

Preparation and characterization of the rhenium silyl esters ($\eta^5\text{-C}_5\text{Me}_5$)(CO)(NO)ReC(O)OSiR₃ (SiR₃ = SiMe₂Ph, SiEt₃)

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Abstract

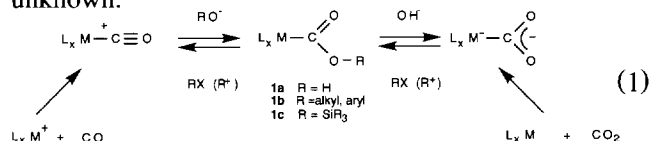
Three synthetic approaches to the rhenium silyl esters Cp*(CO)(NO)ReC(O)OSiEt₃ (**3**) and Cp*(CO)(NO)ReC(O)OSiMe₂Ph (**4**) were evaluated. (a) Treatment of a CH₂Cl₂ solution of Cp*(CO)₂(NO)Re⁺BF₄⁻ with a silanolate NaOSiEt₃ (**5**) or NaOSiMe₂Ph (**6**) provided 90% isolated yields of **3** and **4**. These stable orange-yellow solids are extremely moisture sensitive: traces of water hydrolyze them to Cp*(CO)(NO)ReCO₂H and the parent silanol. IR and NMR spectral data of **3** and **4** are consistent with nonchelating $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ metalloester structures. Less efficient preparative routes to **3** and **4** include treatment of (b) Cp*(CO)(NO)ReCO₂H with the requisite chloroalkylsilane and NⁱPr₂Et, and (c) Cp*(CO)(NO)ReCO₂⁻Na⁺ (7Na⁺) with the chloroalkylsilane. The new rhenium CO₂ adducts Cp*(CO)(NO)ReCO₂⁻M⁺ (7Li⁺, 7Na⁺) were generated by deprotonation of Cp*(CO)(NO)ReCO₂H with excess LiH or NaH THF suspensions at 0°C. Both 7Li⁺ and 7Na⁺ were characterized by their solution IR spectra and by the formation of their derivatives with silyl and tin chlorides.

Keywords: Rhenium; Cyclopentadienyls; Silyls; Metalloalkyl carboxylic acid; Carbon dioxide; Silane

1. Introduction

Metalloalkyl carboxylic acids and their esters are common intermediates for the reactions of coordinated carbon monoxide and carbon dioxide (for reviews on CO₂ complexes see Ref. [1]). Indeed, metalloalkyl carboxylic acids **1a** mediate pH-dependent equilibria that interconvert carbonyl and metalloalkyl carboxylate (i.e. CO₂) complexes, Eq. (1) [2–8]. These equilibria are central to water-gas shift catalysis, which interconverts water and CO with hydrogen and CO₂ [9]. A number of metalloalkyl carboxylates have been prepared by adding excess hydroxide to metal carbonyls¹ and by ligating CO₂ to nucleophilic metal centers.² Only a limited number of examples of

1a have been characterized, however, and most are predisposed either towards decarboxylation to yield their hydrido complexes L_xMH or towards ionization to their carbonyl complexes and hydroxide counterion.³ Although a few examples of the synthesis of **1a** through CO ‘insertion’ into metal hydroxides have been recorded [40,41], the reverse reaction—deinsertion of CO—is unknown.



Organic metalloalkyl carboxylate esters **1b**, which usually

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¹ Cp(NO)(CO)ReCO₂⁻, see Ref. [10]; Cp(N₂Ar)(CO)ReCO₂⁻, see Ref. [11]; Cp(PPh₃)(NO)ReCO₂⁻, see Ref. [12]; Cp(PPh₃)(CO)FeCO₂⁻ [4,7], see Ref. [13]; *t*-(CO)(bpy)₂RuCO₂·3H₂O [6], see Ref. [14].

² *t*-Cl(dmpe)₂IrCO₂, see Ref. [15]; *t*-Cl(diars)₂RhCO₂, see Ref. [16]; (Pr-salen)CoCO₂⁻, see Ref. [17]; [N(CH₂CH₂PPh₂)₃]CoCO₂⁻, see Ref. [18]; Cp(CO)₂FeCO₂⁻ [7], see Refs. [19,20]; Cp*(CO)₂FeCO₂⁻, see Ref. [21]; Cp(CO)₂RuCO₂⁻, see Ref. [22]; (N₄-macrocyclic)CoCO₂⁺ and Co(L)(en)₂CO₂⁺, see Ref. [23]; *t*-(CO)(bpy)₂RuCO₂·3H₂O, see Ref. [24]; (CO)₃WCO₂⁻, see Ref. [25].

