Facile Deoxygenative Reduction of a Bridging Carbonato Ligand with Silyl and Boryl 4,4′-Bipyridinylidene Reagents

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Abstract: The reactivity of CO₂ with a previously described PC₅carbeneP cobalt(I) hydroxide is reported. Insertion of CO₂ into the Co-OH bond followed by a dehydration reaction releasing water results in a cobalt(I) bridging carbonate species featuring fluctional κ¹ : κ¹ and κ¹ : κ² coordination of the central carbonate moiety. The reduction chemistry of the resulting cobalt(I) bridging carbonate species is explored utilizing deoxygenative reducing agents N,N′-bis(trimethylsilyl)- and N,N′-bis(pinacolatoboryl)-4,4′-bipyridinylidene. The three-electron reduction produces the corresponding PC₅carbeneP cobalt(I) siloxide or boroxide complex alongside a PC₅carbeneP cobalt(0) monocarbonyl, silyl/boryl ether, and 4,4′-bipyridine.

Keywords: cobalt • pincer ligands • carbon dioxide activation • carbonate reduction
**Introduction**

Low valent transition metal\(^{[1]}\) complexes or actinides\(^{[2]}\) can mediate reductive carbon oxygen bond cleavage in CO\(_2\) to form metal oxo derivatives and CO. Often, the metal oxo complex formed (whether mono or binuclear) is highly reactive towards further CO\(_2\), resulting in metal carbonate species, with the overall reaction being conversion of two molecules of CO\(_2\) to CO and CO\(_3^{2-}\) with electrons supplied by the low valent metals involved (Scheme 1A). This reaction is potentially useful for the conversion of CO\(_2\) to fuel precursor CO\(^{[3]}\) but the process often stalls due to the stability of the metal carbonates, which must be reduced and/or deoxygenated to regenerate the low valent metal species.

\[
\begin{align*}
\text{A} & \quad 2 \text{L}_m\text{M}^0 + 2 \text{CO}_2 \rightarrow \text{CO} + \text{M}^I – \text{O} – \text{O} – \text{M}^I \\
\text{B} & \quad 2 \text{L}_m\text{M}^I – \text{OH} + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{M}^I – \text{O} – \text{O} – \text{M}^I
\end{align*}
\]

*Scheme 1.* Formation of bridging carbonates *via* reaction of low valent metal complexes (A) or metal hydroxos (B) with carbon dioxide.

Alternatively, in a non-reductive process, carbonates can also be formed *via* insertion of CO\(_2\) into M-OH bonds followed by condensation to lose H\(_2\)O, forming mononuclear\(^{[4]}\) or dinuclear\(^{[5]}\) carbonates in a process relevant to that mediated by carbonic anhydrase enzymes (Scheme 1B). Again, if bridging carbonates form, further conversion of these stable species becomes a challenge. Strong reducing agents such as KC\(_8\) are often employed\(^{[2a]}\) but due to the incompatibility of this reagent with many other reaction components, catalytic systems are difficult to attain.

To circumvent the problems associated with alkali metal-based reductants, silylated\(^{[6]}\) or borylated\(^{[7]}\) pyrazine-based reagents have been employed as milder two electron reducing agents.\(^{[8]}\) Furthermore, these reagents incorporate silicon and boron electrophiles that drive reactions through the formation of thermodynamically favorable silicon/boron halogen or oxygen bonds. For example, Caulton and co-workers have explored these reductants
extensively in the context of reduction and deoxygenation of a nitrogen oxides in a variety of systems.[9] To our knowledge, the use of these reagents for the deoxygenation of coordinated carbonates has been less explored.

Recently, we described a series of $\text{PC_{carbene}P}$ [10] cobalt(I) derivatives featuring ligand frameworks of varying rigidity and donicity.[11] It was found that both the donicity of the pincer ligand as well as the electronic nature of the $X$-ligand $\text{trans}$ to the central ligating carbon atom ($\sigma$ vs. $\pi$-donor) affected the multiplicity of the electronic ground state of the complex. Pincer ligand $L^{\text{NMe2}}$ featuring a linked anthracene ligand backbone with $\text{para}$-substituted dimethylamine moieties was found to be the most donating in the series[12] resulting in more singlet character in the carbene and consequently diamagnetic cobalt(I) complexes. In the $X = \text{OH}$ derivative, $1$-$\text{OH}$, the hydroxo ligand was readily converted to other ligands with Bronsted acids and given its basicity, we were motivated to explore the reactivity of $\text{CO}_2$ with the hydroxo complex. Facile insertion and condensation to a bridging carbonate species[5a] was observed and we have studied its deoxygenation using silyl[6] and boryl[13] bipyridinylidene reducing agents.

