

# Reversible Carbon Dioxide Binding by Simple Lewis Base Adducts with Electron-Rich Phosphines

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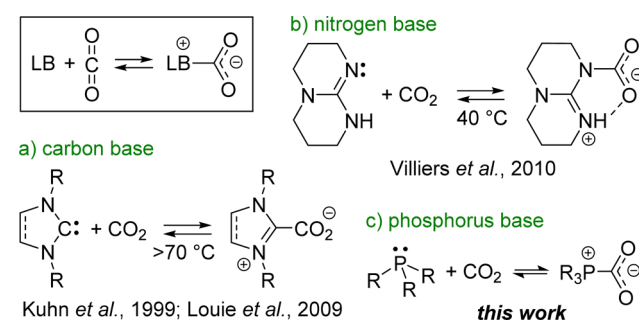
**S** Supporting Information

**ABSTRACT:** For the efficient utilization of carbon dioxide as feedstock in chemical synthesis, low-energy-barrier CO<sub>2</sub> activation is a valuable tool. We report a metal-free approach to reversible CO<sub>2</sub> binding under mild conditions based on simple Lewis base adducts with electron-rich phosphines. Variable-temperature NMR studies and DFT calculations reveal almost thermoneutral CO<sub>2</sub> binding with low-energy barriers or stable CO<sub>2</sub> adduct formation depending on the phosphines donor ability. The most basic phosphine forms an air-stable CO<sub>2</sub> adduct that was used as phosphine transfer agent, providing a convenient access to transition-metal complexes with highly electron-rich phosphine ligands relevant to catalysis.

Carbon dioxide accumulation in our atmosphere as a consequence of human activity is challenging our environment.<sup>1</sup> This issue has prompted the scientific community to develop new approaches to mitigate CO<sub>2</sub> emissions. One strategy to address this problem involves capture and utilization of CO<sub>2</sub> as feedstock for the synthesis of chemicals, materials, and fuels.<sup>2</sup> As an important matter in this respect, the balance between the costs of the required energy input and the created value of the product has to be economically favorable. In this context, a species that can reversibly form weak adducts of CO<sub>2</sub> with almost no energy barrier in either direction would be an incredibly valuable tool.

While CO<sub>2</sub> physisorption in porous materials has applications in CO<sub>2</sub> capture and separation technologies,<sup>3</sup> CO<sub>2</sub> activation associated with the bending of the molecule is typically required to facilitate its chemical transformation. The arguably most straightforward way to achieve this is the formation of simple Lewis base adducts to CO<sub>2</sub> (Chart 1). Strong organic nucleophiles and transition-metal complexes are known to react in this manner,<sup>4</sup> but weakly bonded Lewis base adducts of this type enabling reversible CO<sub>2</sub> binding are very rare.<sup>5</sup> For instance, N-heterocyclic carbenes (NHCs) readily form Lewis base adducts with CO<sub>2</sub>,<sup>6</sup> which makes them valuable organocatalysts for a variety of CO<sub>2</sub> converting reactions (Chart 1a).<sup>7</sup> The reversibility of the carboxylation was investigated by thermogravimetric analysis (TGA) revealing that the decarboxylating ability of NHC-CO<sub>2</sub> adducts

**Chart 1. Examples of Reversible CO<sub>2</sub> Binding by Zwitterionic Lewis Base Adducts**



largely depends on the steric properties of the NHC, while variation of the electronic properties has minor influence.<sup>8</sup>

Despite the fact that amidine and guanidine bases have proven to be useful in promoting a variety of catalytic transformations involving CO<sub>2</sub>,<sup>7</sup> stable nitrogen base-CO<sub>2</sub> adducts are rare.<sup>5</sup> In fact, tertiary amines do not react with CO<sub>2</sub> on their own, and for amidines, it is uncertain whether the presence of water is necessary for the CO<sub>2</sub> capture.<sup>9</sup> Villiers et al. provided the first clear evidence for the formation of a stable nitrogen base-CO<sub>2</sub> adduct, which is stabilized by an additional intramolecular hydrogen-bonding interaction to the carboxylate group and loses CO<sub>2</sub> upon heating at 40 °C under vacuum (Chart 1b).<sup>10</sup>