³ Selected references: (PR₃)₂(R)PtCO₂H, see Ref. [26]; (PR₃)₂₋₄Ir(III)CO₂H [2], see Ref. [27]; Cp(L)(L')ReCO₂H (L = CO, L' = NO [10], N₂Ar [11]), see Ref. [28]; (L = PPh₃, L' = NO), see Ref. [29]; Cp*(CO)(NO)ReCO₂H, see Ref. [30]; Cp(PPh₃)(CO)_xMCO₂H (x = 1, M = Fe [4], Ru [8]), (x = 2, M = Mo), see Ref. [31]; (η⁵-C₆H₇)CO₂FeCO₂H, see Ref. [32]; Cp*(CO)₂RuCO₂H, see Ref. [33]; Cp(PR₃)₂RuCO₂H, see Ref. [34]; (PR₃)_x(CO)_{5-x}ReCO₂H (x = 1,2), see Ref. [35]; (CO)₄FeCO₂H⁻, see Ref. [36]; [HB(pz)₃](CO)Ir(H)CO₂H, see Ref. [37]; Co(OH₂)(en)₂CO₂H²⁺ [5], see Ref. [38]; *t*-(CO)(bpy)₂RuCO₂H⁺ and (trpy)(bpy)RuCO₂H⁺ [6,14], see Ref. [39].

(thin film) 3283 cm^{-1} (br s, ν O–H), 867 cm^{-1} (ν Si–O), (identical to that reported) [59]; $^1\text{H NMR}$ (C_6D_6) δ 7.51 (mult, o-H), 7.21 (mult, m- and p-H), 1.25 (s, OH), 0.24 (s, Me); (CDCl_3) 7.44 (mult, o-H), 7.23 (mult, m- and p-H), 2.29 (br s, OH), 0.24 (s, Me) [Ref. [58] (CDCl_3) δ 7.30 (mult, Ph), 2.62 (br s), 0.55 (s)]; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 139.82 (ipso-C), 133.40 (o-C), 129.65 (p-C), 128.00 (m-C), 0.06 (Me); (CDCl_3) δ 139.09 (ipso-C), 133.38 (o-C), 129.76 (p-C), 128.05 (m-C), -0.09 (Me) [Ref. [60] (CCl_4) δ 139.7 (ipso-C), 134.1 (o-C), 129.8 (m-C), 128.3 (p-C), 0.6 (Me)]; $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6) δ 5.93; (CDCl_3) δ 8.04 [Ref. [61] (d_8 -toluene) δ 5.7]. The rhenium compounds $\text{Cp}^*\text{Re}(\text{NO})(\text{CO})_2^+\text{BF}_4^-$ [62] and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ [30] were prepared by literature procedures and judged pure by IR and $^1\text{H NMR}$ spectroscopy.

2.2. Preparation of silanolates

2.2.1. NaOSiEt_3 (5)

The silanolate **5** was prepared by the same procedure as that reported for $\text{NaOSi}(\text{CH}_3)_3$ [63]. A solution of triethylsilanol (1.31 g, 9.90 mmol) in diethyl ether (20 ml) was cooled in an ice bath and treated with pentane-washed sodium spheres (227.9 mg, 9.91 mmol). After warming to room temperature overnight, the clear solution was filtered through Celite, which was washed with ether (3×5 ml). The combined ether filtrates were evaporated to give a white solid. This solid, which did not crystallize from pentane at -60°C , was dried in vacuo overnight. Yield **5** 1.239 g (81%). IR (CCl_4): 2949 s, 2907 s, 2869 s, 2804 w, 1464 m, 1417 m, 1377 w, 1228 m, 1011 s, 985 s, 958 s, 939 s, cm^{-1} ; (C_6H_{12}): 1418 m, 1227 m, 1010 s, 985 s, 958 s, 939 s, 729 s, 713 s, 668 w, cm^{-1} ; $^1\text{H NMR}$ (C_6D_6) δ 1.07 (t, $^3J_{\text{HH}} = 8.0\text{ Hz}$, CH_3), 0.53 (q, $^3J_{\text{HH}} = 8.0\text{ Hz}$, CH_2); (CDCl_3) δ 0.89 (t, $^3J_{\text{HH}} = 8.1\text{ Hz}$), 0.36 (q, $^3J_{\text{HH}} = 7.9\text{ Hz}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) (inverse gated decoupling) δ 9.00 (t, $^1J_{\text{CH}} = 118\text{ Hz}$, CH_2), 8.15 (q, $^1J_{\text{CH}} = 125\text{ Hz}$, CH_3); (CDCl_3) δ 7.24, 6.56 [Ref. [60] (CCl_4) δ 9.2 (CH_2), 8.4 (CH_3)]; $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6) δ -0.84 [Ref. [61] (d_8 -toluene) δ -0.6].

