 40 °C (initial time 5 min and then at intervals of 15 min) for the reaction of 3 (7.2 mM) with 5 atm of CO₂ (ca. 0.4 M). Middle: Representative plot of the first-order decay of [3] at 60 °C. Bottom: Eyring plot.

from 3/4 generates the analogues of 15, while further dissociation liberates phosphine and a second equivalent of AlX₃. Further competition is provided by the equilibrium governing phosphine-alane adduct formation. This is consistent with the observations that addition of excess AlI₃ slowed the conversion of 3 to 8 and 9, while addition of the [Mes₃PMe][AlI₄] (12) facilitates dissociation of AlI₃ from 3, presumably by an equilibrium involving the generation of the [Al₂I₇]⁻ anion. The participation of free alane in the reaction is also consistent with the slower reduction of 4 to 10 and 11, presumably resulting from the increased Lewis acidity of AlBr₃.

Based on the formation of 13 and 14 from 7, an associative insertion reaction of CO_2 with $[Al_2X_6]$ affording a transient cyclic species of the form $[XC(OAIX_2)_2X]$ is proposed (Scheme 3, bottom left). Probing this notion computationally, scans of the potential energy surface for insertion of CO_2 into AlI₃ at the M06-2X(SCRF) level⁵⁵ led to an estimated barrier of 75 kJ mol⁻¹ (NB.: experimental barrier: 85(5) kJ mol⁻¹). In this case, the reaction energy, calculated at the OG2R3(SCRF) level,^{56,57} was found to be essentially thermoneutral (4 kJ mol⁻¹). However, inclusion of the second AlI₃ resulted in a highly exothermic reaction (-145 kJ mol⁻¹).

Subsequent nucleophilic attack by phosphine could proceed via formation of a phosphonium acyl halide intermediate. Such species are known to be unstable with respect to loss of CO^{53,58,59} and formation of the corresponding halo-phosphonium cation. Alternatively, nucleophilic attack at the halide could yield [Mes3PI]⁺ directly (Scheme 3, bottom middle). Computations at the OG2R3(SCRF) level infer that the





decomposition of [Mes₃PC(O)I][AlI₄] to [Mes₃PI][AlI₄] and CO is endothermic by 46 kJ mol⁻¹ with a reaction barrier in excess of 150 kJ mol⁻¹. In contrast, scans of the potential energy surface for phosphine attack at the carbon-bound halide of the transient cycle indicate that formation of the halophosphonium cation/cyclic anion pair entails only a small barrier (ca. 70 kJ mol⁻¹; the process is barrierless with respect to the exothermicity of the formation of the cyclic intermediate). Subsequent liberation of CO from the cyclic anion is barrierless and exothermic by 53 kJ mol⁻¹ (M06-2X(SCRF) level), clearly supporting the latter reaction pathway. This phosphine oxidation and reduction of CO₂ yields an oxo-bridged Al species ultimately incorporated into 8. Computations at the M06-2X(SCRF) level⁵⁵ show that the exchange of neutral fragment [I2AlOAlI2] for AlI3 in 3 is exothermic by -99 kJ/mol. The overall reaction energy for the conversion of 3 to 8/9 and CO is computed to be exothermic by 37 kJ/mol at the OG2R3(SCRF)//ONI(M06-2x)(SCRF) level.^{56,57} This is consistent with the argument that the formation of 3 represents the kinetic product, while the liberation of CO and formation of 8/9 are the thermodynamically favored products (Scheme 3).

CONCLUSION

The stoichiometric reduction of CO_2 to CO using R_3P/AlX_3 FLPs has been probed, and the kinetic product has been shown to be species of the form $R_3PC(OAlX_3)_2$. Nonetheless a further reaction occurs under CO_2 via a rate-determining associative insertion of CO_2 into the Al–X bond of AlX₃. This view is supported by kinetic data and the isolation of the insertion product of CO_2 with $Al(C_6F_5)_3$, 14. Subsequent nucleophilic attack by phosphine effects phosphine oxidation and affords the generation of the thermodynamic product $Mes_3PC-(OAlX_2)_2OAlX_3$. While this reactivity is interesting, this work suggests that catalytic processes to effect metal-free reduction of CO_2 will require a less oxophilic Lewis acid. Efforts to uncover such main group systems capable of catalytic chemistry are under study.⁶⁰

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an atmosphere of dry, oxygen-free N₂ by means of standard Schlenk or glovebox techniques (Innovative Technology glovebox equipped with a -38 °C freezer). Hexanes and toluene (Aldrich) were dried using an Innovative Technologies solvent system. Fluorobenzene and bromobenzene (-H₃ and -D₅) were purchased from Aldrich and dried on P₂O₅ for several days and vacuum distilled onto 4 Å