To date, no direct evidence for the CO<sub>2</sub> adduct formation with tertiary phosphines has been provided, even though the intermediate formation has been postulated in the carboxylative cyclization of propargyl alcohols in supercritical CO<sub>2</sub>.<sup>11</sup> Phosphine-CO<sub>2</sub> adducts could be stabilized only in the presence of a Lewis acid.<sup>12</sup> The first reversible CO<sub>2</sub> binding of this kind was reported by Grimme, Stephan, Erker et al. in 2009 using frustrated Lewis pairs (FLPs).<sup>13</sup> Since their seminal work, a variety of systems based on phosphines and different Lewis acids have been developed for CO<sub>2</sub> activation,<sup>14</sup> while catalytic transformations of CO<sub>2</sub> are often hampered by the fact that the reaction products form stable adducts with the Lewis pairs.<sup>15</sup>

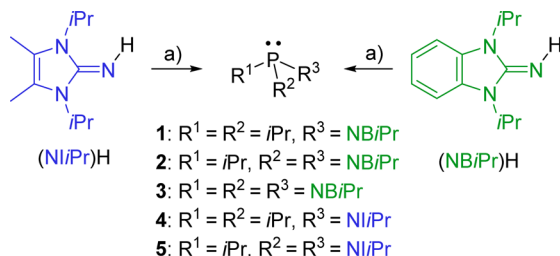
Received: December 22, 2015

Published: January 29, 2016

Herein, we report a metal-free approach to reversible CO<sub>2</sub> binding under mild conditions by simple Lewis base adduct formation with phosphines. This provides low-energy-barrier CO<sub>2</sub> activation associated with the bending of the molecule (Chart 1c). Our study is based on imidazolin-2-ylidenamino-substituted phosphines (IAPs), because they are more electron-rich than alkylphosphines, and their electronic and steric properties can be easily modulated.<sup>16</sup>

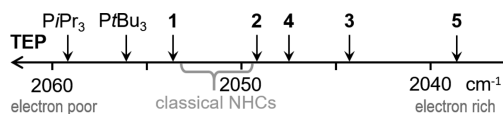
For a selection of electron-rich phosphines with diverse donor ability, we targeted the synthesis of IAPs 1–5 (Scheme 1). Following the reported procedure for the synthesis of IAPs

### Scheme 1. Synthesis of IAPs 1–5<sup>a</sup>



<sup>a</sup>Reagents and conditions (yields): (a) *n*BuLi, THF, –78 °C, and then chlorophosphine, RT; 1 (84%), 2 (86%), 3 (94%), 4 (95%), 5 (87%).

1–3,<sup>16</sup> the 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenamino (Ni*i*Pr) substituted phosphines 4 and 5 were prepared in very good yields by deprotonation of imine (Ni*i*Pr)H with *n*-butyllithium and subsequent treatment with the respective chlorophosphine. Determination of the CO stretching vibrations in [(IAP)Ni(CO)<sub>3</sub>] complexes revealed A<sub>1</sub> bands at 2047.5 cm<sup>–1</sup> for 4 and 2038.6 cm<sup>–1</sup> for 5, indicating superior π-donor ability of the Ni*i*Pr substituent with respect to the NB*i*Pr substituent (Figure 1).

