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Reactivity of the Metallocarboxylates $Cp(NO)(PPh_3)ReCO_2^-M^+$ toward Excess Carbon Dioxide: Degradation to a Bimetallic μ-[η^1-C(Re):η^1-O,O′(Re′)] Carbon Dioxide Complex $Cp(NO)(PPh_3)ReCO_2Re(NO)(CO)(PPh_3)(\eta^1\text{-}C_5H_5)$

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The rhenium η^1-C carboxylate $Cp(PPh_3)(NO)ReCO_2^-$ (**1**Li^+ or **1**K^+) undergoes an unusual reductive disproportionation sequence in the presence of excess CO_2 that generates a new $Re_2(\mu_2\text{-}\eta^3\text{-}CO_2)$ complex $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(\eta^1\text{-}Cp)$ (**2**) plus CO_3^{2-}. The overall stoichiometry entails 3 equiv of CO_2 plus 2 equiv of $Cp(PPh_3)(NO)ReLi$ transforming to ligated CO_2 and CO (i.e., **2**) plus CO_3^{2-}. Three procedures were used to generate **2**: treating (a) $Cp(PPh_3)(NO)ReLi$ with excess CO_2, (b) **1**K^+ with excess CO_2, and (c) **1**K^+ with $Cp(PPh_3)(NO)Re(CO)BF_4$. The results of this study are consistent with the intermediacy of an undetected metalloanhydride $Cp(PPh_3)(NO)ReC(O)OC(O)Re(NO)(PPh_3)Cp$ (**8**), which upon a subsequent $\eta^5 \rightarrow \eta^1$ Cp ring shift on one rhenium center affords **2**. This product undergoes different solvolysis reactions in the presence of methanol and triethylsilanol. The former gives 2 equiv of the methyl ester $Cp(NO)(PPh_3)ReCO_2CH_3$ (**6**), whereas the latter replaces the η^1-Cp group with a silanolate to give the previously characterized $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(OSiEt_3)$ (**5a**).

Introduction

The synthesis of carbon dioxide complexes[1] in which the CO_2 binds η^1-C or η^2-C,O to a metal center is limited by the tendency of these complexes to promote reductive disproportionation[2] of the ligated CO_2, Scheme 1.[3] This disproportionation occurs when an electron-rich transition-metal CO_2 complex incorporates a second equivalent of CO_2 and forms a C_2 ligand that subsequently fragments to carbonate plus carbon monoxide.[4] These C_1 products have been observed as (a) ligated carbonate and CO at the same[2a,c,5] or different[2c,6] metal centers, (b) ligated CO and free carbonate,[2b,7] and (c) ligated carbonate and free CO.[8] We now document an unusual reductive disproportionation sequence for the rhenium η^1-C carboxylate $Cp(PPh_3)(NO)ReCO_2^-$ (**1**Li^+ or **1**K^+)[9,10] that generates a new $Re_2(\mu_2\text{-}\eta^3\text{-}CO_2)$ complex $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(\eta^1\text{-}Cp)$ (**2**) plus free

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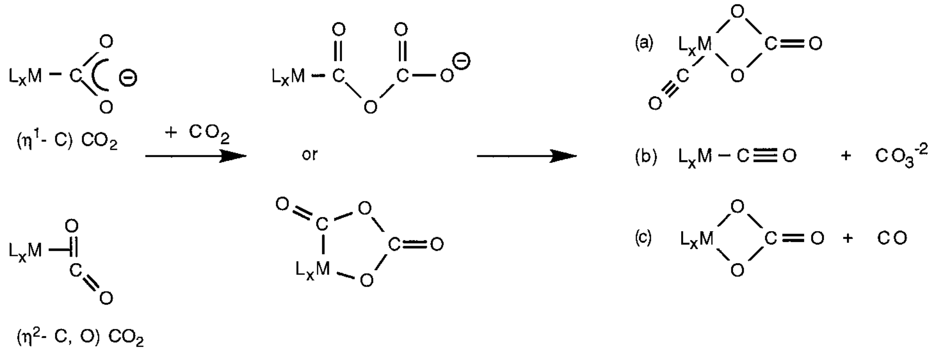
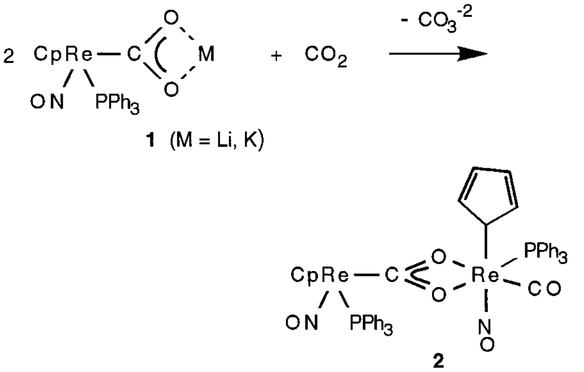
Scheme 1

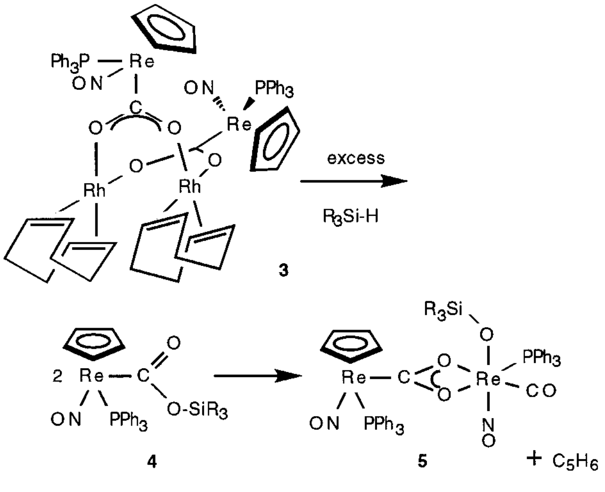


carbonate (eq 1).