molecular sieves prior to use. Mes₃P and (otol)₃P were purchased from Strem, (CF₃)₃COH was purchased from Apollo Scientific, and $B(C_6F_5)_3$ was purchased from Boulder Scientific; all of these reagents were used without further purification. Al $(C_6F_5)_3$ -tol was prepared from $B(C_6F_5)_3$ and Me_3Al in toluene by a known procedure.⁶¹ Al(OC(CF₃)₃)₃·C₆H₅F was prepared from Et₃Al and (CF₃)₃COH in fluorobenzene according to a literature procedure.⁵² AlX₃ (X = Br, I) were purchased from Strem and sublimed three times prior to use under vacuum using a -78 °C coldfinger and an 80 °C (X = Br) or 150 °C (X = I) bath. ¹³CO₂ was purchased from Aldrich and used without further purification. CO2 was purchased from Linde and passed through a Drierite column prior to use. NMR spectra were obtained on a Bruker Avance 400 MHz or a Varian 400 MHz, and spectra were referenced to residual solvent of C6D5Br or externally ${}^{(27}\text{Al: Al}(\text{NO}_3)_3, {}^{31}\text{P: 85\% H}_3\text{PO}_4, {}^{19}\text{F: CFCl}_3)$. Chemical shifts (δ) listed are in ppm, and absolute values of the coupling constants are in Hz. NMR assignments are supported by additional 2D experiments. UV-vis spectra were obtained on an Agilent 8453 UV-vis spectrophotometer using Quartz cells modified with a J-Young NMR cap to ensure a near-perfect seal. Elemental analyses (C, H) and X-ray crystallography were performed in-house. EPR spectra were recorded at the University of Windsor at 25 °C or 77 K on a Bruker EMXplus X-band spectrometer controlled using Xenon software on a PC operating under Linux. The spectra were modeled using PIP4Win v. 1.2.4

Synthesis of (Mes₃P)All₃ (1). A 50 mL round-bottom flask equipped with a magnetic stir bar in the glovebox was charged with PMes₃ (250 mg, 0.64 mmol), All₃ (262 mg, 0.64 mmol), and bromobenzene (6–7 mL). The solution was allowed to stir for 5–10 min while a precipitate formed. The white precipitate was collected on a glass frit, washed with bromobenzene (several drops) and hexanes (ca. 5 mL), and dried (300 mg, 0.38 mmol, 59%). ¹H NMR (C_6D_5Br): 6.84 (bs, 3H, *m*-Mes), 6.68 (bs, 3H, *m*-Mes), 2.71 (s, 9H, *o*-CH₃^{Mes}), 2.02 (s, 9H, *p*-CH₃^{Mes}), 1.79 (s, 9H, *o*-CH₃^{Mes}). ³¹P{¹H} NMR (C_6D_5Br): -19, -29 (bm). ²⁷Al NMR (C_6D_5Br): 37 (bd, ¹ J_{Al-P} = 193 Hz). ¹³C{¹H} NMR (C_6D_5Br): 145.6 (bs), 143.3 (bs), 142.0 (bs), 132.5 (bs, *m*- C_6H_2), 131.5 (*m*- C_6H_2 , signal lost in solvent peak), 120.5 (d, ¹ J_{C-P} = 40.0 Hz, *i*- C_6H_2), 28.6 (bs, *o*- CH_3^{Mes}), 24.4 (bs, *o*- CH_3^{Mes}), 21.0 (s, *p*- CH_3^{Mes}). Anal. Calcd for C₂₇H₃₃AlI₃P: C, 40.73; H, 4.18. Found: C, 40.65; H, 3.81.

Synthesis of Mes₃P(CO₂)(AIX₃)₂ (X = I, 3; Br, 4; CI, 5) and (otol)₃P(CO₂)(AIX₃)₂ (X = I, 6; C₆F₅, 7). These compounds were synthesized in an analogous manner. Thus, only one preparation is detailed. A 50 mL round-bottom flask equipped with a magnetic stir bar in the glovebox was charged with PMes₃ (200 mg, 0.51 mmol) and AlCl₃ (69 mg, 0.51 mmol). Bromobenzene (10 mL) was added to this all at once. The solution was allowed to stir for 30 min, at which point ca. 15 mL of hexanes was added dropwise with rapid stirring. The white precipitate 5 that forms was collected on a glass frit, washed with hexanes (ca. 5 mL) followed by pentane (ca. 5 mL), and dried (215 mg, 0.41 mmol, 81%). Vapor diffusion of a bromobenzene solution of the compound with pentane yielded single crystals suitable for X-ray crystallography.

3: yield: 87%. ¹H NMR (C_6D_5Br): 6.83 (d, ⁴ $J_{H-H} = 4.4$ Hz, 3H, *m*-Mes), 6.70 (d, ⁴ $J_{H-H} = 4.4$ Hz, 3H, *m*-Mes), 2.48 (s, 9H, *o*-CH₃^{Mes}), 2.06 (s, 9H, *p*-CH₃^{Mes}), 1.90 (s, 9H, *o*-CH₃^{Mes}). ³¹P{¹H} NMR (C_6D_5Br): 22.0. ²⁷Al NMR (C_6D_5Br): 20 (bs, $v_{1/2} = ca. 1500$ Hz). ¹³C{¹H} NMR (C_6D_5Br): 167.8 (d, ¹ $J_{C-P} = 119$ Hz, CO₂), 146.5 (d, ⁴ $J_{C-P} = 3.0$ Hz, *p*-C₆H₂), 144.9 (d, ² $J_{C-P} = 11.6$ Hz, *o*-C₆H₂), 144.4 (d, ² $J_{C-P} = 10.3$ Hz, *o*-C₆H₂), 134.5 (d, ³ $J_{C-P} = 12.2$ Hz, *m*-C₆H₂), 133.7 (d, ³ $J_{C-P} = 12.5$ Hz, *m*-C₆H₂), 115.0 (d, ¹ $J_{C-P} = 74.5$ Hz, *i*-C₆H₂), 25.5 (d, ³ $J_{C-P} = 1.5$ Hz, *p*-CH₃^{Mes}). Anal. Calcd for C₂₈H₃₃PO₂Al₂I₆: C, 26.95; H, 2.67. Found: C, 26.91; H, 2.71. ¹³C-3: ³¹P{¹H} NMR (C₆D₅Br): 22.0 (d, ¹ $J_{P-C} = 119$ Hz).