**Results and Discussion**

Terminal hydroxo complex $1$-$\text{OH}$ was prepared as previously described[11] and reacted with an atmosphere of high purity (>99%) carbon dioxide in toluene at room temperature, affording a new diamagnetic species as noted by a shift in the $^{31}\text{P}^{\{1\text{H}\}}$ NMR resonance from 48.1 to 50.4 ppm. An equivalent of water (0.38 ppm[14]) was also detected when the reaction was performed in $\text{C}_6\text{D}_6$ and followed by $^1\text{H}$ NMR spectroscopy. Following work-up, the product, $2$, was isolated.

**Scheme 2.** Synthesis of Co(I) bridging carbonate, $2$, following insertion of $\text{CO}_2$ into the Co-OH bond.
as a dark red powder in 54% yield (Scheme 2). The structure of 2 was confirmed by X-ray crystallography, revealing a dinuclear, Co(I)-CO₃-Co(I), bridging carbonate complex in which the Co(I) centers are ligated in a κ¹:κ² coordination mode (Figure 1). The Co1-O1 and Co1-O2 bond lengths associated with the bidentate interaction were found to be 2.152(3) Å and 2.060(3) Å, respectively, while the Co2-O3 bond length of the unidentate interaction is 1.908(3) Å. These values are comparable to other reported (κ¹: κ²) Co-CO₃-Co complexes supported by β-diketamine[1a] or tris-pyrazolylborate[5a] (Tp) ligands. The Co1-C1 and Co2-C2 cobalt carbene

Figure 1. X-ray molecular structure of 2. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Iso-propyl groups on the phosphine donors are represented as stick models for clarity. Selected bond distances (Å) and angles (deg):

- Co1-C1, 1.854(4); Co2-C2, 1.851(4); Co1-O1, 2.152(3); Co1-O2, 2.060(3); Co2-O3, 1.908(3); Co1-P1, 2.1834(13); Co1-P2, 2.1822(13); Co2-P3, 2.1818(14); Co2-P4, 2.1952(15); C3-O1, 1.256(6); C3-O2, 1.310(6); C3-O3, 1.279(6); C1-Co1-O1, 152.96(18); C1-Co1-O2, 144.46(18); P1-Co1-O1, 94.79(10); P2-Co1-O2, 95.48(11); C3-O1-Co1, 88.8(3); C3-O2-Co1, 91.4(3); C2-Co2-O3, 169.30(19); P3-Co2-O3, 85.63(15); P4-Co2-O3, 85.81(15); C3-O3-Co2, 145.7(4); O1-C3-O2, 117.0(4); O1-C3-O3, 126.2(5); O2-C3-O3, 116.7(4).

bond lengths are 1.854(4) Å and 1.851(4) Å, respectively, similar to the related cobalt hydroxo complex 2 (1.858(3) Å) and benzoate species (1.8456(18) Å) that we previously reported.[11]

The ¹H NMR spectrum of 2 displayed subtle differences compared to 1-OH, most notably the disappearance of the diagnostic hydroxyl proton resonance at 3.71 ppm. The spectrum features seven ligand resonances, suggestive of a fluxional process mediated by a
κ\(^1\)κ\(^1\) structure and an averaged D\(_{2h}\) symmetry. Variable temperature NMR spectroscopic studies to -80 °C suggested that 2 remains fluxional in solution on the NMR time scale even at these low temperatures. A virtual triplet signal at 161.30 ppm in the \(^{13}\)C NMR spectrum is comparable to the previously reported Co(I) κ\(^2\)-benzoate species (160.79 ppm)\(^{[11]}\) confirming the retention of the aryl carbene moiety. Formation of the carbon-13 isotopologue 2-\(^{13}\)C was accomplished by addition of an atmosphere of \(^{13}\)CO\(_2\) to 1-OH and confirms the resonance at 153.18 ppm in the \(^{13}\)C\({}^1\)H) NMR spectrum as the central carbonate carbon atom of the dinuclear structure. In the IR spectrum (Figure S1), a band at 1409 cm\(^{-1}\) was assigned to the ν(C-O) stretching frequency, comparable to previously reported cobalt bridging carbonate species (1400 – 1650 cm\(^{-1}\)).\(^{[15]}\) Unlike the insertion chemistry reported for the tetrahedral TpCoOH species,\(^{[5a]}\) there was no evidence for an equilibrium between complexes 1-OH and 2 in the presence of water.