2.2.2. $\text{NaOSiMe}_2\text{Ph}$ (6)

The same procedure was used with phenyldimethylsilanol (2.0669 g, 13.6 mmol), ether (20 ml), and sodium spheres (0.3185 g, 13.85 mmol). The resulting cloudy solution (10 h, room temperature) was filtered and evaporated; the product was dissolved in pentane (10 ml) and cooled at -20°C overnight to produce a white crystalline product. After the solution was drained with a cannula, the crystals were washed with cold (-30°C) pentane (3 ml) and dried in vacuo for 4 h. Yield **6** 1.594 g (67%). IR (CCl_4): 3066 m, 2945 m, 1495 w, 1426 m, 1245 m, 1110 s, 986 s, 980 s, 972 sh, cm^{-1} ; (C_6H_{12}) 1426 m, 1243 m, 1110 m, 988 s, 968 sh, 816 s,

787 w, 765 s, 737 m, 704 m, 687 w, 664 w, 636 m, cm^{-1} . $^1\text{H NMR}$ (C_6D_6) δ 7.50 (dd, $J = 7.85, 1.25\text{ Hz}$, o-H), 7.25 (t, $J = 7.05\text{ Hz}$, m-H), 7.18 (tt, $J = 7.30, 1.50\text{ Hz}$, p-H), 0.24 (s, Me); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 145.86 (ipso-C), 132.50 (o-C), 129.12 (p-C), 128.93 (m-C), 2.89 (Me) [Ref. [60] (CCl_4) δ 145.8 (ipso-C), 132.6 (o-C), 129.1 (p-C), 129.1 (m-C), 3.1 (Me)]; $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6) δ -12.56 [Ref. [61] (d_8 -toluene) δ -12.3].

2.3. Synthesis of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SiEt}_3$ (3)

2.3.1. Reaction between $\text{Cp}^*(\text{CO})_2(\text{NO})\text{Re}^+\text{Bf}_4^-$ and NaOSiEt_3 (5)

A lemon yellow CH_2Cl_2 solution (20 ml) of $\text{Cp}^*\text{Re}(\text{NO})(\text{CO})_2^+\text{BF}_4^-$ (0.300 g, 0.607 mmol) was treated with a solution of **5** (94 mg, 0.61 mmol) in CH_2Cl_2 (1.0 ml). During the dropwise addition of **5** over 5 min the reaction solution turned orange, which left an orange solid after evaporation of the solvent. A pentane solution (3×5 ml) of the residue was filtered through Celite, reduced in volume to 5 ml, and cooled to -78°C . The resulting yellow-orange microcrystalline precipitate was separated from the pentane solution (cannula), and the crystals were washed with cold (-78°C) pentane (2×1.0 ml) and dried in vacuo. Yield **3** 302 mg (92%). IR (pentane, CH_2Cl_2 , Et_2O , THF): (1982, 1975, 1976, 1972 cm^{-1} , $\nu_{\text{C}=\text{O}}$), (1721, 1706, 1715, 1709 cm^{-1} , ν_{NO}), (1607, 1596, 1606, 1604 cm^{-1} , $\nu_{\text{C}=\text{O}}$). $^1\text{H NMR}$ (C_6D_6) δ 1.68 (s, Cp^*Me), 1.20 (psuedo t of simulated A_3BC spin system, $^3J_{\text{HH}\alpha} = 7.50\text{ Hz}$, $^3J_{\text{HH}\beta} = 8.40\text{ Hz}$, 9H, SiCH_2CH_3), 0.96 (m, $^2J_{\text{H}\alpha\text{H}\beta} = 14.7\text{ Hz}$, $^3J_{\text{H}\alpha\text{H}} = 7.50\text{ Hz}$, 3H, CH_αH), 0.93 (m, $^2J_{\text{H}\beta\text{H}\alpha} = 14.7\text{ Hz}$, $^3J_{\text{H}\beta\text{H}} = 8.40\text{ Hz}$, 3H, CH_βH); $^{13}\text{C}\{^1\text{H}\}$ (APT) (C_6D_6) δ 208.5 (ReCO), 190.9 (ReCO₂), 104.5 (Cp^*), 9.7 (Cp^*Me), 7.3 (SiCH_2CH_3); 6.0 (SiCH_2CH_3); $^{29}\text{Si}\{^1\text{H}\}$ NMR δ 17.91. Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{NO}_4\text{ReSi}$: %C, 40.13; %H, 5.61. Found: %C, 39.87; %H, 5.41.

2.3.2. Reaction between $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ and $\text{Et}_3\text{SiCl}/\text{NEt}(i\text{-Pr})_2$

An orange CH_2Cl_2 solution (2 ml) of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ (53.9 mg, 0.127 mmol), pre-cooled to 5°C , was treated with $\text{NEt}(i\text{-Pr})_2$ (25 μl , 0.14 mmol). No color change was noted after ClSiEt_3 (21.5 μl , 0.128 mmol) was added dropwise (microliter syringe). After stirring for 30 min at 5°C , the solvent was evaporated, and the orange residue was extracted with pentane (2×5 ml) and filtered. The pentane was concentrated in vacuo to 2 ml; the orange solution was cooled to -78°C ; and the temperature was maintained for 1 h. Supernatant solution was removed with a cannula from the resulting orange crystals, which were dried in vacuo for 1 h. These were identified by quantitative $^1\text{H NMR}$ spectroscopy (anisole internal standard)

as spectroscopically pure $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SiEt}_3$ (**3**) (61% yield).