(1)

The starting rhenium CO_2 complex **1** originally was synthesized by Gladysz and co-workers by deprotonation of $Cp(PPh_3)(NO)ReCO_2H$.[9] Once generated, **1**Li^+ and **1**K^+ are stable in solution. Both metallocarboxylates and their Sn, Ge, and Pb(IV) derivatives $Cp(PPh_3)(NO)ReCO_2MPh_3$ were characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, as well as by an X-ray structure determination of the tin ester (M = Sn). In a more recent study, we used **1** as precursers to a $Re_2Rh_2(\mu_3\text{-}CO_2)_2$ complex $[Cp(PPh_3)(NO)Re(CO_2)Rh(\eta^4\text{-}COD)]_2$ (**3**) in which each μ_3-[η^1-C(Re):η^1-O(Rh):η^1-O′(Rh′)] rhenium carboxylate ligand bridges two rhodium(I) (η^4-COD) moieties.[11] Treatment of **3** with $PhMe_2SiH$ or Et_3SiH initially produced the silyl esters $Cp(PPh_3)(NO)ReCO_2SiR_3$ (**4**) (eq 2),[12] but these promptly degraded in solution to Re_2(μ_2-η^3 CO_2) silanolate compounds **5**.[13] The depicted structure of **5** conforms to the result of a X-ray crystallographic study for the phenyldimethylsilanolate **5b** ($SiR_3 = SiMe_2Ph$)[12] and moreover is comparable to the structure that we now are reporting for **2**. In this study we demonstrate that the reductive disproportionation of ligated CO_2 on **1** plus exogenous CO_2 to yield **2**, a net degradation of a metallocarboxylate to a bimetallic CO_2 complex, resembles the rearrangement of **4** to **5**.



(2)

Experimental Section

Synthetic manipulations were performed using a combination of standard Schlenk line, glovebox, and vacuum line procedures.[14] Infrared spectra of THF solutions were recorded on a Perkin-Elmer FT spectrophotometer, Model No. 1600, over the carbonyl ν(CO) frequency range (2200−1600 cm^{-1}). NMR spectral data were obtained in C_6D_6 and were reported as δ values relative to residual C_6D_5H (^{1}H: 7.15 ppm) and C_6D_6 (^{13}C: 128.00 ppm) using Varian 300 MHz INOVA and Unity 500 spectrometers. Experimental details for working with purified CO_2 have been reported.[15] Combustion microanalyses were done by Quantitative Technologies, Bound Brook, NJ. Organic and inorganic reagents were obtained commercially and used as received; silanes and C_6D_6 were stored in a glovebox under nitrogen. THF and benzene were distilled from sodium benzophenone ketyl. Trialkylsilanols, Et_3SiOH, and $PhMe_2SiOH$ were prepared as previously reported.[10c] The rhenium compounds $Cp(PPh_3)(NO)ReCO_2H$,[16] $Cp(PPh_3)(NO)ReH$,[17] and $Cp(NO)(PPh_3)ReCO^+BF_4^-$ [18] were prepared by literature procedures and judged pure by IR and ^{1}H NMR spectroscopy.

Carboxylation of [Cp(NO)(PPh$_3$)Re]$^-$Li$^+$. To a precooled (−20 °C) suspension of $Cp(NO)(PPh_3)ReH$ (194 mg, 0.356 mmol) in 10 mL of THF was added 0.28 mL of n-BuLi solution (1.6 M in hexane, 0.45 equiv). Within 30 min a solution color change from orange to red was observed; IR spectral monitoring was consistent with conversion to $Cp(NO)(PPh_3)ReLi$ [ν(NO) 1460, 1458, 1433, and 1396 cm^{-1}].[17] This red solution was frozen by immersing the reaction flask (which remained attached to a vacuum line) in liquid nitrogen. After three freeze−pump−thaw cycles of the reaction mixture, excess CO_2 (1 mmol) was condensed onto the frozen solution. An immedi-

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ate reaction was evident as the red reaction mixture turned orange and melted at −78 °C; after warming to room temperature over 30 min, the reaction was judged complete by IR spectral monitoring. The IR spectrum was dominated by one ν(CO) band at 1972 cm^{-1} and two ν(NO) bands at 1718 and 1684 cm^{-1} that indicate the presence of Cp(NO)(PPh$_3$)ReCO$_2$-Re(η^1-Cp)(CO)(NO)(PPh$_3$) (**2**). (Identical results were obtained in the presence of 1 equiv of freshly distilled *N*,*N′*-tetramethylethylenediamine.)