Figure 2. The CV of 2 recorded under argon at 0.1 V/s in 0.3 M TBAPF\(_6\) in THF with GC disk WE, Pt mesh CE and Ag/AgCl pseudo-reference electrodes.

As mentioned in the Introduction, reduction of bridging carbonates to regenerate low valent metal centers is an important process for the goal of realizing catalytic turnover in the conversion of CO\(_2\) to CO/CO\(_3^{2-}\). We therefore performed cyclic voltammetry on 2 to examine its electrochemical response; experiments were performed in 0.3 M tetrabutylammonium
hexafluorophosphate (TBAPF$_6$) in THF in an argon filled glovebox. Two reversible reduction features were observed at $E_p = -0.86$ V and -1.20 V vs Fc$^+/$/Fc likely corresponding to subsequent one electron reduction of each Co center in the complex (Figure 2). These reductions remain reversible even at slow scan rates suggestive of reductive stability of the presumed Co(0)-CO$_3$-Co(0) species (Figure S4). An irreversible oxidation can also be observed at $E_{p,a} = -0.02$ V vs Fc$^+/$/Fc, likely corresponding to the Co(I/II) couple. No other redox features were observed outside of this range.

Despite the clean reversibility of the two reduction events, attempts to chemically reduce 2 with KC$_8$ failed to give interpretable results. Reactions conducted in either THF or C$_6$D$_6$ gave NMR silent solutions which may be indicative of Co(0) species but no clean products were isolable from these experiments at the small scales at which they were conducted. We

**Scheme 3.** Reduction of bridging carbonate complex 2 using $N,N'$-bis(trimethylsilyl)- or $N,N'$-bis(pinacolatoboryl)-4,4'-bipyridinylidene.
therefore explored the reaction of 2 with the reducing agents N,N'-bis(trimethylsilyl)[6] and N,N'-bis(pinacolatoboryl)-4,4'-bipyridinylidene[13] that have been successfully applied in reductive deoxygenation reactions of coordinated nitrogen oxides.[9] Starting with the silyl substituted reagent, addition of 1.5 equivalents of N,N'-bis(trimethylsilyl)-4,4'-bipyridinylidene (Me₃Si-bipy) to 2 in toluene and heating to 80 °C over 18h (Scheme 3) resulted in the formation of a new diamagnetic Co(I) species noted by the appearance of a new resonance at 44.2 ppm in the ³¹P{¹H} NMR spectrum. Analysis of the ¹H NMR spectrum of the reaction mixture displayed a peak at 0.09 ppm corresponding to the silyl methyl protons in the product, suggesting the formation of a Co(I) siloxide species, 3. Trimethylsilyl ether Si-O-Si (0.5 eq.) was also formed as noted in the ¹H NMR spectrum with the methyl protons appearing at 0.12 ppm.[14a, 16] An identical reduction reaction was performed using 2-¹³C and followed by NMR spectroscopy. The ¹³C{¹H} NMR spectrum of the reaction mixture showed no evidence for the formation of free ¹³CO, which typically features a peak at approximately 180 ppm.[17] However, an IR spectrum of the crude solid isolated from this reaction suggested the formation of a PCarbeneP cobalt(0)

Figure 3. IR spectra (KBr pellet) of complex 2 (top) and the reaction mixture upon reduction with N,N'-bis(trimethylsilyl)-4,4'-bipyridinylidene (bottom) featuring the formation of a Co-CO carbonyl stretch.
monocarbonyl species, 4, featuring a $\nu$(C-O) stretching frequency at 1828 cm$^{-1}$ (Figure 3). That this carbonyl ligand arises from the carbonato group was supported by the observation of the shift of this band to 1833 cm$^{-1}$ when the reaction was performed with 2-$^{13}$C (Figure S3).

Due to sluggish kinetics utilizing Me$_3$Si-bipy, the reducing agent N,N'-bis{pinacolatoboryl}-4,4'-bipyridinylidene (PinB-bipy) was also applied in this reaction. Addition of 1.5 equivalents of PinB-bipy to 2 at room temperature in toluene resulted in an immediate colour change to bright red. Analysis of the reaction mixture by $^1$H NMR spectroscopy displayed the formation of a Co(I) boroxide species 5 featuring a peak at 1.13 ppm corresponding to the pinacol methyl protons. The $^{31}$P{$^1$H} and $^{11}$B{$^1$H} NMR spectra displayed peaks at 45.5 ppm and 22.3 ppm respectively; the expected formation of 0.5 equivalents of bis(pinacolato)diboryl ether (B-O-B) was also observed.$^{[18]}$ IR analysis of the reaction mixture displayed an identical $\nu$(C-O) stretching frequency at 1828 cm$^{-1}$ confirming the formation of Co(0) carbonyl complex 4.