2.4. Synthesis of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SiMe}_2\text{Ph}$ (**4**)

2.4.1. Reaction between $\text{Cp}^*(\text{CO})_2(\text{NO})\text{Re}^+\text{BF}_4^-$ and $\text{NaOSiMe}_2\text{Ph}$ (**6**)

$\text{Cp}^*(\text{CO})_2(\text{NO})\text{Re}^+\text{BF}_4^-$ (300 mg, 0.607 mmol) in CH_2Cl_2 (20.0 ml) was treated with a CH_2Cl_2 solution (1.0 ml) of **6** (174 mg, 0.607 mmol) over 5 min. The resulting orange colored solution was immediately evaporated, extracted into pentane (3×5.0 ml), and filtered through Celite. The volume was reduced in vacuo to 5 ml before cooling to -78°C . The yellow-orange $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SiMe}_2\text{Ph}$ (**4**) that precipitated was separated, washed with cold (-78°C) pentane (2×1.0 ml), and dried in vacuo. Yield of the microcrystalline solid **4** was 301 mg (89%). IR (pentane, CH_2Cl_2 , Et_2O , THF): (1982, 1976, 1978, 1972 cm^{-1} , $\nu_{\text{C}=\text{O}}$), (1720, 1706, 1715, 1709 cm^{-1} , ν_{NO}), (1612, 1602, 1610, 1608 cm^{-1} , $\nu_{\text{C}=\text{O}}$). $^1\text{H NMR}$ (C_6D_6) δ 7.87 (m, o-H), 7.27 (m, m-H); 7.20 (m, p-H, Ph), 1.63 (s, Cp^*Me), 0.69 (s, 3H, SiMe_α), 0.68 (s, 3H, SiMe_β); (CD_2Cl_2) δ 7.66 (m, o-H), 7.38 (m, m- and p-H), 2.10 (s, Cp^*Me), 0.50 (s, 3H, SiMe_α), 0.49 (s, 3H, SiMe_β); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 207.95 (ReCO), 191.30 (ReCO₂), 139.10 (ipso-C), 134.23 (o-C), 129.50 (p-C), 127.91 (m-C), 104.44 (Cp^*), 9.66 (Cp^*Me), 0.05 (SiMe_α), -0.14 (SiMe_β); (CD_2Cl_2) δ 207.63 (ReCO), 191.92 (ReCO₂), 138.83 (ipso-C), 133.73 (o-C), 129.41 (p-C), 127.75 (m-C), 104.92 (Cp^*), 10.08 (Cp^*Me), -0.53 (SiMe_α), -0.61 (SiMe_β); $^{29}\text{Si}\{^1\text{H}\}$ NMR δ 4.32. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_4\text{ReSi}$: %C, 42.99; %H, 4.69. Found: %C, 43.46; %H, 4.80.

2.4.2. Reaction between $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ and $\text{PhMe}_2\text{SiCl}/\text{NEt}(i\text{-Pr})_2$

To a CH_2Cl_2 solution (2 ml) of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ (51.5 mg, 0.121 mmol), pre-cooled to 5°C , was added a slight excess of NEt^iPr_2 (23.5 μl , 0.135 mmol). Then PhMe_2SiCl (20 μl , 0.119 mmol) was added dropwise with rapid stirring. The solution was kept at 5°C for 10 min before the CH_2Cl_2 was evaporated in vacuo and the orange residue was extracted with pentane (2×2 ml). The combined extracts were filtered and cooled to -78°C . Orange crystals of **3** appeared within minutes; after 20 min, the pentane was removed with a cannula and the orange solid was dried in vacuo. It was identified as spectroscopically pure **4**; yield 39 mg (58%).

2.5. Preparation of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^-M^+$ (**7**): IR spectral studies

2.5.1. $M = \text{Li}$

A 50 ml round-bottom flask with a side arm was charged with LiH (750 mg, 94 mmol),

$\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ (251 mg, 0.592 mmol), and a stirbar. The flask was then capped with a septum and immersed in ice-water. THF (10 ml) was added. After 1 h stirring, an IR spectrum of the orange supernatant solution indicated complete conversion to $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^-\text{Li}^+$ (**7Li**⁺). IR (THF) 1950 ($\nu_{\text{C}=\text{O}}$), 1675 (ν_{NO}), 1514, 1484 ($\nu_{\text{OCO asym}}$), 1332, 1257 ($\nu_{\text{OCO sym}}$), 1380 (ν_{Cp^*}) cm^{-1} .