4: Yield: 83%. ¹H NMR (C_6D_5Br): 6.84 (bs, 3H, *m*-Mes), 6.76 (bs, 3H, *m*-Mes), 2.32 (bs, 9H, *o*-CH₃^{Mes}), 2.08 (s, 9H, *p*-CH₃^{Mes}), 1.90 (bs, 9H, *o*-CH₃^{Mes}). ³¹P{¹H} NMR (C_6D_5Br): 22.3. ²⁷Al NMR (C_6D_5Br): not observed. ¹³C{¹H} NMR (C_6D_5Br): 172.5 (d, ¹ J_{C-P} = 119 Hz, CO₂), 147.2 (d, ⁴ J_{C-P} = 3.0 Hz, *p*-C₆H₂), 145.3 (bs, *o*-C₆H₂),

144.1 (bs, $o \cdot C_6H_2$), 133.9 (s, $m \cdot C_6H_2$), 133.8 (s, $m \cdot C_6H_2$), 114.1 (d, ${}^1J_{C-P} = 76 \text{ Hz}$, $i \cdot C_6H_2$), 24.9 (bs, $o \cdot CH_3^{\text{Mes}}$), 23.8 (bs, $o \cdot CH_3^{\text{Mes}}$), 21.3 (s, $p \cdot CH_3^{\text{Mes}}$). Anal. Calcd for $C_{28}H_{33}PO_2Al_2Br_6$: C, 34.82; H, 3.44. Found: C, 34.78; H, 3.64. ${}^{13}C-4$: Yield: 83%. ${}^{31}P\{{}^{1}H\}$ NMR (C_6D_5Br): 21.0 (d, ${}^1J_{P-C} = 121 \text{ Hz}$).

5: yield: 82%. ¹H NMR (C_6D_5Br): 6.80 (bs, 3H, *m*-Mes), 6.68 (bs, 3H, *m*-Mes), 2.32 (bs, 9H, *o*-CH₃^{Mes}), 2.03 (s, 9H, *p*-CH₃^{Mes}), 1.85 (bs, 9H, *o*-CH₃^{Mes}). ³¹P{¹H} NMR (C_6D_5Br): 20.1 (d, ¹ $J_{P-C} = 123$ Hz). ²⁷Al NMR (C_6D_5Br): 105 (bs, $v_{1/2} = 750$ Hz). ¹³C{¹H} NMR (C_6D_5Br): 171.5 (d, ¹ $J_{C-P} = 123$ Hz, CO₂), 146.8 (d, ⁴ $J_{C-P} = 3.2$ Hz, *p*-C₆H₂), 145.0 (bs, *o*-C₆H₂), 144.4 (bs, *o*-C₆H₂), 133.6 (bs, 2 × *m*-C₆H₂), 114.6 (d, ¹ $J_{C-P} = 76$ Hz, *i*-C₆H₂), 24.5 (bs, *o*-CH₃^{Mes}), 23.6 (bs, *o*-CH₃^{Mes}), 21.2 (s, *p*-CH₃^{Mes}). Anal. Calcd for C₂₈H₃₃PO₂Al₂Cl₆: C, 48.10; H, 4.76. Found: C, 48.24; H, 4.71. ¹³C-5: Yield: 82%. ³¹P{¹H} NMR (C₆D₅Br): 19.8.

6: Heating to 60 °C for 1 h. Yield: 72%. ¹H NMR (C_6D_5Br): 7.57–7.51 (m, 3H), 7.36–7.32 (m, 3H), 7.16–7.09 (m, 6H), 2.08 (bs, 9H, o-CH₃). ³¹P{¹H} NMR (C_6D_5Br): 27.5. ²⁷Al NMR (C_6D_5Br): 23 (bs, $v_{1/2} = ca. 1500$ Hz). ¹³C{¹H} NMR (C_6D_5Br): 164.3 (d, ¹ $J_{C-P} = 123$ Hz, CO₂), 144.5 (d, $J_{C-P} = 9.3$ Hz), 136.9 (d, $J_{C-P} = 3.0$ Hz), 135.7 (d, $J_{C-P} = 12.7$ Hz), 134.5 (d, $J_{C-P} = 11.6$ Hz), 128.5 (d, $J_{C-P} = 13.6$ Hz), 111.2 (d, $J_{C-P} = 81.2$ Hz, $i-C_6H_4$), 23.4 (d, ³ $J_{C-P} = 4.9$ Hz, $o-CH_3$). Anal. Calcd for C₂₂H₂₁PO₂Al₂I₆: C, 22.71; H, 1.82. Found: C, 23.22; H, 2.00.