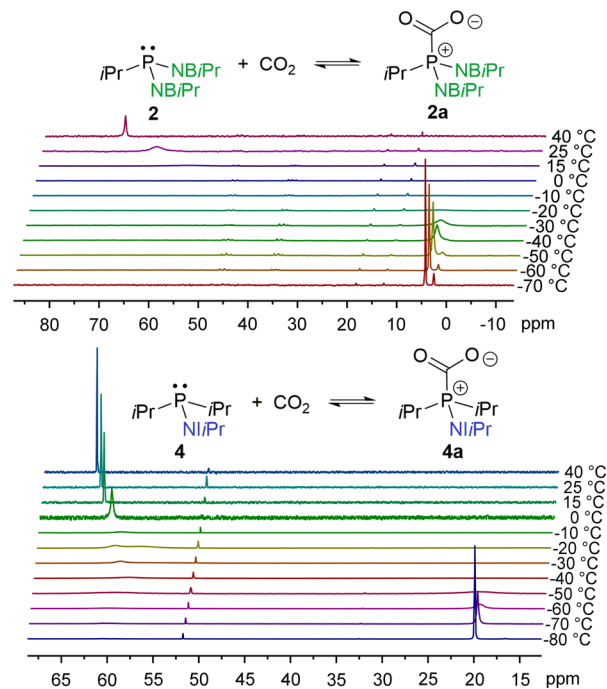


**Figure 1.** An overview: Tolman electronic parameter (TEP) of IAPs 1–5 and selected alkylphosphines.

We began our investigation into the possibility of forming Lewis base–CO<sub>2</sub> adducts using alkylphosphines PtBu<sub>3</sub> and PiPr<sub>3</sub>. A recent computational study on the solvent effect of the CO<sub>2</sub> activation mechanism with FLPs indicated the intermediate formation of a solvated tBu<sub>3</sub>P–CO<sub>2</sub> adduct.<sup>17</sup> However, the IR spectra of both phosphines in dichloromethane saturated with CO<sub>2</sub> showed the asymmetric stretch of CO<sub>2</sub> at 2350 cm<sup>–1</sup>, but no bands in the expected region of a CO<sub>2</sub> adduct (2300–1500 cm<sup>–1</sup>). Furthermore, the NMR spectra of PtBu<sub>3</sub> and PiPr<sub>3</sub> in THF-*d*<sub>8</sub> under 2 bar CO<sub>2</sub> pressure showed no line-broadening and were identical to those recorded without CO<sub>2</sub> atmosphere. In a similar manner, pressurizing a benzene solution of 1 with 2 bar carbon dioxide showed no difference in the <sup>1</sup>H and <sup>31</sup>P NMR spectra compared to those of 1 under argon atmosphere. Collectively, these experiments indicate that alkylphosphines as well as IAP 1 are not electron-rich enough to form stable CO<sub>2</sub> adducts.

We next pressurized a THF solution of phosphine 2 with 2 bar CO<sub>2</sub>. A broad signal appears at 57.0 ppm in the room-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, shifted upfield compared

to that of 2 (74.4 ppm).<sup>16</sup> A variable-temperature NMR study identified the presence of an equilibrium between the free phosphine 2 and its zwitterionic CO<sub>2</sub> adduct 2a (Figure 2). At

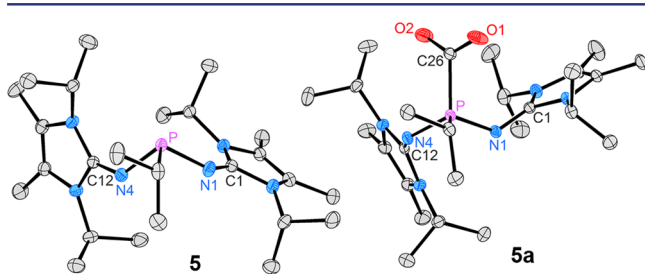


**Figure 2.** Variable-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectra of IAP 2 (top) and 4 (bottom) with 2 bar CO<sub>2</sub> in THF-*d*<sub>8</sub>.

–70 °C the signals of two isomeric adducts 2a appear in the <sup>31</sup>P NMR spectrum (*vide infra*), while subsequent warming to 40 °C shifts the equilibrium to the free IAP 2. Similar equilibrium behavior was observed for phosphine 4, showing a broad signal at 62.9 ppm in the room-temperature <sup>31</sup>P NMR spectrum and a resonance for the zwitterionic adduct 4a at 19.9 ppm upon cooling to –70 °C. In both cases, release of the CO<sub>2</sub> atmosphere from the NMR tube gave the signals of the free phosphines in the NMR spectra, clearly indicating the reversibility of the CO<sub>2</sub> binding.