![Scheme 4. Synthesis of complexes 3 and 5 by salt metathesis and condensation reactions.](image)

The identity of the products 3-5 were confirmed unambiguously by their separate synthesis (Schemes 4, 5). Complex 3 was prepared in 60% yield by treating the L$^{\text{NMe}_2}$Co(I) chloro complex$^{[11]}$ 1-Cl with an excess of NaOSiMe$_3$ in toluene and heating to 80 °C over 18 hours (Scheme 4A). Dark red crystals grown from a saturated solution of pentane at -30 °C over several days were analyzed by X-ray crystallography (Figure 4). Complex 3 was found to be $C_{2v}$ symmetric with a Co1-C1 bond length of 1.860(2) Å; this, alongside a $^{13}$C NMR resonance at 161.68 ppm, confirmed the retention of the aryl carbene moiety. Complex 5 was synthesized in
**Figure 4.** Molecular structure of compound 3; thermal ellipsoids are given at the 50% probability level. Selected bond distances (Å) and angles (deg): Co1-C1, 1.860(2); Co1-O1, 1.8782(18); Co1-P1, 2.2030(8); Co1-P2, 2.1800(8); C1-Co1-O1, 177.22(9); P1-Co1-O1, 97.20(6); P2-Co1-O1, 92.83(6); P1-Co1-P2, 167.20(3).

38% by the addition of HOBPin to 1-OH in toluene and heating for 18 h at 80 °C (Scheme 4B). A $^1$H NMR spectrum of the crude reaction mixture revealed the formation of water (0.40 ppm) and, following work-up, analysis of the complex by $^{13}$C NMR spectroscopy featured a triplet resonance at 161.65 ppm (t, $^2J_{C-P} = 24.8$ Hz) consistent with retention of the cobalt carbene bond. The $^{11}$B{$^1$H} NMR spectrum revealed a peak at 22.3 ppm. These compounds were in all ways spectroscopically identical to the products formed in the reduction reactions described above.
The identity of the cobalt(0) monocarbonyl complex 4 was confirmed by a two-step independent synthesis (Error! Reference source not found.) starting from either 1-Cl or its bromo analog 1-Br.\cite{11} To a suspension of 1-Cl in toluene at -196 °C was added approximately 1 equivalent of CO utilizing a glass gas addition bulb of calibrated volume.\cite{19} The mixture was warmed to room temperature and allowed to stir for 10 minutes before solvent was removed in vacuo. Following work-up, cobalt(I) chloro carbonyl 6-Cl was isolated as a red powder in 76% yield. An identical reaction using 1-Br resulted in the formation of 6-Br, albeit in a lower yield (32%). The bromo analog was characterized by X-ray crystallography (vide infra), allowing us to confirm the nature of these compounds.

Crystals of 6-Br were grown from a saturated solution of toluene layered with pentane at -30 °C and were analyzed by X-ray crystallography (Figure 5). The connectivity map of 6-Br shows the structure is trigonal bipyramidal at cobalt consisting of two isomers, one in which the halogen is trans to the carbon atom donor of the pincer ligand and the other which features the carbonyl ligand trans to the donor carbonyl (Figure S10). Note that, in addition to the isomers of 6-Br, samples contained crystals of a second product in which the carbene bond had been protonated and two carbonyl ligands were bound to the cobalt center in place of the halide (see SI and Figure S11 for details). Nevertheless, the analysis confirms the nature of complex 6-Br, which displays an elongated Co1-C1 bond (1.958(11) Å) compared to the square planar
Figure 5. X-ray structures of complexes 6-Br (top) and 4 (bottom); thermal ellipsoids are given at the 50% probability level. Selected bond distances (Å) and angles (deg) for 6-Br: Co1-C1B, 1.958(11); Co1-Br1, 2.3584(13); Co1-C2, 1.759(2); C2-O2, 1.152(3); Co1-P1, 2.196(3); Co1-P2, 2.150(3); C1B-Co1-Br1, 145.8(3); C1B-Co1-C2, 102.5(3); P1-Co1-Br1, 92.39(4); P1-Co1-C2, 97.37(7); C2-Co1-Br1, 111.69(8); P1-Co1-P2, 160.34(2). For 4: Co1A-C1A, 1.946(14); Co1A-C33A, 1.71(2); C33A-O1A, 1.124(15); Co1A-P1, 2.196(3); Co1A-P2, 2.150(3); C1A-Co1A-C33A, 172.5(11); P1-Co1A-C33A, 92.0(11); P2-Co1A-C33A, 99.9(11); P1-Co1A-P2, 164.80(16).