7: Yield, 90%. ¹H NMR (C_6D_3Br): 7.60–6.85 (m, 12H), 1.81 (bs, 9H, o-CH₃), 1.27–1.13 (m, 4H, 0.5·(CH₃(CH₂)CH₃)), 0.84 (t, ³J_{H-H} = 6.8 Hz, 3H, 0.5·(CH₃(CH₂)CH₃)). ³¹P{¹H} NMR (C_6D_5Br): 30.0. ²⁷Al NMR (C_6D_5Br): not observed. ¹⁹F{¹H} NMR (376 MHz, C_6D_5Br): -121.8 (bd, ³J_{F-F} = 19.2 Hz, 12F, o-C₆F₅), -152.5 (t, ³J_{F-F} = 19.9 Hz, 6F, p-C₆F₅), -161.4 (m, 12F, m-C₆F₅). ¹³C{¹H} NMR (C_6D_5Br): 167.3 (d, ¹J_{C-P} = 128 Hz, CO₂), 149.9 (dm, ¹J_{C-F} = 234 Hz), 144.2 (d, ²J_{C-P} = 8.4 Hz, C-Me), 141.7 (dm, ¹J_{C-F} = 252 Hz), 136.7 (dm, ¹J_{C-F} = 253 Hz), 136.4 (d, J_{C-P} = 1.8 Hz), 135.2 (d, J_{C-P} = 11.8 Hz), 133.7 (d, J_{C-P} = 78 Hz, i-C₆H₄), 31.8 (s, C₆H₁₄), 22.9 (s, C₆H₁₄), 22.4 (bs, o-CH₃), 14.4 (s, C₆H₁₄). Anal. Calcd for C₆₁H₂₈Al₂F₃₀O₂P-0.5C₆H₁₄: C, 50.61; H, 1.95. Found: C, 50.36; H, 2.06.

Isolation of $Mes_3PC(OAIX_2)_2OAIX_3$ (X = I, 8; Br, 10). Small portions of these products were separated from reactions yielding 3 and 4, respectively, upon standing for 24 h and after slow cooling of the fluorobenzene solutions to -38 °C.³³ Crystals obtained were suitable for X-ray crystallography. The crystals were partly soluble in deuterated bromobenzene.

8: Small portions of **8** were isolated from reactions. ¹H NMR (C_6D_5Br) : 7.09–6.83 (m, 7–8H, 1.5· C_6H_5F), 6.82 (bs, 3H, *m*-Mes), 6.70 (bs, 3H, *m*-Mes), 2.33 (bs, 9H, *o*-CH₃^{Mes}), 2.06 (s, 9H, *p*-CH₃^{Mes}), 1.83 (bs, 9H, *o*-CH₃^{Mes}). ³¹P{¹H} NMR (C_6D_5Br) : 19.5. ²⁷Al NMR (C_6D_5Br) : 31 (s, $v_{1/2} = ca. 170 Hz$). ¹³C{¹H} NMR (C_6D_5Br) : 19.5. ²⁷Al NMR (C_6D_5Br) : 31 (s, $v_{1/2} = ca. 170 Hz$). ¹³C{¹H} NMR (C_6D_5Br) : 173.9 (d, ¹ $J_{C-P} = 118 Hz, CO_2$), 162.8 (d, ¹ $J_{C-F} = 244 Hz, i-C_6H_5F$), 147.0 (d, ⁴ $J_{C-P} = 3.0 Hz, p-C_6H_2$), 144.7 (bs, 2C, *o*-C₆H₂), 133.5 (bs, 2C, *m*-C₆H₂), 130.0 (d, ³ $J_{C-F} = 7.7 Hz, m-C_6H_3F$), 124.1 (d, ⁴ $J_{C-F} = 3.1 Hz, p-C_6H_5F$), 115.3 (d, ² $J_{C-F} = 20.6 Hz, o-C_6H_3F$), 113.6 (d, ¹ $J_{C-P} = 76.2 Hz, i-C_6H_2$), 26.0 (bs, *o*-CH₃^{Mes}), 23.8 (bs, *o*-CH₃^{Mes}), 21.3 (s, *p*-CH₃^{Mes}). ¹⁹F NMR (376 MHz, C₆D₅Br): -112.4. Anal. Calcd for C₂₈H₃₃Al₃I₇O₃P·3C₆H₃F (**8**·3C₆H₃F)): C, 28.45; H, 2.61. Found: C, 28.36; H, 2.60.

10: Small portions of **10** were isolated from reactions. ¹H NMR (CD_2Cl_2) : 7.52–7.24 (m, 5H, C_6H_3Br), 7.17 (bs, 6H, *m*-Mes), 2.41 (s, 9H, *p*-CH₃^{Mes}), 2.32 (bs, 9H, *o*-CH₃^{Mes}), 2.11 (bs, 9H, *o*-CH₃^{Mes}). ³¹P{¹H} NMR (CD_2Cl_2) : 19.5. ²⁷Al NMR (CD_2Cl_2) : 88 (bs). ¹³C{¹H} NMR (CD_2Cl_2) : 176.8 (d, ¹ J_{C-P} = 123 Hz, CO₂), 147.9 (d, ⁴ J_{C-P} = 3.0 Hz, *p*-C₆H₂), 145.5 (bd, ² J_{C-P} = 11 Hz, *o*-C₆H₂), 134.0 (bd, ³ J_{C-P} = 12.4 Hz, *m*-C₆H₂), 131.9 (s, C₆H₅Br), 130.5 (s, C₆H₅Br), 127.4 (s, C₆H₅Br), 122.7 (s, C₆H₅Br), 113.7 (d, ¹ J_{C-P} = 76.6 Hz, *i*-C₆H₂), 25.1 (bs, *o*-CH₃^{Mes}), 24.3 (bs, *o*-CH₃^{Mes}), 21.5 (d, ⁵ J_{C-P} = 1.6 Hz, *p*-CH₃^{Mes}). Anal. Calcd for C₂₈H₃₃Al₃Br₇O₃P·C₆H₅Br (**10**·C₆H₅Br): C, 32.78; H, 3.07. Found: C, 32.52; H, 3.11. Synthesis of [Mes₃PX][AIX₄] (X = I, 9; Br, 11). These compounds were synthesized in an analogous manner. Thus only one preparation is detailed. A 50 mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with PMes₃ (0.300 g, 0.77 mmol) and AII₃ (0.315 g, 0.77 mmol). Toluene (20 mL) was added to this all at once. To this mixture was then added dropwise a solution of I₂ (0.196 g, 0.77 mmol) in ca. 5 mL of toluene. The mixture turned to a pale yellow, oily solution and was allowed to stir for 30 min. The solvent was removed *in vacuo* to obtain a pale orange solid. The solid was stirred in hexanes (ca. 10 mL) for 10 min, and the mixture was filtered on a glass frit, washed with hexanes (ca. 5 mL), and dried (0.72 g, 89%).