2.5.2. $M = \text{Na}$

A 40 ml centrifuge tube was charged with a 60 wt.% NaH oil dispersion (100 mg, 2.50 mmol) and a stirbar and then capped with a septum. A nitrogen atmosphere was established in the centrifuge tube via a syringe needle attached to a Schlenk line. The NaH dispersion was washed with THF (2×4 ml); the washings were removed with a syringe, and the remaining NaH was dried in vacuo for 5 min. $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ (53 mg, 0.12 mmol) was added to the centrifuge tube by momentarily removing its septum. The nitrogen atmosphere was re-established, and the centrifuge tube was placed in an ice-water bath and chilled THF (10 ml) was added. After stirring for 15 min, the tube was centrifuged, and an IR spectrum of the orange solution revealed quantitative conversion of the starting material to $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^-\text{Na}^+$ (**7Na**⁺). IR (THF): 1947 ($\nu_{\text{C}=\text{O}}$), 1676 (ν_{NO}), 1490 (br, $\nu_{\text{OCO asym}}$), 1320, 1248 ($\nu_{\text{OCO sym}}$), 1382 (ν_{Cp^*}) cm^{-1} .

2.6. Silylation of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^- \text{Na}^+$ (**7Na**⁺)

2.6.1. PhMe_2SiCl

In a centrifuge tube $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ (24 mg, 0.058 mmol) plus THF-washed NaH (51 mg, 1.3 mmol NaH) in THF (5 ml) were transformed into **7Na**⁺ at 5°C . After stirring the suspension for 15 min, the tube was centrifuged, and the supernatant was transferred via cannula to a 50 ml round-bottom flask. This orange solution, chilled to 5°C , was treated with PhMe_2SiCl (9.8 μl , 0.060 mmol). An IR spectrum indicated the presence of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SiMe}_2\text{Ph}$ (**4**) as the only detectable $\text{Cp}^*(\text{CO})(\text{NO})\text{Re}$ compound ($\nu_{\text{C}=\text{O}}$ 1973, $\nu_{\text{N}=\text{O}}$ 1709, $\nu_{\text{C}=\text{O}}$ 1608). An NMR spectrum of the red-brown oil, after evaporation of solvent, in C_6D_6 (anisole internal standard) was consistent with a 60% yield of **4** as the major product, along with 5% $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$ and another 5% contribution of an unidentified $\text{Cp}^*(\text{CO})(\text{NO})\text{Re}$ compound (δ 1.48).

2.6.2. Et_3SiCl

A THF solution (5 ml) containing 0.058 mmol of **7Na**⁺ was treated with Et_3SiCl (7.0 μl , 0.042 mmol) at 5°C . In several experimental runs, IR spectra of the resultant solutions revealed variable amounts of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SiEt}_3$ (**3**) and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$.

NMR spectra were consistent with yields of 44–58% **3** and 15–33% $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$ as the only detectable Cp^*Re compounds.

2.7. Reaction of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^- \text{Li}^+$ (7Li^+) and Ph_3SnCl

A suspension of LiH (50 mg, 6.3 mmol) and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ (26 mg, 0.062 mmol) in 5 ml of THF (5 °C) was stirred for 1 h. The orange suspension was filtered and the filtrate was transferred to a second flask that contained Ph_3SnCl (24 mg, 0.062 mmol). An IR spectrum of this solution indicated the presence of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SnPh}_3$ as the only $\text{Cp}^*(\text{CO})(\text{NO})\text{Re}$ material present ($\nu_{\text{C}=\text{O}}$ 1973, $\nu_{\text{N}=\text{O}}$ 1710). The THF was removed in vacuo and NMR spectral analysis (CDCl_3 , anisole internal standard) of the yellow-brown oil revealed a 67% yield of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{SnPh}_3$ [30,51]: δ 2.04 (s, Cp^*).

2.8. Reaction of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^- \text{Na}^+$ (7Na^+) with $^{13}\text{CO}_2$

A solution of 7Na^+ , prepared as described above, was subjected to a freeze–pump–thaw cycle. The frozen solution was treated with $^{13}\text{CO}_2$ (8.0 Torr, 4.60×10^2 ml, at 23.5 °C, 0.20 mmol); the $\text{N}_{2(1)}$ bath was removed, and after the THF had melted the solution was stirred for 15 min. An IR spectrum of the orange solution indicated the presence of only $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$, $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$, CO_2 , and $^{13}\text{CO}_2$.

2.9. Reaction of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^- \text{Li}^+$ (7Li^+) with $^{13}\text{CO}_2$

A frozen suspension of 7Li^+ was treated with $^{13}\text{CO}_2$ (4.60×10^2 ml, 4 Torr, 23 °C, 0.1 mmol). After the THF had melted, the solution was stirred for 5 min and a nitrogen atmosphere was re-established. IR spectral analysis revealed the presence of $^{13}\text{CO}_2$, $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$, and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{Li}$. Within 15 min a suspension had formed; an IR spectrum of the supernatant solution showed $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ in addition to a broad peak centered at 1450 cm^{-1} .