cobalt carbene complexes likely due to π-backbonding imparted by the carbonyl ligand. The NMR spectra of 6-Cl, although somewhat broadened, indicate the presence of two isomers as found in the X-ray analysis of 6-Br. Infrared analysis of 6-Cl also confirms the presence of two isomeric structures featuring two ν(C-O) stretching frequencies at 1924 and 1872 cm\(^{-1}\) (Figure S2). These values are consistent with previously reported PC\(_{aryl}\)P Co(II) chloro carbonyl species (1948 cm\(^{-1}\))\(^{[20]}\) and PC\(_{carbene}\)P Ir(I) mono and di-carbonyl species (1960-2060 cm\(^{-1}\))\(^{[21]}\).

Complex 6-Cl could be converted to 4 by reducing with KC\(_8\) in THF at room temperature (Scheme 4). The complex is silent in all NMR spectra, featuring a magnetic moment of 1.702 \(\mu_B\)
consistent with an $S = \frac{1}{2}$ ground state. Infrared spectroscopic analysis of $4^{\text{13}}\text{C}$ displays a $\nu(\text{C-O})$ stretching frequency at 1833 cm$^{-1}$ consistent with species produced during the reduction reaction of $2^{\text{13}}\text{C}$. X-ray quality crystals were grown by dissolving the compound in minimal toluene, layering with pentane, and placing in the freezer at -30 °C over 5 days. Structural analysis (Figure 5) revealed formation of the Co(0) monocarbonyl. Complex 4 features $C_{2v}$ symmetry as well as an elongated Co1-C1 bond of 1.946(14) Å due to π-backbonding between the cobalt d-orbitals and the carbonyl ligand. Having successfully synthesized the products of the reduction of PC$_{\text{carbene}}$P Co(I) bridging carbonate with N,N'-bis(trimethylsilyl)- and N,N'-bis(pinacolatoboryl)-4,4'-bipyridinylidene, we can confirm the three-electron reduction of Co-CO$_3$-Co to form Co(I) siloxide/boroxide and Co(I) monocarbonyl alongside bipyridine and silyl/boryl ether.

Conclusions

Insertion of CO$_2$ into the Co-O bond of PC$_{\text{carbene}}$P Co(I) hydroxo complex 1-OH results in the formation of a dinuclear bridging carbonate species featuring fluctional $\kappa^1:\kappa^1$ and $\kappa^1:\kappa^2$ binding at the central CO$_3$ fragment on the NMR spectroscopic timescale. The further reduction of Co-CO$_3$-Co was therefore explored using the deoxygenative reducing agents N,N'-bis(trimethylsilyl)- and N,N'-bis(pinacolatoboryl)-4,4'-bipyridinylidene. Addition of 1.5 equivalents of reducing agent to complex 2 resulted in formation of the corresponding Co(I) siloxide (3) or boroxide (5) species, trimethylsilyl ether or bis(pinacolato)diboryl ether, 4,4'-bipyridine, and a Co(0) monocarbonyl species (4). Separate syntheses of complexes 3-5 confirmed their identity as the products from the reduction of bridging carboxylate with N,N'-bis(trimethylsilyl)- and N,N'-bis(pinacolatoboryl)-4,4'-bipyridinylidene.