9: ¹H NMR (C_6D_5Br): 6.82 (d, ⁴ J_{H-P} = 4.4 Hz, 3H, *m*-Mes), 6.63 (d, ⁴ J_{H-P} = 6.0 Hz, 3H, *m*-Mes), 2.17 (s, 9H, *o*-CH₃^{Mes}), 2.12 (s, 9H, *p*-CH₃^{Mes}), 1.73 (s, 9H, *o*-CH₃^{Mes}). ³¹P{¹H} NMR (C_6D_5Br): -14.5. ²⁷Al NMR (C_6D_5Br): -25 (s). ¹³C{¹H} NMR (C_6D_5Br): 146.4 (d, ⁴ J_{C-P} = 3.4 Hz, *p*-C₆H₂), 145.4 (d, ² J_{C-P} = 11.8 Hz, *o*-C₆H₂), 143.4 (d, ² J_{C-P} = 12.1 Hz, *o*-C₆H₂), 133.4 (d, ³ J_{C-P} = 6.4 Hz, *o*-C₆H₂), 119.3 (d, ¹ J_{C-P} = 6.5 Hz, *i*-C₆H₂), 26.3 (d, ³ J_{C-P} = 1.8 Hz, *p*-CH₃^{Mes}), 24.4 (d, ³ J_{C-P} = 4.3 Hz, *o*-CH₃^{Mes}), 21.4 (d, ⁵ J_{C-P} = 1.8 Hz, *p*-CH₃^{Mes}). Anal. Calcd for C₂₇H₃₃PAII₅: C, 30.88; H, 3.17. Found: C, 31.22; H, 3.05.

11: Yield: 89%. ¹H NMR (C_6D_5Br): 6.87 (d, ⁴ $J_{H-P} = 4.4$ Hz, 3H, m-Mes), 6.71 (d, ⁴ $J_{H-P} = 6.4$ Hz, 3H, m-Mes), 2.14 (s, 9H, p-CH₃^{Mes}), 2.13 (s, 9H, o-CH₃^{Mes}), 1.76 (s, 9H, o-CH₃^{Mes}). ³¹P{¹H} NMR (C_6D_5Br): 38.5. ²⁷Al NMR (C_6D_5Br): 81 (s). ¹³C{¹H} NMR (C_6D_5Br): 147.2 (d, ⁴ $J_{C-P} = 3.0$ Hz, p-C $_6H_2$), 145.4 (d, ² $J_{C-P} = 10.3$ Hz, o-C $_6H_2$), 143.7 (d, ² $J_{C-P} = 15.4$ Hz, o-C $_6H_2$), 133.7 (d, ³ $J_{C-P} = 12.1$ Hz, m-C $_6H_2$), 133.2 (d, ³ $J_{C-P} = 13.5$ Hz, m-C $_6H_2$), 119.0 (d, ¹ $J_{C-P} = 74.4$ Hz, i-C $_6H_2$), 24.9 (d, ³ $J_{C-P} = 1.5$ Hz, p-CH₃^{Mes}), 24.4 (d, ³ $J_{C-P} = 5.5$ Hz, o-CH₃^{Mes}), 21.5 (d, ⁵ $J_{C-P} = 1.5$ Hz, p-CH₃^{Mes}). Anal. Calcd for C₂₇H₃₃PAlBr₅: C, 39.79; H, 4.08. Found: C, 39.87; H, 4.05.