The reaction solution was evaporated, and the orange residue was extracted with benzene (5 × 5 mL). These extracts were filtered (medium-porosity sintered glass), combined, and evaporated. The resulting orange residue was dissolved in 10 mL of THF and treated with 1.0 mL of methanol (25 mmol). IR spectra of the yellow solution were consistent with quantitative conversion to Cp(NO)(PPh$_3$)ReCO$_2$Me (**6**),[18a] ν(NO) 1678, ν(C=O) 1592 cm^{-1}. The product was isolated as a yellow solid (112 mg, 57%) after crystallization at −20 °C from 11 mL of 1:10 CH$_2$Cl$_2$/pentane; it was established as spectroscopically pure **6** by multinuclear NMR spectroscopy.

A portion of the remaining white benzene-insoluble residue (49 mg) was immediately dissolved by 6 M HCl with vigorous effervescence of presumed CO$_2$. The remaining solid was extracted with deionized water (3 × 1 mL) and treated with 0.5 mL of a 0.1 M Pb(NO$_3$)$_2$ solution. The resulting white precipitate was centrifuged, washed with water, recentrifuged, and dried in a vacuum desiccator over P$_2$O$_5$. An IR spectrum of this solid as a KBr pellet was identical to one run of an authentic sample of PbCO$_3$: a broad band at 1410 cm^{-1} and a weaker absorption at 840 cm^{-1}.[19]

Reaction of Cp(NO)(PPh$_3$)ReCO$_2$$^-K^+$ (1K$^+$) with Excess CO$_2$. To a mixture of KH (0.199 g, 4.96 mmol) and Cp(NO)(PPh$_3$)ReCO$_2$H (0.115 g, 0.195 mmol) was added THF (20 mL), and the yellow suspension was stirred at room temperature for 1 h. This gave an orange suspension, which was filtered. An IR spectrum of the filtrate was consistent with **1**K$^+$: 1634, 1622, (NO), 1440 (v br), 1240 (br) (OCO region) cm^{-1}. After a CO$_2$ atmosphere (1 atm) was maintained over this vigorously stirred solution for 5 min the IR spectrum of the red-orange solution was dominated by the diagnostic ν(CO) and ν(NO) bands for **5**, although weak, unassigned ν(NO) bands at 1657, 1636, and 1608 cm^{-1} also were present. The solvent was removed in vacuo; the residue was extracted with benzene (2 × 5 mL) and filtered, and the benzene was evaporated prior to redissolving the orange residue in dichloromethane (5 mL). Addition of pentane (10 mL) afforded a cloudy solution, which upon maintaining overnight at −20 °C produced salmon-colored crystals. These were filtered, washed with hexane, and dried in vacuo: yield 0.052 g of **5** (46%).

Reaction of Cp(NO)(PPh$_3$)ReCO$^+$BF$_4$$^-$ and Cp(NO)(PPh$_3$)ReCO$_2$$^-K^+$ (1b). To a yellow suspension of Cp(NO)(PPh$_3$)ReCO$_2$H[16] (105 mg, 0.179 mmol) in 10 mL of THF was transferred by cannula a white slurry of KH (100 mg, 2.49 mmol) in 3 mL of THF. Within 30 min of stirring at room temperature, this slurry afforded a yellow-orange supernatant solution of **1b**K$^+$ (identified by IR spectroscopy: ν(NO) 1622 (br) cm^{-1}, ν(OCO) 1474 (br), 1240 cm^{-1})[9] with noticeable gas evolution (presumably hydrogen). This suspension was transferred by a cannula to a Schlenk filter (the frit was covered with Celite) and was filtered with nitrogen pressure into a precooled (−78 °C) slurry of Cp(NO)(PPh$_3$)ReCO$^+$BF$_4$$^-$ (122 mg, 0.184 mmol) in 5 mL of THF. Another 2 mL of THF was used to wash the frit, and the resulting orange suspension was stirred at −78 °C for 10 min before the reaction mixture was warmed to and stirrred at room temperature for 1 h.