Inspired by these results we were curious to see if more basic IAPs would form room-temperature stable CO<sub>2</sub> adducts. In fact, IAP 3 turned out to be just electron-rich enough to form a stable adduct. Pressurizing a solution of 3 in benzene with CO<sub>2</sub> resulted in the clean formation of (NB*i*Pr)<sub>3</sub>P–CO<sub>2</sub> (3a), which was isolated as a white solid in quantitative yield. The <sup>31</sup>P NMR spectrum shows a singlet at –22.0 ppm, which is markedly upfield shifted compared to that of 3 (74.9 ppm).<sup>16</sup> The characteristic carboxylate signal appears at 167.6 ppm (<sup>1</sup>J<sub>PC</sub> = 170 Hz) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. In a similar manner, pressurizing a hexane solution of 5 with 2 bar CO<sub>2</sub> resulted in the immediate precipitation of a white solid, which was isolated in quantitative yield. The product exhibits a resonance in the <sup>31</sup>P NMR spectrum at 2.9 ppm, upfield shifted compared to that of 5 (82.4 ppm) and a doublet at 169.4 ppm (<sup>1</sup>J<sub>PC</sub> = 130 Hz) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, clearly indicating the formation of (Ni*i*Pr)<sub>2</sub>*i*PrP–CO<sub>2</sub> (5a). The IR spectrum of 5a shows three strong absorption bands at 1630, 1570, and 1523 cm<sup>–1</sup> for the CO and CN stretches. Comparison of these frequencies with the scaled values obtained from the DFT calculations indicates that the ν<sub>as</sub>(CO) vibration appears at 1630 cm<sup>–1</sup> (cf. Table S7).

An X-ray diffraction (XRD) study of **5a** confirmed that carbon dioxide binds to the phosphine with a P–C bond of 1.8814(10) Å. The metric parameters of the CO<sub>2</sub> fragment [C26–O1:1.2437(13) Å, C26–O2:1.2284(14) Å, O1–C26–O2:129.62(10) Å] are comparable to those reported for Villiers adduct (cf. Chart 1b) [C–O: 1.257(3) Å, 1.229(2) Å, O–C–O: 128.59(19) Å].<sup>10</sup> Compared to the free phosphine **5**, the exocyclic N–C bonds in **5a** are elongated by average 0.038 Å, while the P–N bonds and the endocyclic N–C bonds are shortened by average 0.082 and 0.014 Å, respectively. These geometric parameters indicate a more pronounced N to P hyperconjugation upon CO<sub>2</sub> complexation.

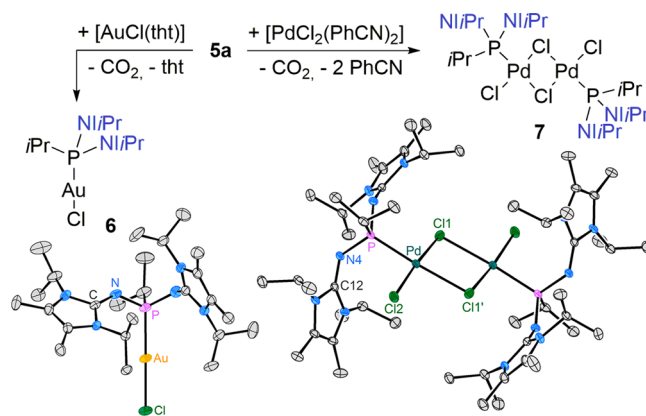


**Figure 3.** Molecular structures of **5** (left) and **5a** (right). Hydrogen atoms are omitted for clarity; thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **5**: P–N1 1.6876(16), P–N4 1.6968(14), N1–C1 1.293(2), N4–C12 1.294(2), P–N1–C1 131.66(13), P–N4–C12 128.43(12). **5a**: P–N1 1.6124(8), P–N4 1.6083(8), N1–C1 1.3287(12), N4–C12 1.3333(12), P–N1–C1 128.14(7), P–N4–C12 122.72(7), P–C26 1.8814(10), C26–O1 1.2437(13), C26–O2 1.2284(14), O1–C26–O2 129.62(10).