Synthesis of [Mes₃PMe][All₄] (12). A 50 mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with PMes₃ (1.0 g, 2.57 mmol) and AlI₃ (1.1 g, 2.7 mmol). Fluorobenzene (15 mL) was added to this all at once. To this mixture was added dropwise a solution of MeI (0.384 g, 2.7 mmol) in fluorobenzene (5 mL). The mixture turned to a pale yellow solution and was allowed to stir for 1 h. The solvent was removed in vacuo to obtain a beige, oily residue. The residue was stirred in hexanes (ca. 20 mL) for 10 min. An off-white precipitate formed, which was filtered on a glass frit, washed with hexanes (ca. 2 \times 5 mL), and dried (2.1 g, 87%). ¹H NMR (C_6D_5Br) : 6.87 (s, 3H, m-Mes), 6.69 (s, 3H, m-Mes), 2.39 (d, ${}^2J_{H-P}$ = 11.6 Hz, 3H, Me), 2.14 (s, 9H, p-CH₃^{Mes}), 1.99 (s, 9H, o-CH₃^{Mes}), 1.72 (s, 9H, o-CH₃^{Mes}). ${}^{31}P{}^{1}H{}^{1}NMR$ (C₆D₅Br): 7.0. ${}^{27}AI$ NMR (C_6D_5Br) : -25 (s). ¹³C{¹H} NMR (C_6D_5Br): 145.1 (d, ⁴ J_{C-P} = 2.9 $\begin{aligned} &(C_6D_5D_1). -23 \text{ (s)}. \quad C_1 \text{ II } \text{ NMR } (C_6D_5D_1). \text{ I+3.1 } (d, \ J_{C-P} = 2.8) \\ &\text{Hz}, p\text{-}C_6H_2), \text{ 143.6 } (d, \ ^2J_{C-P} = 10.6 \text{ Hz}, o\text{-}C_6H_2), \text{ 142.8 } (d, \ ^2J_{C-P} = 10.4 \text{ Hz}, o\text{-}C_6H_2), \text{ 133.1 } (d, \ ^3J_{C-P} = 11.4 \text{ Hz}, m\text{-}C_6H_2), \text{ 133.1 } (d, \ ^3J_{C-P} = 11.6 \text{ Hz}, m\text{-}C_6H_2), \text{ 119.6 } (d, \ ^1J_{C-P} = 79.0 \text{ Hz}, i\text{-}C_6H_2), \text{ 25.7 } (d, \ ^1J_{C-P} = 62.4 \text{ Hz}, PMe), \text{ 24.1 } (d, \ ^3J_{C-P} = 4.7 \text{ Hz}, o\text{-}CH_3^{\text{Mes}}), \text{ 24.0 } (d, \ ^3J_{C-P} = 5.2 \text{ Hz}, o\text{-}CH_3^{\text{Mes}}), \text{ 21.4 } (s, p\text{-}CH_3^{\text{Mes}}). \text{ Anal. Calcd for } C_{28}H_{36}\text{PAII}_4\text{: C}, \text{ PAII}_4 \text{ Constants} \\ &\text{PAII}_4 \text{ Constants} \text{ PAII}_4 \text{ Constants} \text{ PAII}_4 \text{ Constants} \text{ Constants} \text{ PAII}_4 \text{ Constants} \text{ Constants} \text{ Constants} \text{ Constants} \text{ PAII}_4 \text{ Constants} \text{ Co$ 35.85; H, 3.87. Found: C, 35.88; H, 3.94.

Synthesis of $[(C_6F_5)C(0)OAI(C_6F_5)_2]_2$ (14). A 50 mL Schlenk bomb equipped with a Teflon screw cap and a magnetic stirbar was charged with Al(C_6F_5)_3·tol (300 mg, 0.48 mmol) and fluorobenzene (5 mL). The bomb was transferred to the Schlenk line equipped with a CO₂ outlet. The bomb was degassed, filled with CO₂ (1 atm), and sealed. The solution was heated to 90 °C and stirred rapidly for 24 h, after which the CO₂ atmosphere was removed. The product was isolated by crystallization at -38 °C and filtered (220 mg, 0.38 mmol, 79%). Slow cooling of a fluorobenzene solution to -38 °C of the compound yielded single crystals suitable for X-ray crystallography. ²⁷Al NMR (C_6D_5Br): blank. ¹⁹F{¹H} NMR (376 MHz, C_6D_5Br): -122.8 (bd, ² J_{F-F} = 18.0 Hz, 4F, o-C₆ F_5 -Al), -131.5 (bs, 2F, o-C₆ F_5 -CO₂), -135.0 (tt, ³ J_{F-F} = 22.6 Hz, ⁴ J_{F-F} = 11.3 Hz, 1F, p-C₆ F_5 -CO₂), -148.3 (t, ³ J_{F-F} = 19.9 Hz, 2F, p-C₆ F_5 -Al), -156.5 (m, 2F, m-C₆ F_5 -CO₂), -159.1 (m, 4F, m-C₆ F_5 -Al), ^{13}C {¹H} NMR (C₆ D_5Br), partial: 168.0 (s, CO₂). Anal. Calcd for C₁₉AlF₁₅O₂: C, 39.88. Found: C, 39.79.

Synthesis of (otol)₃PC(O)OAI(OC(CF₃)₃)₃ (15). A 50 mL Schlenk bomb equipped with a Teflon screw cap and a magnetic stirbar was charged with $P(otol)_3$ (20 mg, 66 μ mol), PhF-Al(OC(CF₃)₃)₃ (54 mg, 66 μ mol), and fluorobenzene (0.7 mL). The bomb was transferred to the Schlenk line equipped with a CO₂ outlet. The bomb was degassed, filled with CO₂ (1 atm), and sealed. The solution was stirred for 10 min, after which time the CO₂ atmosphere was removed. Slow cooling of the solution to -38 °C yielded single crystals suitable for X-ray crystallography (66 mg, 61 µmol, 93%). ¹H NMR (C₆H₅F): 7.84 (m, 3H, o-CH), 7.59 (m, 3H, p-CH), 7.39 (m, 3H, m-CH), 7.36 (m, 3H, *m*-CH), 2.29 (s, 9H, CH₃). ${}^{31}P{}^{1}H{}$ NMR (C₆H₅F): 11.2. ${}^{27}AI$ NMR (C_6H_5F) : 37 (bs). ¹⁹F{¹H} NMR (376 MHz, C_6H_5F): -75.2 (s, 27F, (CF_3) . ¹³C{¹H} NMR (C₆H₅F): 159.1 (d, ¹J_{P-C} = 124 Hz, CO₂), 144.4 115.5 (d, ${}^{1}J_{P-C} = 82$ Hz, $i-C_{6}H_{4}$), 78.9 (m, OC(CF₃)₃), 21.5 (d, ${}^{3}J_{P-C}$ = 5 Hz, CH₃). Anal. Calcd for C₃₄H₂₁AlF₂₇O₅P: C, 37.80; H, 1.96. Found: C, 37.72; H, 2.04.