Experimental Section

General Considerations. The storage and manipulation of all compounds were performed under an argon atmosphere either in an IT glovebox or with a double-manifold high-vacuum line using standard techniques. Passage of argon through an OxisorBW scrubber (Matheson Gas Products) removed any residual oxygen and moisture. Toluene, hexanes, pentane and
tetrahydrofuran were dried and purified using a solvent purification system and stored in 500 mL thick-walled glass vessels over sodium/benzophenone ketal and distilled under reduced pressure. C₆D₆ was dried over sodium/benzophenone ketal. All dried solvents were degassed, and vacuum distilled prior to use. ¹H and ¹³C NMR spectrometry chemical shifts were referenced to residual protio-solvent resonances and naturally abundant ¹³C resonances for all deuterated solvents. Chemical shift assignments are based on ¹H, ¹³C{¹H}, ³¹P{¹H}, ¹¹B{¹H}, ¹H–¹³C-HSQC, and ³H–¹³C-HMBC NMR experiments performed on Ascend-500 or Avance-600 MHz spectrometers. UV–vis near IR absorption spectra were collected using an Agilent Technologies Cary 60 spectrophotometer. IR spectra were collected using a Thermo-Nicolet Nexus 470 spectrophotometer. 1-X (X = OH, Cl, Br)¹¹, N,N′-bis(pinacolatoboryl)-4,4′-bipyridinylidene,¹³ and N,N′-bis(trimethylsilyl)- 4,4′-bipyridinylidene⁶ were prepared per literature procedures. All other reagents were purchased from Sigma-Aldrich and used as received. All elemental and high-resolution mass spectrometry analyses were obtained by the Instrumentation Facility of the Department of Chemistry, University of Calgary. Diffraction patterns were collected with Cu Kα radiation on a Bruker Smart diffractometer equipped with an Apex II detector, fixed-CHI goniometer, and sealed-tube (Cu) source or with Mo Kα radiation on a Nonius Kappa CCD diffractometer. CCDC entries 2195249-2195252 contain the supplementary crystallographic data for this paper (compounds 2, 3, 4 and 6-Br, respectively). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. All electrochemical measurements were performed on a CHI 660D or 660E potentiostat at room temperature (20 ± 2 °C) in a three-electrode configuration. A glassy carbon working, Pt mesh counter and Ag/AgCl wire reference electrode were used in dry (Na/benzophenone) tetrahydrofuran (THF) containing 0.3 M TBAPF₆ (Sigma, electrochemical grade, ≥99.0%) as supporting electrolyte and 1.0 mM analyte. The Ag/AgCl wire was immersed into a glass tube filled with electrolyte solution and separated via a CoralPor frit from the analyte-containing solution. Ferrocene (Fc) was added as an internal standard at the end of each measurement, and potentials were referenced against the Fc⁺/Fc redox couple (0 V). Cyclic voltammograms were recorded in a
glovebox under an Ar atmosphere (unless otherwise noted). Redox potentials are reported as peak potential of the cathodic wave (E_{pc}).

**Synthesis of PC_{carbene}PCo(I)CO_3, (2):** To a 50 mL round bottom flask was added 2 (0.221 g, 0.368 mmol) and dissolved in 10 mL of toluene. At room temperature 1 atmosphere of CO_2 was added to the reaction mixture and allowed to stir for 1 h. Solvent was removed in vacuo and the resulting residue triturated with 2 x 5 mL pentane. The solid was collected under argon utilizing a 2 mL filter frit, washing with an additional 2 mL pentane. The solid was dried to yield a dark red powder (0.121 g, 0.099 mmol. 54%). Crystals suitable for X-ray structural analysis were grown from a saturated solution of toluene layered with pentane at -30 °C over several days. ³¹P NMR (203 MHz, benzene-d_6) δ 50.4. ¹H NMR (500 MHz, benzene-d_6) δ 6.91 (q, J = 2.9 Hz, 4H, Ar-H), 5.88 (d, J = 2.4 Hz, 4H, Ar-H), 3.86 (s, 8H, CH(CH_3)_2), 2.23 (s, 24H, N(CH_3)_2), 1.86 (q, J = 6.4 Hz, 24H, CH(CH_3)_2), 1.66 (q, J = 7.4 Hz, 24H, CH(CH_3)_2), 1.43 (s, 12H, C(CH_3)_2). ¹³C NMR (126 MHz, benzene-d_6) δ 161.30 (vt, Co=C), 158.18 (¹³C=O), 147.21 (s, N-C_Ar), 134.25 (s, C_Ar-C(CH_3)_2), 132.45 (C_Ar-C=Co), 131.58 (C_Ar-P), 119.42 (s, Ar-C_H), 117.62 (s, Ar-CH), 45.01 (s, C(CH_3)_2), 23.99 (t, J = 7.8 Hz, CH(CH_3)_2), 22.76 (s, C(CH_3)_2), 20.57 (s, CH(CH_3)_2), 19.19 (s, CH(CH_3)_2). Infrared (KBr pellet): ν (C=C) and (C-O) stretches, 1584, 1410, 1333 cm⁻¹.

Elemental analysis: Calcd (%): C, 63.61; H, 8.21; N, 4.57. Found: C, 63.12; H, 8.49; N, 4.19.