The resulting orange solution was evaporated in vacuo, the residue was extracted with benzene (3 × 3 mL), and the combined extracts were filtered through Celite and evaporated. An orange residue remained that was redissolved over 10 min in methylene chloride (10 mL); pentane (20 mL) was added slowly to form a cloudy orange solution. Upon cooling at −20 °C overnight, the resulting orange crystals were filtered, washed with pentane (3 × 5 mL), and dried in vacuo overnight. This material was identified as Cp(NO)(PPh$_3$)ReCO$_2$Re(CO)(NO)(PPh$_3$)(η^1-C$_5$H$_5$)·1.0CH$_2$Cl$_2$ (**2**), yield 0.159 g (75%). The relative amount of the methylene chloride solvate was confirmed in the ^{1}H NMR spectrum of this complex (4.26 ppm in C$_6$D$_6$). Anal. Calcd for C$_{49}$H$_{42}$Cl$_2$N$_2$O$_5$P$_2$Re$_2$: C, 47.31; H, 3.40. Found: C, 47.11; H, 3.61. IR (KBr): 1970 (CO), 1707, 1676 (NO), 1482, 1436, (PPh$_3$), 1362 (vw) 1288, 1263, 1236, 1217, 1187 (OCO region) cm^{-1}. IR (CH$_2$Cl$_2$): 1970 (CO), 1716 1679 (NO), 1482, 1435 (PPh$_3$), 1358 (m), 1300−1200 (v br), cm^{-1}. IR (THF): 1971 (CO), 1718, 1684 (NO), 1482, 1436 (PPh$_3$), 1358 (m), 1300−1200 (v br), 1218 (m) (OCO region) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.65 (mult., 2H, *o*-H, PPh$_3$), 7.61 (dd, $^3J_{\mathrm{H,P}}$ = 10.2, $^3J_{\mathrm{(H(o),H(m)}}$ = 7.8 Hz, 4H, *o*-H, PPh$_3$), 7.55 (br mult, 6H, *o*-H, PPh$_3$), 6.9−7.14 (mult, 18H, *m*- and *p*-H, PPh$_3$), 6.32 and 6.28 (br s, $\Delta\nu_{1/2}$ = 8 Hz, 48/29 (by area), 5H, η^1-C$_5$H$_5$), 4.59 and 4.53 (s, 5H, $\Delta\nu_{1/2}$ = 2 Hz, 25/51 (by area), η^5-Cp). ^{13}C{^{1}H} NMR: δ 134.62 (d, $^2J_{\mathrm{C,P}}$ = 11.5 Hz, *o*-C), 134.54 (d, $^2J_{\mathrm{C,P}}$ = 11.4 Hz, *o*-C), 134.12 (d, $^2J_{\mathrm{C,P}}$ = 8.4 Hz, *o*-C), 134.04 (d, $^2J_{\mathrm{C,P}}$ = 9.1 Hz, *o*-C), 133.20 (d, $^1J_{\mathrm{C,P}}$ = 40.5 Hz, *ipso*-C), 132.71 (d, $^1J_{\mathrm{C,P}}$ = 41.2 Hz, *ipso*-C), 130.76 (*p*-C), 130.53 (*p*-C), 130.46 (*p*-C), 128.86 (d, $^3J_{\mathrm{C,P}}$ = 9.9 Hz, *m*-C), 128.82 (d, $^3J_{\mathrm{C,P}}$ = 9.2 Hz, *m*-C), 128.66 (d, $^3J_{\mathrm{C,P}}$ = 10.7 Hz, *m*-C), 128.63 (d, $^3J_{\mathrm{C,P}}$ = 10.9 Hz, *m*-C), 128.29 (*m*-C), 128.11 (*p*-C), 127.88 (*m*-C), 127.69 (*m*-C), 127.50 (*m*-C), 117.17 (br, $\Delta\nu_{1/2}$ = 75 Hz, η^1-C$_5$H$_5$), 92.72 and 92.61 (s, 1/2 (by area), η^5-Cp), 53.24 (CH$_2$Cl$_2$). ^{31}P{^{1}H} NMR: δ 18.75, 15.38 (major); 17.99, 14.22 (minor).

Reaction of Cp(NO)(PPh$_3$)ReCO$_2$Re(η^1-Cp)(CO)(NO)(PPh$_3$) (2) with Et$_3$SiOH. An orange solution containing **5** (0.0179 mmol) in 600 mg of C$_6$D$_6$ was quantified by ^{1}H NMR spectroscopy via an anisole internal standard. Then Et$_3$SiOH (3.0 μL, 19.6 μmol) was added with a 10 μL syringe, and an ^{1}H NMR spectrum was recorded after standing for 18 h. Prominent absorptions were assigned to Cp(NO)(PPh$_3$)ReCO$_2$-Re(CO)(NO)(PPh$_3$)(OSiEt$_3$) (**5b**), 53% yield as a 33:24 mixture of the major and minor diastereoisomers[12] (Cp, δ 5.13 and 5.10, respectively). The identity of **5b** was confirmed by ^{13}C and ^{31}P NMR spectroscopy. Free cyclopentadiene was evident (yield, 49%) from the signals at δ 6.45, 6.28, and 2.67. In addition to (Et$_3$Si)$_2$O (1.00, 0.57), unreacted silanol (δ 0.94, 0.49), unreacted starting material (10%, δ 4.59 and 4.53 resonances, 4:7), and Cp(NO)(PPh$_3$)ReCO$_2$SiEt$_3$ (**4**)[12] were found (19%), δ 4.85 (Cp), 1.13 (dd, J = 8.5, 7.3 SiCH$_2$*CH$_3$*), 0.81 (dq, J = 15.1, 7.3, SiC*H$_\alpha$*H$_\beta$), 0.72 (dq, J = 15.1, 8.5, SiCH$_\alpha$*H$_\beta$*). After 41 h, all of the starting **2** and **4** had been replaced by free cyclopentadiene (63%) and **5b** (74%) as a 51/28 ratio of diastereoisomers. IR (THF): 1971 (CO), 1694, 1685 (NO), 1290, 1249 (OCO). ^{1}H NMR (C$_6$D$_6$): δ 7.70−6.80 (m, Ph), 5.13 (s, Cp) (major diast), 1.22 (t, J = 7.8, CH$_3$), 0.84 (q, J = 7.8, CH$_2$), 5.10 (s, Cp) (minor diast), 1.21 (t, J = 7.8, CH$_3$), 0.86 (q, J = 7.8, CH$_2$). ^{13}C{^{1}H} NMR: δ 136.20−130.42 (m, Ph), 93.29 (C$_5$H$_5$) (major diast), 8.25 (CH$_3$), 8.03 (CH$_2$), 93.09 (C$_5$H$_5$) (minor diast), 8.37 (CH$_3$), 8.15 (CH$_2$). ^{31}P{^{1}H} NMR: δ 22.10, 15.06 (major); 20.41, 17.47 (minor). ^{29}Si{^{1}H} NMR: δ 7.60.