Synthesis of Al(C₆F₅)₃(C₆H₅Br)₂ (16). Single crystals suitable for X-ray diffraction of this compound were obtained by slow cooling a bromobenzene solution of Al(C₆F₅)₃·tol to -38 °C, over several days. ¹H, ²⁷Al, ¹⁹F, ¹³C{¹H} NMR: as reported for the known complex Al(C₆F₅)₃·tol.⁶¹

Kinetic Study. All kinetic experiments were performed in thickwalled J-Young NMR tubes (total volume of 2 mL) under CO_2 pressure. Saturated solutions of 5 (7.2 mM) were prepared by dissolving 36 mg (29 μ mol) in 4.0 mL of C_6D_5Br , and aliquots of 0.50 mL were used. The concentration of CO_2 in solution was determined using Raoult's law for CO_2 in bromobenzene at 1 atm.⁵⁴ The reactions were monitored by ³¹P{¹H} NMR spectroscopy, samples were placed directly in the prewarmed spectrometer, and the spectra were acquired after a 5 min equilibration period. Data were obtained over a 30 K range (303–333 K).

Computational Studies. The Gaussian suite (G09)⁶² was utilized for all calculations. Optimizations employed the ONIOM^{63,64} composite approach, within which the DFT model M06-2X55 was used. The appropriateness of this approach was affirmed by observation of good agreement between computationally and X-ray diffraction-determined structural parameters. Single-point energy calculations at the ONIOM-determined geometries were performed using the ONIOM G2R3 $({\rm OG2R3})^{56,57}$ composite approach, which approximates a CCSD(T)/6-311+G(2df, 2p) calculation, providing a more accurate prediction at modest cost.^{65,66} Bromobenzene solvent effects were examined using both explicit bromobenzene molecules and/or a polarized continuum solvent model (indicated by the abbreviation SCRF).^{67,68} Inclusion of solvent in either form had only a small effect on predicted structures but showed a detectable effect on the reaction energetics, presumably because all species were extremely polar. Energies were corrected using unscaled zero-point energies from the frequency analyses, since scaling factors for ONIOM-based frequency determinations are undetermined.

ASSOCIATED CONTENT

Supporting Information

X-ray data (CIF) have been deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) IPCC. Climate Change 2007: Synthesis Report, IPCC, 2007.
- (2) Sakakura, T.; Choi, J.-C.; Yasuda, H. Chem. Rev. 2007, 107, 2365.
- (3) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kuhn, F. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8510.
- (4) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. Chem. Rev. 2001, 101, 953.
- (5) Sunley, G. J.; Watson, D. J. Catal. Today 2000, 58, 293.
- (6) Olah, G. A.; Prakash, G. K. S.; Goeppert, A. J. Org. Chem. 2009, 74, 487.
- (7) Olah, G. A. C&E News 2003, 81, 5.
- (8) Hebrard, F. d. r.; Kalck, P. Chem. Rev. 2009, 109, 4272.
- (9) Laitar, D. S.; Muller, P.; Sadighi, J. P. J. Am. Chem. Soc. 2005, 127, 17196.
- (10) Hegg, E. L. Acc. Chem. Res. 2004, 37, 775.
- (11) Ettedgui, J.; Diskin-Posner, Y.; Weiner, L.; Neumann, R. J. Am. Chem. Soc. 2010, 133, 188.
- (12) Lin, W.; Frei, H. J. Am. Chem. Soc. 2005, 127, 1610.
- (13) Morris, A. J.; Meyer, G. J.; Fujita, E. Acc. Chem. Res. 2009, 42, 1983.
- (14) Takeda, H.; Ishitani, O. Coord. Chem. Rev. 2010, 254, 346.
- (15) Woolerton, T. W.; Sheard, S.; Reisner, E.; Pierce, E.; Ragsdale, S. W.; Armstrong, F. A. J. Am. Chem. Soc. **2010**, 132, 2132.
- (16) Rosen, B. A.; Salehi-Khojin, A.; Thorson, M. R.; Zhu, W.; Whipple, D. T.; Kenis, P. J. A.; Masel, R. I. *Science* **2011**, *334*, 643.
- (17) Simon-Manso, E.; Kubiak, C. P. Organometallics 2004, 24, 96.
- (18) Castro-Rodriguez, I.; Meyer, K. J. Am. Chem. Soc. 2005, 127, 11242.
- (19) Silvia, J. S.; Cummins, C. C. J. Am. Chem. Soc. 2010, 132, 2169.
- (20) Huff, C. A.; Sanford, M. S. J. Am. Chem. Soc. 2011, 133, 18122.
- (21) Jessop, P. G.; Ikariya, T.; Noyori, R. Chem. Rev. 1995, 95, 259.
- (22) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. Nat. Chem. **2011**, *3*, 609.
- (23) Leitner, W. Angew. Chem., Int. Ed. 1995, 34, 2207.
- (24) Tanaka, R.; Yamashita, M.; Nozaki, K. J. Am. Chem. Soc. 2009, 131, 14168.
- (25) Langer, R.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. Angew. Chem., Int. Ed. 2011, 50, 9948.
- (26) Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, 49, 9777.
- (27) Sgro, M. J.; Stephan, D. W. Chem. Commun. 2013, 49, 2610.
- (28) Sgro, M. J.; Stephan, D. W. Angew. Chem., Int. Ed. 2012, 51, 11343.
- (29) Sgro, M. J.; Dömer, J.; Stephan, D. W. Chem. Commun. 2012, 48, 7253.
- (30) Neu, R. C.; Ménard, G.; Stephan, D. W. Dalton Trans. 2012, 41, 9016.
- (31) Li, J.; Hermann, M.; Frenking, G.; Jones, C. Angew. Chem., Int. Ed. 2012, 51, 8611.
- (32) Ménard, G.; Stephan, D. W. Angew. Chem., Int. Ed. 2011, 50, 8396.
- (33) Ménard, G.; Stephan, D. W. J. Am. Chem. Soc. 2010, 132, 1796.
- (34) Berkefeld, A.; Piers, W. E.; Parvez, M. J. Am. Chem. Soc. 2010, 132, 10660.
- (35) Gu, L.; Zhang, Y. J. Am. Chem. Soc. 2009, 132, 914.
- (36) Ashley, A. E.; Thompson, A. L.; O'Hare, D. Angew. Chem., Int. Ed. 2009, 48, 9839.