Examination of the thermal stability of **3a** and **5a** revealed that both carbon dioxide adducts can be handled at ambient conditions without appreciable decomposition. Under vacuum, **3a** slowly loses CO<sub>2</sub> at room temperature (50% in 4 h), while no decarboxylation was observed for **5a** after 4 h. Heating **5a** to 70 °C for 2 h under vacuum resulted in complete decarboxylation and clean regeneration of **5**, which was confirmed by NMR spectroscopy and TGA (cf. Figure S18).

Due to the exceptional donor ability, IAP **5** is a promising ancillary ligand in catalysis but is also very air-sensitive. Conveniently, IAP–CO<sub>2</sub> adduct **5a** is a crystalline solid and can be handled in air, which inspired us to utilize **5a** as a phosphine transfer reagent. In fact, the reaction of **5a** with [AuCl(tht)] or [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] proceeds upon CO<sub>2</sub> elimination to afford complexes **6** and **7** as crystalline solids in good yield (Figure 4). The <sup>31</sup>P NMR resonances of **6** (54.8 ppm) and **7** (35.4 ppm) appear upfield with respect to **5a** (2.9 ppm) and downfield compared to **5** (82.4 ppm), indicating the formation of complexes with IAP **5**. The molecular structures of **6** and **7** were established by single crystal XRD studies (Figure 4) confirming the expected connectivity. Remarkably, the metal–Cl bonds in trans position to the phosphine [6: Au–Cl 2.3264(7) Å, 7: Pd–Cl1' 2.5335(4) Å] are significantly elongated compared to those of the analogue complexes with PCy<sub>3</sub> ([AuCl(PCy<sub>3</sub>)]: 2.279(5) Å, [PdCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>]: 2.4370(7) Å).<sup>18</sup> This suggests weakening of the metal–Cl bond due to the strong donor character of IAP **5**, which can be beneficial for catalytic applications.

The reversible CO<sub>2</sub> binding with IAPs was further probed by DFT calculations. Ionization potentials, pK<sub>a</sub> values and the free energies for binding of CO<sub>2</sub> (ΔG<sub>298</sub>) were determined for **1–5**



**Figure 4.** Synthesis of complexes **6** and **7** by phosphine transfer and their molecular structures.

with PW6B95-D3//TPSS-D3/def2-TZVP using the COSMO-RS solvation model.<sup>19</sup>

The results (Table 1) agree very well with the experiments: Formation of **1a** from **1** and CO<sub>2</sub> is endergonic by 5.3 kcal/

**Table 1.** Free Energies for Binding of CO<sub>2</sub> by IAPs **1–5**,<sup>a</sup> P–CO<sub>2</sub> Bond Lengths, and O–C–O Bond Angles

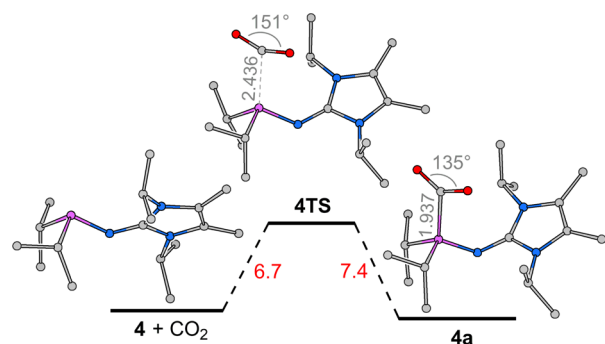
CO <sub>2</sub> adduct	ΔG <sub>298</sub> [kcal/mol]	r(P–CO <sub>2</sub> ) [Å]	α(O–C–O) [°]
<b>1a</b>	5.3	1.967	136.3
<b>2a</b> <sup>b</sup>	–3.2/–2.8	1.942/1.938	134.9/135.0
<b>3a</b>	–5.8	1.923	132.7
<b>4a</b>	–0.7	1.937	135.0
<b>5a</b>	–10.3	1.912	132.8

<sup>a</sup>PW6B95-D3//TPSS-D3/def2-TZVP+COSMO-RS. <sup>b</sup>Two conformers were found for **2a**.