Reaction of Cp(NO)(PPh$_3$)ReCO$_2$Re(η^1-Cp)(CO)(NO)(PPh$_3$) (2) with CH$_3$OH. To a C$_6$D$_6$ solution (600 mg) containing **2** (3.7 μmol, quantified vs an anisole internal standard) was added anhydrous and deoxygenated MeOH (0.4 μL, 9.9 μmol). NMR spectra of the yellow solution after 8 h

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(18) In addition to deprotonating metallocarboxylic acids, the other common synthetic route to anionic metallocarboxylates entails carboxylation of metallocarboxylates.[1] Thus, treatment of Cp(CO)$_2$FeM (M = Li, Na, K) [which is isolobal to Cp(PPh$_3$)(NO)ReM] with CO$_2$ under comparable conditions cleanly generates the extensively studied η^1-C CO$_2$ adduct Cp(CO)$_2$FeCO$_2$$^-$. Pinkes, J. R.; Masi, C. J.; Chiulli, R.; Steffey, B. D.; Cutler, A. R. *Inorg. Chem*. **1997**, *36*, 70, and references therein.

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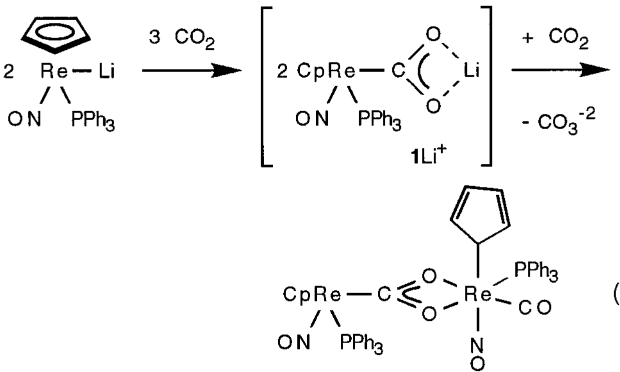
were consistent with the presence of 6% remaining **2** and an 82% yield of $Cp(NO)(PPh_3)ReCO_2CH_3$ (**6**):[18a] ^1H NMR δ 4.85 (Cp), 3.42 (Me); $^{13}C\{^1H\}$ NMR δ 91.89 (Cp), 49.15 (OMe).

Results and Discussion

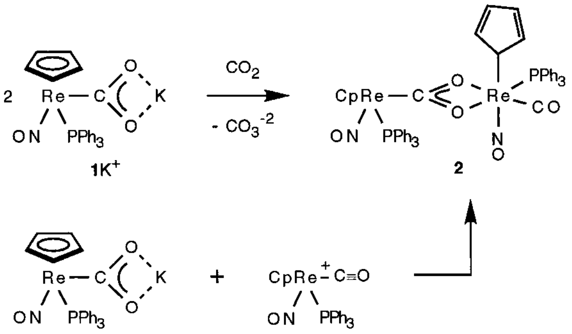
The rhenium η^1-C CO_2 adduct $Cp(PPh_3)(NO)ReCO_2^-$ (**1**Li^+ or **1**K^+), originally prepared by deprotonating $Cp(PPh_3)(NO)ReCO_2H$ with LiH or KH in THF at 25 °C,[9] is among the more stable and easily handled metallocarboxylates.[1] It was thus surprising that attempts to generate **1**Li^+ by treating the well-known metalate $Cp(PPh_3)(NO)ReLi$[17] with excess dry CO_2 between −78 °C and room temperature failed.[18] An immediate reaction occurred at −78 °C as a red solution of $Cp(PPh_3)(NO)ReLi$ plus CO_2 turned orange; no further changes in the IR spectra were noted as the cold solutions warmed to room temperature. We never detected **1**Li^+ in these reaction mixtures, although a single, THF- and benzene-soluble product **2** appeared to form that had three dominant and equally intense absorptions: a ν(CO) absorption at 1972 $cm^{-1}$and two ν(NO) bands at 1718 and 1684 cm^{-1}.

Two other salient observations helped to further this characterize this unusual reaction in which CO_2 gets incorporated as a neutral rhenium carbonyl (eq 3). First, treating the benzene extract of the reaction mixture with methanol in C_6D_6 quantitatively afforded the known[19] $Cp(NO)(PPh_3)ReCO_2CH_3$ (**6**), as deduced from its ^1H NMR spectrum. This material was isolated in 65−82% yields. Second, an insoluble white material that also formed during the carboxylation of **1**Li^+ dissolved in water and reprecipitated upon treatment with aqueous $Pb(NO_3)_2$. An IR spectrum of the resulting white solid as a KBr pellet matched that of an authentic sample of $PbCO_3$.[20]



(**3**)

Two other reactions also gave **2** as the only organorhenium product (eq 4). Brief exposure of **1**K^+ to CO_2 (1 atm) generated **2**, as did the reaction between **1**K^+ and the rhenium carbonyl $Cp(NO)(PPh_3)ReCO^+BF_4^-$. From these reactions **2** was isolated as a stable light orange solid after crystallization from CH_2Cl_2/pentane at −20 °C. Isolated yields ranged from 46 to 75% for a material that was characterized as a mono-CH_2Cl_2 solvate. Its NMR and IR spectral data are consistent with the presence of two diastereomers, each having two rhenium centers that retain a total of two Cp, two PPh_3, two NO, one terminal CO, and one μ_2-η^3 CO_2 as ligands.