3. Results and discussion

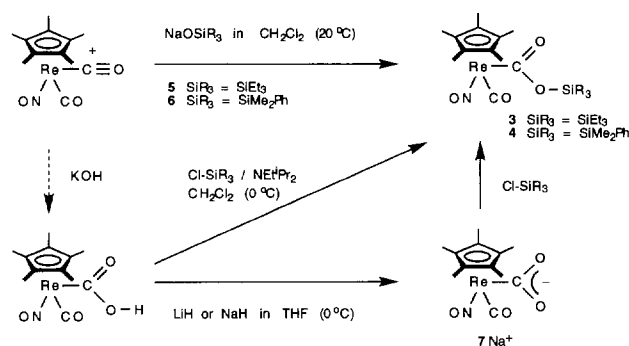
The silanolates used in this study, NaOSiEt_3 (**5**) and $\text{NaOSiMe}_2\text{Ph}$ (**6**), were prepared by deprotonation of the requisite silanols. These silanols were obtained by modification of literature procedures for the basic hydrolysis of chlorosilanes in a nonaqueous medium [64]. The hydrolysis of ClSiMe_2Ph must be done carefully in

order to prevent subsequent condensation of HOSiMe_2Ph to its disiloxane $\text{PhMe}_2\text{SiOSiMe}_2\text{Ph}$, a side reaction which is not problematic for the preparation of HOSiEt_3 . Both silanols were easily purified by vacuum distillation.

Treatment of these silanols with sodium in diethyl ether, analogous to the procedure of Belmonte and Own for the preparation of NaOSiMe_3 [63], provided the silanolates NaOSiEt_3 (**5**) and $\text{NaOSiMe}_2\text{Ph}$ (**6**) in 67% and 81% yields respectively. Both **5** and **6** were obtained as white solids, although only the latter was crystallized (pentane, –20 °C). These white, free-flowing powders are soluble in hydrocarbon, arene, ether, and halocarbon solvents. ^1H NMR spectra of these silanolates revealed that diethyl ether was not coordinated to sodium; presumably their solid state structures retain $[\text{NaOSiR}_2\text{R}']_n$ oligomers similar to those reported for the alkali metal salts of trimethylsilanol [65].

Solution IR spectra of these silanolates in CCl_4 and cyclohexane exhibit shifts in their intense $\nu(\text{Si}-\text{O})$ stretching frequencies from 867 cm^{-1} (HOSiMe_2Ph) and $839, 834\text{ cm}^{-1}$ (HOSiEt_3) to ca. $950\text{--}1000\text{ cm}^{-1}$. Exact assignments of the $\nu(\text{Si}-\text{O})$ stretches for **5** and **6** were precluded as this region also has $\nu(\text{C}-\text{C})$ modes. Similar spectral features were noted by Caulton and coworkers in the spectra for the silanolates of triphenylsilanol and t-butyltrimethylsilanol [66]. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these silanolates are unremarkable and only demonstrate small shifts with respect to the silanols (see Section 2). $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra in C_6D_6 reveal that deprotonation of the silanols resulted in upfield chemical shifts of 18.2 ppm (SiEt_3) and 18.5 ppm (SiMe_2Ph).

Scheme 1 outlines the three synthetic procedures that we used to obtain the rhenium silyl esters $\text{Cp}^*(\text{CO})(\text{NO})\text{ReC}(\text{O})\text{OSiR}_3$ [**3** ($\text{SiR}_3 = \text{SiEt}_3$); **4** ($\text{SiR}_3 = \text{SiMe}_2\text{Ph}$)]. In the first and most effective route, treatment of the rhenium carbonyl salts $[\text{Cp}^*\text{Re}(\text{CO})_2(\text{NO})]\text{BF}_4$ [62] with the silanolates **5** and **6** in dichloromethane yielded **3** and **4** respectively in ca. 90% yields. Substitution of tetrahydrofuran as the solvent provided lower yields (< 55%) of **3**, which cannot



Scheme 1.

be attributed to the lack of stability of **3** in tetrahydrofuran. Isolated samples of **3** are stable as tetrahydrofuran solutions for at least 3 h. Both silyl ester complexes are yellow–orange microcrystalline solids that are readily soluble in hydrocarbon and ether solvents. Although both **3** and **4** in these solutions are thermally stable, traces of water hydrolyze them to $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ [30] and the parent silanol.