**Synthesis of PC_{carbene}PCo(I)OSi(CH_3)_3, (3):** To a 50 mL thick-walled reaction flask was added 1 (0.100 g, 0.161 mmol) and NaOSiMe_3 (0.030 g, 0.267 mmol) and dissolved in 10 mL of toluene. The reaction was heated at 80 °C over 18 h. The resulting solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo and the solid triturated with pentane and dried under vacuum. The sample was recrystallized in 1 mL of pentane over 5 days at -30 °C to yield dark red crystals (0.065 g, 0.097, 60%). ³¹P NMR (203 MHz, benzene-d_6) δ 44.2. ²⁹Si NMR (99 MHz, benzene-d_6) δ -113.26. ¹H NMR (500 MHz, benzene-d_6) δ 6.88 (q, J = 3.0 Hz, 2H, Ar-H), 5.83 (d, J = 2.4 Hz, 2H, Ar-H), 3.62 (ddq, J = 10.7, 7.0, 3.7 Hz, 4H, CH(CH_3)_2), 2.15 (s, 12H, N(CH_3)_2), 1.78 (q, J = 7.5 Hz, 6H, CH(CH_3)_2), 1.69 (q, J = 6.6 Hz, 12H, CH(CH_3)_2), 1.41 (s, 6H, C(CH_3)_2), 0.09 (s, 9H, Si(CH_3)_3). ¹³C NMR (126 MHz, benzene-d_6) δ 161.68 (t, J = 27.1 Hz, Co=C), 150.86 (s, N-C_Ar), 146.93 (s, C_Ar-C(CH_3)_2), 133.72 (t, J = 14.5 Hz, C_Ar-C=Co), 133.21 (s, C_Ar-P), 119.27 (s, Ar-CH), 117.80 (s, Ar-CH), 45.53 (s, C(CH_3)_2), 40.09 (s,
N(CH₃)₂), 23.47 (s, CH(CH₃)₂), 22.04 (s, C(CH₃)₂), 20.82 (s, CH(CH₃)₂), 19.17 (s, CH(CH₃)₂), 5.83 (s, Si(CH₃)₃). Elemental analysis: Calcd (%): C, 62.48; H, 8.84; N, 4.16. Found: C, 63.03; H, 8.71; N, 3.48.

**Synthesis of PCarbenePCo(0)CO, (4):** To a 50 mL flask was added 7 (0.020 g, 0.031 mmol) and KCS₈ (0.006 g, 0.044 mmol) and dissolved in 3 mL of THF. The reaction was stirred over 1 h at room temperature. The solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed *in vacuo*. The resulting residue was triturated with pentane and dried under high vacuum to yield a red-brown solid (0.012 g, 0.020 mmol, 63%). X-ray quality crystals were grown by dissolving the compound in minimal toluene, layering with pentane, and placing in the freezer at -30 °C over 5 days.

31P NMR (243 MHz, benzene-d₆) δ silent. 1H NMR (500 MHz, benzene-d₆) δ silent. 13C NMR (151 MHz, benzene-d₆) δ silent. μeff (benzene-d₆): 1.702 μB. Infrared (4-13C): ν(C=O) stretch, 1833 cm⁻¹. HRMS (APCI) Calcd: 612.28012. Found: 612.28031 (M+H)*.

**Synthesis of PCarbenePCo(I)OBPin, (5):** To a 50 mL thick-walled reaction flask was added 2 (0.058 g, 0.096 mmol) and HOBPin (0.022 g, 0.153 mmol) and dissolved in 10 mL of toluene. The reaction was heated at 80 °C over 18 h. The resulting solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed *in vacuo*. The solid was triturated with pentane and dried under vacuum to yield a red solid (0.026 g, 0.036 mmol, 38%). 31P NMR (243 MHz, benzene-d₆) δ 45.5. 11B NMR (161 MHz, benzene-d₆) δ 22.3. 1H NMR (600 MHz, benzene-d₆) δ 6.86 (q, J = 3.0 Hz, 2H, Ar-H), 5.79 (d, J = 2.4 Hz, 2H, Ar-H), 3.71 (ddd, J = 10.3, 6.9, 3.3 Hz, 4H, C(CH₃)₂), 2.14 (s, 12H, N(CH₃)₂), 1.80 (dq, J = 10.6, 7.0 Hz, 24H, CH(CH₃)₂), 1.39 (s, 6H, C(CH₃)₂), 1.13 (s, 12H, BOC(CH₃)₂). 13C NMR (151 MHz, benzene-d₆) δ 161.65 (t, J = 24.8 Hz, Co=C), 147.13 (s, Ar=C), 133.91 (t, J = 15.4 Hz, Ar=C), 133.33 (t, J = 6.4 Hz, Ar=C), 132.47 (d, J = 9.5 Hz, Ar=C), 119.34 (s, Ar=CH), 117.90 (s, Ar=CH), 45.72 (s, C(CH₃)₂), 40.10 (s, N(CH₃)₂), 25.34 (s, BOC(CH₃)₂), 23.82 (t, J = 7.8 Hz, CH(CH₃)₂), 21.77 (s, C(CH₃)₂), 20.41 (d, J = 3.0 Hz, BOC(CH₃)₂), 19.49 (s, CH(CH₃)₂). HRMS (APCI) Calcd: 726.3672. Found: 726.36552 (M+H)*.