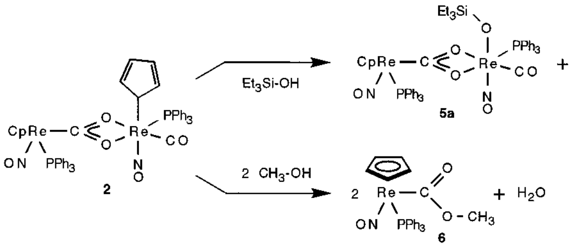


(**4**)

These major and minor diastereomers of **2** varied from 2:1 to 1.7:1 mixtures (as judged from ^1H, ^{13}C, and ^{31}P NMR spectra), which proved to be invariant with time and handling. The ^{31}P NMR spectra of **2** accordingly indicate the presence of two different PPh_3 ligands: two pairs of absorptions are evident, two signals for each diastereomer.

Both the ^1H and ^{13}C NMR spectra of **2** are dominated by the presence of absorptions for both η^1- and η^5-C_5H_5 ligands. Two narrow η^5-C_5H_5 resonances come at 4.55 and 4.53 ppm (ca. 1:2 relative intensities) and the two broadened η^1-C_5H_5 singlets are at 6.32 and 6.28 ppm (1:2). The ^{13}C NMR spectra likewise exhibit two sets of Cp resonances: two singlets at 92.72 and 92.61 ppm (1:2 intensities) and one broad absorption at 117 ppm. We observed no major changes in the ^1H NMR spectrum (toluene-d_8) upon cooling to −75 °C, which is consistent with similar rapid fluxional rearrangement of the η^1-C_5H_5 group that recently has been reported for related rhenium complexes $Re(CO)_3(PR_3)_2(\eta^1$-$C_5H_5)$.[21g] Further support for the presence of a η^1-C_5H_5 ligand on **2** originates with the observation that its solvolysis with a silanol (vide infra) also releases 1 equiv of free cyclopentadiene (identified by ^1H and ^{13}C NMR spectroscopy).

Since the μ-CO_2 ligand on **2** was not detected in the ^{13}C NMR spectrum, we resorted to nonspectroscopic procedures for establishing its presence. Treatment of **2** with Et_3SiOH accordingly provided the $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(OSiEt_3)$ (**5a**) in 74% NMR spectral yield (along with C_5H_6, 63%), eq 5. This rhenium silanolate previously had been characterized; an X-ray crystallographic structure determination of its phenyldimethylsilanolate congener **5b** established the presence of a μ-[η^1-C(Re_1):η^2-O,O′(Re_2)] bridging car-



(**5**)

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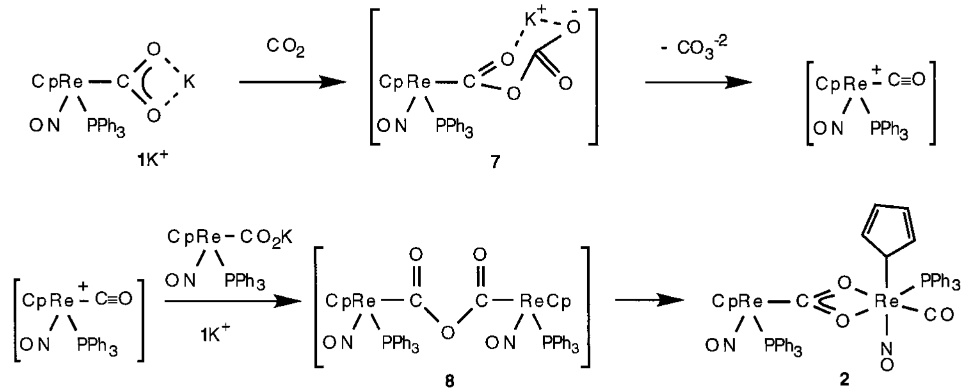
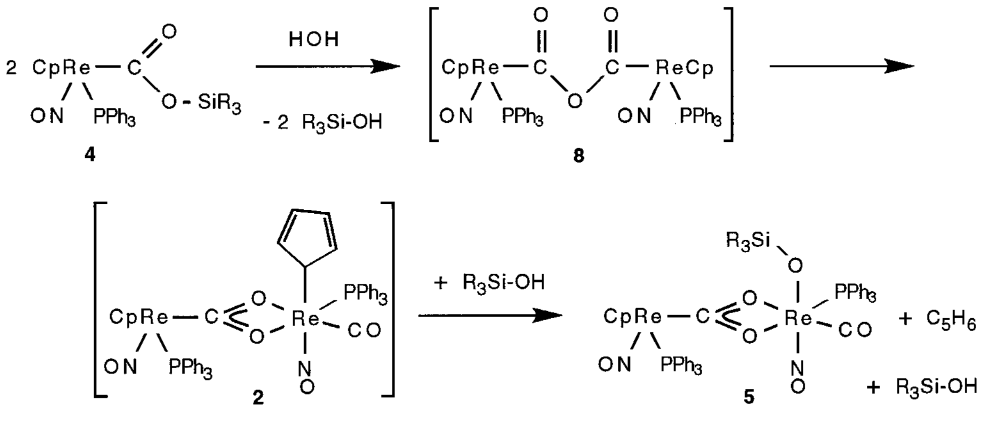
[20] Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952**, *24*, 1253.