Solution IR spectra of **3** and **4** are consistent with the nonchelating metalloester structures depicted. Their silyl ester $\nu(\text{C}=\text{O})$ bands, at 1604 and 1608 cm^{-1} (THF) respectively, are only slightly lower than the corresponding absorptions for the parent acid $\text{Cp}^*(\text{CO})(\text{NO})\text{ReC}(\text{O})\text{OH}$ and its methyl ester $\text{Cp}^*(\text{CO})(\text{NO})\text{ReC}(\text{O})\text{OCH}_3$ [54] (1627 and 1630 cm^{-1}). For comparison, the corresponding tin ester $\text{Cp}^*(\text{CO})(\text{NO})\text{ReC}(\text{O})\text{OSnMe}_3$ has its ester $\nu(\text{C}=\text{O})$ band at 1524 cm^{-1} (THF) or at 1510 cm^{-1} (KCl), whereas $\text{Cp}^*(\text{CO})(\text{NO})\text{Re}(\text{CO}_2)\text{SnPh}_3$ shows its $\nu(\text{OCO})_{\text{asym}}$ absorption at 1429 cm^{-1} (KCl) [30,51]. Results of X-ray structure determinations of these ReSn metalloesters confirmed that the former has a nonchelating $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ ester linkage, whereas the latter retains a bimetalloxy carboxylate $\mu(\eta^1\text{-C}:\eta^2\text{-O},\text{O}')$ ligand [30,51]. IR stretching frequencies for the CO and NO ligands on **3** and **4** resemble those of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReC}(\text{O})\text{OH}$ and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReC}(\text{O})\text{OCH}_3$.

The presence of the chiral rhenium center yields diastereotopic methylene hydrogens for **3** and diastereotopic methyl groups for **4**, which are observed in their NMR spectra. Other NMR spectral assignments were routine with the possible exception of the ^{13}C NMR chemical shifts for the Re–CO and Re–CO₂. We assigned the lower field resonances (ca. 208 ppm) to Re–CO and the δ 191 peaks to the ester CO in consonance with very similar observations for the analogous rhenium acid, methyl ester, and the aforementioned tin esters. The $^{29}\text{Si}\{^1\text{H}\}$ NMR chemical shifts for **3** and **4** are remarkably close to those of their respective silanols.

The second synthetic procedure for **3** and **4** entailed treating $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ with the appropriate chlorosilane in the presence of diisopropylethylamine. This procedure was patterned after that commonly used to siliate organic carboxylic acids [67]. We obtained moderate conversions (55–60%) to **3** and **4**, which were isolated spectroscopically pure in these small-scale reactions. No further attempts were made to optimize these reactions.

In the third route to **3** and **4** we generated the unknown rhenium CO₂ adducts $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{M}^+$ (7Li^+ , 7Na^+), which then were siliated with the requisite silyl chlorides. Treatment of THF solutions of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ with excess LiH or NaH at 5°C afforded orange supernatant solutions of the carboxylate anion 7Li^+ and 7Na^+ .

Interestingly, 7Li^+ proved to be rather stable, surviving for at least 20 min at room temperature; in contrast, reactions with 7Na^+ had to be carried out within 20 min at 5°C, since it degraded to give $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$ [68]: IR ($\nu_{\text{C}=\text{O}} = 1749$, $\nu_{\text{NO}} = 1683$). We did not attempt to purify 7Li^+ and 7Na^+ beyond separating them from excess metal hydride. Similar attempts to prepare 7K^+ using KH or $\text{KN}(\text{Si}(\text{CH}_3)_3)_2$ (between 0 and –78°C) provided only mixtures of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$, as deduced by IR spectral monitoring. Attempts to trap 7K^+ with ClSiEt_3 afforded only variable mixtures of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ and $\text{Cp}^*(\text{CO})_2(\text{NO})\text{Re}^+$.

Degradation of **7** evidently does not involve reversible CO₂ dissociation to give the unknown metalates $\text{Cp}^*(\text{CO})(\text{NO})\text{Re}^-\text{M}^+$. Treatment of solutions containing 7Na^+ or 7Li^+ with two or three equivalents of 99% ^{13}C CO₂ (between 0 and –78°C) provided no evidence for $\text{Cp}^*(\text{CO})(\text{NO})\text{Re}^{13}\text{CO}_2^-\text{M}^+$. Furthermore, 7Na^+ decomposed to $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$ as observed for reactions in the absence of exogenous ^{13}C CO₂. With 7Li^+ the presence of ^{13}C CO₂ decomposed 7Li^+ within 15 min to $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$. Apparently, excess CO₂ induces decomposition of 7Li^+ . Under similar conditions, $\text{Cp}(\text{CO})_2\text{FeCO}_2^-\text{Na}^+$ readily exchanged ligated CO₂ and incorporated ^{13}C CO₂ [20].