mol. **4** is predicted to be isoenergetic with **4a** (ΔG<sub>298</sub> ≈ 0 kcal/mol), but the other three IAPs form stable CO<sub>2</sub> adducts. We find two conformers of **2a** within a free energy range of 0.3 kcal/mol, suggesting that the two peaks in the variable-temperature NMR spectrum (Figure 2) might arise from these distinct species. The formation of **3a** and **5a** by CO<sub>2</sub> addition to the respective phosphines is even more exergonic. This nicely correlates with the higher donor ability of **3** and **5**, indicated in Figure 1. The stronger binding is also reflected in shorter P–CO<sub>2</sub> bond lengths of **5a** and **3a**, which go along with a smaller O–C–O angle. In line with observations, CO<sub>2</sub> is more strongly bound in **5a** than in **3a**.

The free energy barriers for the CO<sub>2</sub> addition of **2** and **4** have been evaluated by locating the transition structures of P–C bond formation (Figure 5). With ΔG<sub>298</sub><sup>‡</sup> = 6.5 kcal/mol (**2**) and 6.7 kcal/mol (**4**), the CO<sub>2</sub> addition and release are fast processes, in agreement with the observed NMR spectra.

In conclusion, the first phosphine–CO<sub>2</sub> adducts were synthesized and characterized. Their stability closely correlates with the phosphines donor ability, which enables tuning of the adduct stability. Variable-temperature NMR studies and DFT calculations reveal the almost thermoneutral CO<sub>2</sub> binding with low-energy barriers of 6.5 and 6.7 kcal/mol for phosphines **2** and **4**, respectively. The more electron-rich phosphines **3** and **5** form room-temperature stable CO<sub>2</sub> adducts. Moreover, the crystalline CO<sub>2</sub> adduct **5a** can be handled in air, providing a convenient access to transition-metal complexes with highly electron-rich phosphine ligands relevant to catalysis. This was exemplified in the clean formation of complexes **6** and **7** by



**Figure 5.** Relative energies (kcal/mol) for stationary points on the  $4 + \text{CO}_2$  hypersurface. Bond distances in Å.

phosphine transfer reaction using **5a**. Considering the reversible, almost thermoneutral, low-energy-barrier  $\text{CO}_2$  activation, IAPs should be promising catalysts for a variety of transformations involving  $\text{CO}_2$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13116.

X-ray crystallographic data for **5** (CIF)

X-ray crystallographic data for **5a** (CIF)

X-ray crystallographic data for **6** (CIF)

X-ray crystallographic data for **7** (CIF)

Experimental details, characterization data and DFT-optimized structures, including Tables S1–S11 and Figures S1–S36 (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the DFG (IRTG 2027, SFB 858) and from the FCI for a Liebig Fellowship (F.D.). Thanks are due to Prof. F. E. Hahn for his generous support.

## ■ REFERENCES

- (1) (a) Karl, T. R.; Trenberth, K. E. *Science* **2003**, *302*, 1719. (b) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15729.
- (2) (a) Aresta, M. *Carbon Dioxide as Chemical Feedstock*. Wiley-VCH: Weinheim, 2010. (b) Aresta, M.; Dibenedetto, A.; Angelini, A. *Chem. Rev.* **2014**, *114*, 1709.
- (3) (a) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724. (b) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2010**, *43*, 58. (c) Ferey, G.; Serre, C.; Devic, T.; Maurin, G.; Jobic, H.; Llewellyn, P. L.; Weireld, G. D.; Vimont, A.; Daturi, M.; Chang, J.-S. *Chem. Soc. Rev.* **2011**, *40*, 550.
- (4) (a) Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 2391. (b) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914. (c) Tanaka, H.; Nagao, H.; Peng, S.-M.; Tanaka, K. *Organometallics* **1992**, *11*, 1450. (d) Zhang, X.; Gross, U.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1858. (e) Murphy, L. J.

Robertson, K. N.; Harroun, S. G.; Brosseau, C. L.; Werner-Zwanziger, U.; Moilanen, J.; Tuononen, H. M.; Clyburne, J. A. C. *Science* **2014**, *344*, 75.