[21] (a) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (b) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1982**, *2*, 535. (c) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241. (d) Young, K. M.; Miller, T. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 1529. (e) Hubbard, J. L.; Kimball, K. L.; Burns, R. M.; Sum, V. *Inorg. Chem.* **1992**, *31*, 4224. (f) Casey, C. P.; Widenhoefer, R. A.; O'Connor, J. M. *J. Organomet. Chem.* **1992**, *428*, 99. (g) Dahlenburg, L.; Hillman, G.; Markus, E.; Moll, M.; Knoch, F. *J. Organomet. Chem.* **1996**, *525*, 115.

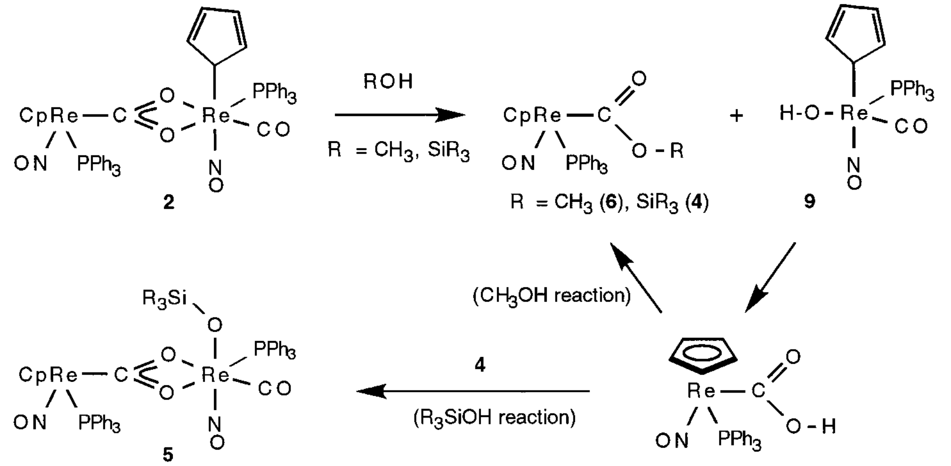
Scheme 2



Scheme 3



Scheme 4



boxylate,[12] as well as the *fac*-stereochemistry of the O-ligands depicted for the carboxylate-chelated rhenium center.

The IR spectra of **2** in THF, C_6H_6, and CH_2Cl_2 solutions or as a KBr pressed pellet exhibit comparable ν(CO) and ν(NO) absorptions, but differ somewhat in the appearance of the ν(OCO) region. Although we find what appears to be the $\nu_{OCO(sym)}$ band at 1218 cm^{-1} in THF (or C_6H_6 and CH_2Cl_2) solution, this peak corresponds to a local maximum on a broad envelope encompassing 1300–1200 cm^{-1}. The IR spectrum as a KBr pellet clearly shows five medium to strong intensity bands in this region: 1288, 1263, 1236, 1217, and 1187 cm^{-1}. We rule out either of the 1482 and 1436 cm^{-1} bands (weak and medium relative intensities, respectively) as candidates for the $\nu_{OCO(asym)}$ assignment, since absorptions with identical energies and relative band shapes are found for $Cp(PPh_3)(NO)ReH$ and $Cp(PPh_3)(NO)ReCH_3$. Previously, we had assigned the medium to strong intensity $\nu_{OCO(sym)}$ and $\nu_{OCO(asym)}$ bands for **5a** (in THF) at 1290 and 1249 cm^{-1} and those for **5b** at 1287 and 1248 cm^{-1}; both molecules likewise exist as 1:1 to 1:2 diastereomeric mixtures.[12] It therefore seems plausible that the ν_{OCO} bands for **2** fall within the 1300–1200 cm^{-1} region. Although such an assignment would lead to a $\Delta\nu = \{[\nu_{OCO(asym)}] - [\nu_{OCO(sym)}]\} < 100$ cm^{-1}, a corresponding value of 80 cm^{-1} was measured for $Cp(CO)_2RuCO_2ZrClCp_2$ ($\nu_{OCO(asym)}$ 1349, $\nu_{OCO(sym)}$ 1292 cm^{-1}), and these assignments followed from the results of a labeling study after incorporating $^{13}CO_2$.[15a,22]

A plausible pathway for transforming the rhenium (η^1-C) carboxylate $Cp(PPh_3)(NO)ReCO_2^-$ (**1**Li$^+$ or **1**K$^+$) plus excess CO_2 to **2** appears in Scheme 2. The presumed C_2O_4 adduct **7**[4] incorporates a second equivalent of CO_2 needed for the observed reductive disproportionation that releases carbonate. Although the anticipated $Cp(NO)(PPh_3)ReCO^+$ byproduct was not detected, we independently established that treatment of it (as the BF_4^- salt, eq 4) with **1**K$^+$ provided **2**. The transience of another postulated intermediate, the metalloanhydride **8**, followed by an $\eta^5-\eta^1$ Cp ring shift[21] commensurate with O,O′-chelation of the rhenium carboxylate and deinsertion of the rhenium carbonyl group accounts for **2**. Irreversible Cp ligand slippage[21a] has been documented for other Re(I) compounds as a means of opening up coordination sites.[21b−g]

The metalloanhydride **8** represents a viable intermediate in the three procedures that we used to generate **2**, even though it was not detected by IR spectral monitoring. Transience of other η^2-C,C′ metalloanhydride intermediates involving a single metal center $L_xMC(O)OC(O)$[23] (as opposed to a bridging metalloanhydride),[23c] although precedented, apparently is not germane to the present work and to the analogous degradation of the silyl esters $Cp(PPh_3)(NO)ReCO_2SiR_3$ (**4**).