- Article
- (37) Roters, S.; Hepp, A.; Slootweg, J.; Lammertsma, K.; Uhl, W. Chem. Commun. 2012, 48, 9616.
- (38) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. Angew. Chem., Int. Ed. **2011**, *50*, 3925.
- (39) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. Angew. Chem., Int. Ed. 2009, 48, 6643.
- (40) Menard, G.; Hatnean, J. A.; Cowley, H. J.; Lough, A. J.; Rawson, J. M.; Stephan, D. W. J. Am. Chem. Soc. **2013**, 135, 6446.
- (41) Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. J. Org. Chem. 1991, 56, 3537.
- (42) Tojo, S.; Yasui, S.; Fujitsuka, M.; Majima, T. J. Org. Chem. 2006, 71, 8227.
- (43) Sasaki, S.; Sutoh, K.; Murakami, F.; Yoshifuji, M. J. Am. Chem. Soc. 2002, 124, 14830.
- (44) Kwaan, R. J.; Harlan, C. J.; Norton, J. R. Organometallics 2001, 20, 3818.
- (45) Kloo, L.; Rosdahl, J.; Taylor, M. J. Polyhedron 2002, 21, 519.
- (46) Rawson, J. M.; Nilges, M. Vol. PIP for Windows v. 1.2, 2011.
- (47) Tolman, C. A. Chem. Rev. 1977, 77, 313.
- (48) Timoshkin, A. Y.; Bodensteiner, M.; Sevastianova, T. N.; Lisovenko, A. S.; Davydova, E. I.; Scheer, M.; Graßl, C.; Butlak, A. V. *Inorg. Chem.* **2012**, *51*, 11602.
- (49) Kwon, H. J.; Kim, H. W.; Rhee, Y. M. Chem.—Eur. J. 2011, 17, 6501.
- (50) Menard, G.; Stephan, D. W. Dalton Trans. 2013, 42, 5447.
- (51) Timoshkin, A. Y.; Frenking, G. Organometallics 2008, 27, 371–380.
- (52) Müller, Lutz O.; Himmel, D.; Stauffer, J.; Steinfeld, G.; Slattery, J.; Santiso-Quiñones, G.; Brecht, V.; Krossing, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 7659.
- (53) Plack, V.; Goerlich, J. R.; Fischer, A.; Schmutzler, R. Z. Anorg. Allg. Chem. 1999, 625, 1979.
- (54) Perisanu, S. T. J. Soln. Chem. 2001, 30, 183.
- (55) Zhao, Y.; Truhlar, D. Theor. Chem. Acc. 2008, 120, 215.
- (56) Vreven, T.; Morokuma, K. J. Chem. Phys. 1999, 111, 8799.
- (57) Vreven, T.; Morokuma, K. J. Phys. Chem. A 2002, 106, 6167.
- (58) Kolesinska, B. Cent. Eur. J. Chem. 2010, 8, 1147.
- (59) Wells, A. Syn. Commun. 1994, 24, 1715.
- (60) Dobrovetsky, R.; Stephan, D. W. Angew. Chem., Int. Ed. 2013, 52, 2516.
- (61) Hair, G. S.; Cowley, A. H.; Jones, R. A.; McBurnett, B. G.; Voigt, A. J. Am. Chem. Soc. **1999**, 121, 4922.
- (62) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, H. P. H.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. M., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian09; Gaussian, Inc.: Wallingford, CT, 2009.
- (63) Dapprich, S.; Komaromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. J. Mol. Stuct. (THEOCHEM) **1999**, 461–462, 1.
- (64) Vreven, T.; Morokuma, K. J. Comput. Chem. 2000, 21, 1419.
- (65) Dutmer, B. C.; Gilbert, T. M. Organometallics 2011, 30, 778.
- (66) Gilbert, T. M. J. Comput. Chem. 2011, 32, 1493.
- (67) Tomasi, J.; Mennucci, B.; Cammi, R. Chem. Rev. 2005, 105, 2999.
- (68) Vreven, T.; Mennucci, B.; da Silva, C. O.; Morokuma, K.; Tomasi, J. J. Chem. Phys. **2001**, 115, 62.