**Synthesis of PCarbenePCo(I)ClCO, (6-Cl):** To a 50 mL flask was added 1 (0.053 g, 0.086 mmol) and dissolved in toluene. While stirring, carbon dioxide (ca. 77 mmHg, 0.081 mmol) was condensed into the evacuated flask at -196 °C utilizing a 19 mL gas addition bulb. The reaction was allowed
to stir for 10 minutes before solvent was removed \textit{in vacuo}. The resulting residue was re-dissolved in 5 mL toluene and filtered through a small filter frit. The solid was washed with pentane and dried. The filtrate was placed into a 50 mL round bottom flask and solvent removed \textit{in vacuo}. The resulting residue was re-dissolved in 5 mL toluene and filtered through a small filter frit. The solid was washed with pentane and dried. The filtrate was placed into a 50 mL round bottom flask and solvent removed \textit{in vacuo}. The resulting solid was washed with 2 x 2 mL pentane and dried under high vacuum resulting in a red powder (0.042 g, 0.065 mmol, 76%). X-ray quality crystals were grown by dissolving the compound in minimal toluene, layering with pentane, and placing in the freezer at -30 °C over 3 days. $^{31}$P NMR (243 MHz, benzene-$d_6$) δ silent. $^1$H NMR (500 MHz, benzene-$d_6$) δ 7.39 (s, 2H, Ar-H), 6.58 (s, 2H, Ar-H), 3.89 (s, 2H, CH(CH$_3$)$_2$), 2.77 (s, 2H, CH(CH$_3$)$_2$), 2.46 (s, 12H, N(CH$_3$)$_2$), 1.87 (s, 6H, CH(CH$_3$)$_2$), 1.66 (d, J = 2.9 Hz, 3H, C(CH$_3$)$_2$), 1.56 (d, J = 3.0 Hz, 3H, C(CH$_3$)$_2$), 1.38 (s, 6H, CH(CH$_3$)$_2$), 1.32 (d, J = 5.8 Hz, 6H, CH(CH$_3$)$_2$), 1.09 (s, 6H, CH(CH$_3$)$_2$). $^{13}$C NMR (151 MHz, benzene-$d_6$) δ 218.88 (vt, Co=, 163.06 (s, Ar-C), 140.23 (s, Ar-C), 128.12 (s, Ar-CH), 114.34 (s, Ar-C), 113.42 (s, Ar-CH), 40.49 (s, C(CH$_3$)$_2$), 39.32 (s, N(CH$_3$)$_2$), 32.26 (s, C(CH$_3$)$_2$), 29.75 (s, C(CH$_3$)$_2$), 18.45 (s, CH(CH$_3$)$_2$), 18.15 (s, CH(CH$_3$)$_2$), 17.59 (s, CH(CH$_3$)$_2$), 16.38 (s, CH(CH$_3$)$_2$). Note: The carbonyl peak was not identified. Assignment of peaks was performed using both $^1$H-$^{13}$C-HSCQ and $^1$H-$^{13}$C-HMBC. $\mu_{\text{eff}}$ (benzene-$d_6$): 1.557 $\mu_B$. Infrared (KBr pellet): ν(C-O) stretch, 1924, 1872 cm$^{-1}$. HRMS (APCI) Calcd: 611.27154. Found: 611.27249 (M$^+$).

Acknowledgements

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References


Supporting Information

Facile Deoxygenative Reduction of a Bridging Carbonato Ligand with Silyl and Boryl 4,4’-Bipyridinylidene Reagents

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### Crystal Data Collection and Refinement Parameters

**Table S1.** Crystal data collection and refinement parameters for compounds 2, 3, 4, and 6-Br.

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