In a previous study we had postulated the intermediacy of both the metalloanhydride **8** and **2** during the degradation of the silyl esters **4** to **5** (Scheme 3).[12] Hydrolysis of **4** evidently yields the rhenium acid $Cp(PPh_3)(NO)ReCO_2H$, which then interacts with additional **4** to give **8** and releases another equivalent of silanol. Rearrangement of **8** to **2** followed by silanolysis of the Re-η^1-Cp yields the observed products. Indeed, treatment of $Cp(NO)(PPh_3)ReCO^+BF_4^-$ with 1 equiv of **1**K$^+$ followed by addition of silanol R_3SiOH conveniently gave **5** (even though **2** had not been detected).[12] In the present study, we found that treating the isolated and fully characterized **2** with Et_3SiOH delivered **5a** (eq 5).

The intriguing solvolysis reactivity of **2** toward methanol and silanol (eq 5) warrants comment. Methanolysis of **2** surprisingly retains both Cp ligands and generates 2 equiv of **6**, whereas Et_3SiOH transforms **2** to the dirhenium silanolate **5** plus free cyclopentadiene. Since silanols are more acidic than alcohols,[24] Et_3SiOH could preferentially abstract cyclopentadiene from **2** via solvolysis of the η^1-Cp. Prior ionization of the Cp^- ligand,[21c] however, is unlikely since methanolysis of **2** under these conditions also would have given cyclopentadiene. In Scheme 4 we speculate on a mechanism in which both Et_3SiOH and methanol initially solvolyze the carboxylate ligand on **2** and provide their respective rhenium esters **4** or **6** plus the hypothesized η^1-Cp hydroxyrhenium intermediate **9**. This latter intermediate rearranges via a an $\eta^1 \rightarrow \eta^5$ ring shift to give the rhenium acid, which either undergoes methanolysis to yield the second equivalent of **6** or (with silanol) reacts with **4** to generate **5**. Both reactions of the rhenium acid have been established independently.[12]

Conclusions

Reductive disproportionation of ligated CO_2 is regarded as a deleterious process that irreversibly destroys the CO_2 complexation in favor of forming CO and carbonate, either of which may remain coordinated.[1,2] In the present study the otherwise stable rhenium η^1-C carboxylate $Cp(PPh_3)(NO)ReCO_2^-$ (**1**Li$^+$ or **1**K$^+$)[9] readily incorporated additional CO_2, but its ensuing reductive disproportionation generated a new CO_2 complex in addition to CO_3^{2-}. This new CO_2 complex, $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(\eta^1\text{-}Cp)$ (**2**), retains a Re_2-(μ_2-η^3 CO_2) motif and ligated CO. It evidently originates via an initial reductive disproportionation of $Cp(PPh_3)(NO)ReCO_2^-$ (**1**) plus CO_2 to $Cp(PPh_3)(NO)ReCO^+$ and free carbonate (Scheme 2); the rhenium carbonyl, however, subsequently intercepts **1** to generate the stable bimetallic CO_2 complex **2**. The overall stoichiometry (eq 3) requires 3 equiv of CO_2 plus 2 equiv of the electron-rich metalate [i.e., $Cp(PPh_3)(NO)ReLi$], transforming to ligated CO_2 and CO (i.e., **2**) plus CO_3^-.

Three procedures were used to generate **2**: treating (a) $Cp(PPh_3)(NO)ReLi$ with excess CO_2, (b) **1**K$^+$ with excess CO_2, and (c) **1**K$^+$ with $Cp(PPh_3)(NO)Re(CO)BF_4$. Results of studying these reactions are consistent with the intermediacy of an undetected metalloanhydride $Cp(PPh_3)(NO)ReC(O)OC(O)Re(NO)(PPh_3)Cp$ (**8**), which upon subsequent $\eta^5-\eta^1$ Cp ring shift on one rhenium center affords **2**. This product undergoes different solvolysis reactions in the presence of methanol and triethylsilanol. The former gives 2 equiv of the methylester $Cp(NO)(PPh_3)ReCO_2CH_3$ (**6**), whereas the latter replaces the η^1-Cp group with a silanolate, to give $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(OSiEt_3)$ (**5a**).

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Science, and from the National Science Foundation, Grant CHE 9412837, is gratefully acknowledged.

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[23] Considerably more evidence is available for transience of η^2-C,C′ metalloanhydride intermediates involving a single metal center, $L_xMC(O)OC(O)$,[18,23a,b] as opposed to those involving a bridging metalloanhydride ligand.[23c] (a) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794. (b) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363. (c) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1467.

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