(5) Murphy, L. J.; Robertson, K. N.; Kemp, R. A.; Tuononen, H. M.; Clyburne, J. A. C. *Chem. Commun.* **2015**, *51*, 3942.

(6) Kuhn, N.; Steimann, M.; Weyers, G. Z. *Naturforsch., B: J. Chem. Sci.* **1999**, *54b*, 427.

(7) Fiorani, G.; Guoa, W.; Kleij, A. W. *Green Chem.* **2015**, *17*, 1375.

(8) (a) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112. (b) Van Ausdall, B. R.; Glass, J. L.; Wiggins, K. M.; Aarif, A. M.; Louie, J. *J. Org. Chem.* **2009**, *74*, 7935.

(9) (a) Heldebrant, D. J.; Jessop, P. G.; Thomas, C. A.; Eckert, C. A.; Liotta, C. L. *J. Org. Chem.* **2005**, *70*, 5335. (b) Perez, E. R.; Santos, R. H. A.; Gambardella, M. T. P.; de Macedo, L. G. M.; Rodrigues-Filho, U. P.; Launay, J.-C.; Franco, D. W. *J. Org. Chem.* **2004**, *69*, 8005. (c) Pereira, F. S.; Agostini, D. L. d. S.; Santo, R. D. d. E.; deAzevedo, E. R.; Bonagamba, T. J.; Joba, A. E.; Gonzalez, E. R. P. *Green Chem.* **2011**, *13*, 2146.

(10) Villiers, C.; Dognon, J.-P.; Pollet, R.; Thury, P.; Ephritikhine, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 3465.

(11) Kayaki, Y.; Yamamoto, M.; Ikariya, T. *J. Org. Chem.* **2007**, *72*, 647.

(12) For early examples see: (a) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1987**, *26*, 3087. (b) Buhro, W. E.; Chisholm, M. H.; Martin, J. D.; Huffman, J. C.; Folting, K.; Streib, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8149. (c) Kroner, J.; Nöth, H.; Polborn, K.; Stolpmann, H.; Tacke, M.; Thomann, M. *Chem. Ber.* **1993**, *126*, 1995. (d) Schumann, H.; Girgsdies, F.; Heymer, B.; Kaufmann, J.; Marschall, C.; Wassermann, W. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2268. (e) Habereeder, T.; Nöth, H.; Paine, R. T. *Eur. J. Inorg. Chem.* **2007**, 2007, 4298.

(13) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643.

(14) For reversible  $\text{CO}_2$  binding see: (a) Sgro, M. J.; Stephan, D. W. *Chem. Commun.* **2013**, *49*, 2610. (b) Harhausen, M.; Fröhlich, R.; Kehr, G.; Erker, G. *Organometallics* **2012**, *31*, 2801. (c) Dickie, D. A.; Coker, E. N.; Kemp, R. A. *Inorg. Chem.* **2011**, *50*, 11288. (d) Dickie, D. A.; Barker, M. T.; Land, M. A.; Hughes, K. E.; Clyburne, J. A. C.; Kemp, R. A. *Inorg. Chem.* **2015**, *54*, 11121. (e) Courtemanche, M.-A.; Larouche, J. r. m.; Légaré, M.-A.; Bi, W.; Maron, L.; Fontaine, F. d. r.-G. *Organometallics* **2013**, *32*, 6804. (f) Barry, B. M.; Dickie, D. A.; Murphy, L. J.; Clyburne, J. A. C.; Kemp, R. A. *Inorg. Chem.* **2013**, *52*, 8312. (g) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 3925.

(15) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 6400.

(16) Wünsche, M. A.; Mehlmann, P.; Witteler, T.; Buß, F.; Rathmann, P.; Dielmann, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 11857.

(17) Pu, M.; Privalov, T. *Chem. - Eur. J.* **2015**, *21*, 17708.

(18) (a) Angermaier, K.; Zeller, E.; Schmidbaur, H. *J. Organomet. Chem.* **1994**, *472*, 371. (b) Sui-Seng, C.; Belanger-Gariepy, F.; Zargarian, D. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, 620.

(19) For details see [Supporting Information](#).