The metalloxy carboxylates 7Li^+ and 7Na^+ were characterized by their solution IR spectra. Their terminal carbonyl and nitrosyl stretching frequencies exhibit the expected [19,20,46–48] shifts to lower energies (20–26 cm^{-1} and 32–34 cm^{-1} respectively) with respect to $\nu_{\text{C}=\text{O}}$ and ν_{NO} stretches for the neutral silyl esters **5** and **6** and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$. The metalloxy carboxylate $\nu(\text{OCO})$ absorptions for 7Li^+ and 7Na^+ closely resemble those that we recently reported for $\text{Cp}(\text{CO})_2\text{FeCO}_2^-\text{M}^+$ (Li^+ , Na^+) [20]. Two sets of $\nu(\text{OCO})_{\text{asym}}$ and $\nu(\text{OCO})_{\text{sym}}$ absorptions were observed for 7Li^+ , whereas a single, broad $\nu(\text{OCO})_{\text{asym}}$ and two $\nu(\text{OCO})_{\text{sym}}$ absorptions were noted for 7Na^+ . This doubling of the anticipated carboxylate $\nu(\text{OCO})$ absorptions has been attributed to the presence of metalloxy carboxylate monomers and dimers with, for example, chelating and bridging Li^+ respectively. For 7Li^+ and 7Na^+ , we measured separations of the metalloxy carboxylate absorptions, $\Delta\nu(\text{OCO}) = [\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}]$, of 208 cm^{-1} and 206 cm^{-1} respectively, which is consistent with an ionic or $(\eta^1\text{-C}:\eta^2\text{-O},\text{O}')$ metalloxy carboxylate structure.⁶ These values are somewhat lower than those observed for $\text{Cp}(\text{CO})_2\text{FeCO}_2^-\text{Li}^+$ and Na^+ (323–305 cm^{-1}), but only slightly higher than the $\Delta\nu(\text{OCO})$

⁶ The well established IR spectral correlations involving absorptions for ligated organic carboxylate RCO_2^-M^+ , $\Delta\nu(\text{CO}_2) = [\nu(\text{CO}_2)_{\text{asym}} - \nu(\text{CO}_2)_{\text{sym}}]$, were used [69].

value of 187 cm^{-1} that Gladysz and coworkers reported for $\text{Cp}(\text{PPh}_3)(\text{NO})\text{ReCO}_2^-\text{Li}^+$ [12].

Deprotonation of a metallocarboxylic acid appears to be a viable synthetic route to rhenium metallocarboxylates. Gladysz group's $\text{Cp}(\text{PPh}_3)(\text{NO})\text{ReCO}_2^-\text{Li}^+$ and K^+ , for example, were generated by LiH or KH deprotonation of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{ReCO}_2\text{H}$ at room temperature [12]. Previous examples include generating basic aqueous solutions of $\text{Cp}(\text{NO})(\text{CO})\text{ReCO}_2^-\text{Na}^+$ or Et_3NH^+ and $\text{Cp}(\text{N}_2\text{Ar})(\text{CO})\text{ReCO}_2^-\text{Li}^+$, Na^+ , or Ca^{+2} [10,11]. Recent attempts to deprotonate $(\text{dppe})(\text{CO})_3\text{ReCO}_2\text{H}$, however, yielded only its hydrido derivative $(\text{dppe})(\text{CO})_3\text{ReH}$ [35].

The ready availability of the new rhenium metallocarboxylates 7Li^+ and 7Na^+ , unfortunately, did not prove to be particularly useful for the current study. Silylation of 7Na^+ with Et_3SiCl or PhMe_2SiCl provided **3** or **4** in only moderate 40–60% yields. Attempts to silylate 7Li^+ gave varying amounts of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReH}$ and very little of the desired silyl esters **3** or **4**. Although these small-scale procedures admittedly were not optimized, considerable effort nonetheless would have been required in order to isolate and purify **3** or **4** from 7Na^+ . We do, however, include an experimental for transforming 7Li^+ and Ph_3SnCl to the known stanlyl ester $\text{Cp}^*(\text{NO})(\text{CO})\text{ReCO}_2\text{SnPh}_3$ in 67% yield [30,51]. Future reports will detail on using 7Li^+ and 7Na^+ for the synthesis of ReRh [53] and ReZr [70] $\mu\text{-CO}_2$ complexes.

4. Conclusions

We used three procedures to synthesize the rhenium silyl esters $\text{Cp}^*(\text{CO})(\text{NO})\text{Re}-\text{C}(\text{O})\text{OSiEt}_3$ (**3**) and $\text{Cp}^*(\text{CO})(\text{NO})\text{ReC}(\text{O})\text{OSiMe}_2\text{Ph}$ (**4**). Their synthesis by treatment of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{H}$ with the requisite chloroalkylsilane and diisopropylethylamine was limited by the moderate conversion (55–60%) to **3** and **4**. Reactions between the new metallocarboxylate $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2^-\text{Na}^+$ (7Na^+) and the chloroalkylsilane likewise provided only moderate yields of **3** and **4** (40–60%), whereas 7Li^+ gave only trace amounts of the same products. The most efficient preparation of **3** and **4** was to add a silanolate NaOSiEt_3 (**5**) or $\text{NaOSiMe}_2\text{Ph}$ (**6**) to a methylene chloride solution of $\text{Cp}^*(\text{CO})_2(\text{NO})\text{Re}^+\text{BF}_4^-$. These reactions afforded 90% isolated yields of **3** and **4** as stable orange-yellow solids; their IR and NMR spectral data are consistent with nonchelating $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ metalloester structures.

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