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Unusual Degradation of the Rhenium Silyl Ester $Cp(NO)(PPh_3)ReCO_2SiMe_2Ph$ to the Bimetallic μ-η^1(C(Re)):η^1(O,O′(Re)) Carbon Dioxide Complex $Cp(NO)(PPh_3)ReCO_2Re(NO)(CO)(PPh_3)OSiMe_2Ph$

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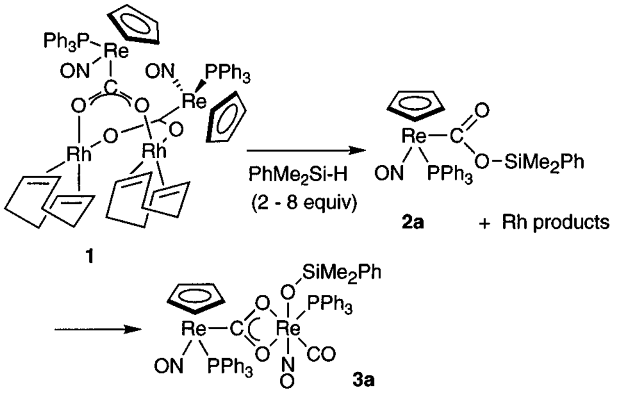
*Summary: The silyl esters $Cp(PPh_3)(NO)ReCO_2SiR_3$ (**2**) are produced from treatment of $Cp(PPh_3)(NO)ReCOBF_4$ with the silanolates R_3SiONa ($R_3Si = PhMe_2Si$, Et_3Si) in CH_2Cl_2 (0 °C) or of $Cp(PPh_3)(NO)ReCO_2K$ with R_3SiCl in THF. Upon handling, **2** degraded to the bimetallocarboxylates $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(OSiR_3)$ (**3**), one of which ($SiR_3 = SiMe_2Ph$) was characterized by X-ray crystallography as a μ-η^1(C(Re$_1$)):η^2(O,O′(Re$_2$)) bimetallocarboxylate.*

Several tetrametallic bis(carbon dioxide) complexes $[(\eta^5\text{-}C_5R_5)(L)(L')M(CO_2)Rh(\eta^4\text{-COD})]_2$ (C_5R_5 = Cp* (R = Me), M = Fe, Ru (L, L′ = CO) and Re (L = NO, L′ = CO); C_5R_5 = Cp (R = H), M = Re (L = NO, L′ = PPh_3) (**1**)) recently have been reported.[1] An X-ray crystallographic structure determination of $[Cp^*(CO)(NO)Re(CO_2)Rh(\eta^4\text{-COD})]_2$ and spectroscopic data for the others established a $M_2Rh_2(\mu_3\text{-}CO_2)_2$ structural motif in which each μ_3-η^1(C(Re)):η^1(O(Rh)):η^1(O′(Rh′)) carboxylate ligand bridges two Rh^I (η^4-COD) moieties.[1a] The resulting "open-book" structure resembles that of the catalytically active Rh(I) carboxylates $[(RCO_2)Rh(diene)]_2$.[2] In preliminary studies on the reactions of hydrosilanes with **1**, the most stable and least reactive of the $M_2Rh_2(\mu_3\text{-}CO_2)_2$ complexes, we have observed that the initially formed rhenium silyl esters $Cp(PPh_3)(NO)ReCO_2SiR_3$ experience an unexpected reaction chemistry.

Treatment of **1** with 1.1−8.0 equiv of $PhMe_2SiH$ in C_6D_6 at room temperature produced complex reaction mixtures in which the predominant $Cp(PPh_3)(NO)Re$-containing product was identified as $Cp(PPh_3)(NO)ReCO_2SiMe_2Ph$ (**2a**; 75% yield with 4.0 equiv of $PhMe_2SiH$) (Scheme 1). The chemistry at the rhodium appears to be dominated by the formation and subsequent reactions of $(COD)Rh(H)_2SiMe_2Ph$.[3,4] In the presence of only 1.1−2.0 equiv of $PhMe_2SiH$ with respect to **1**, however, the initially formed **2a** degraded to another compound, **3a** (28% conversion, 1 h for 2.0 equiv of silane). IR and ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectral data for **3a** indicated the presence of two rhenium centers that are ligated by a total of one Cp, two PPh_3, two NO, one terminal CO, and one $OSiMe_2Ph$.[5] To further characterize **3a** and to document its origin, we independently synthesized its silyl ester precursor **2a** as well as $Cp(PPh_3)(NO)ReCO_2SiEt_3$ (**2b**) using synthetic procedures that were reported for several examples of $Cp^*(CO)(NO)ReCO_2SiR_3$.[6]

Scheme 1



Treatment of Gladysz's $Cp(PPh_3)(NO)ReCO_2K$[7] with $PhMe_2SiCl$ or Et_3SiCl quantitatively generated **2a** and **2b**, as judged by IR spectral monitoring (Scheme 2).[5] Evaporation of solvent followed by either concentration of ether extracts and precipitation (−78 °C) or evaporation using a Schlenk line produced varying mixtures of **2** and **3** (15−50% **3**) as yellow solids. Similar results were obtained for the reaction of $Cp(PPh_3)(NO)(CO)ReBF_4$ and 1.1 equiv of $NaOSiMe_2Ph$ in CH_2Cl_2 (0 °C). This degradation of **2** to **3** is attributed to the

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(1) (a) Tetrick, S. M.; Tham, F. S.; Cutler, A. R. *J. Am. Chem. Soc.* **1997**, *119*, 6193. (b) Tetrick, S. M.; Xu, C.; Pinkes, J. R.; Tham, F. S.; Cutler, A. R. *Organometallics*, in press.

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(3) Marciniec, B.; Krzyzanowski, P. *J. Organomet. Chem.* **1995**, *493*, 261.

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(5) Selected spectroscopic data are as follows: $Cp(PPh_3)(NO)ReCO_2SiMe_2Ph$ (**2a**): IR (CH_2Cl_2) ν(NO) 1682, ν(C=O) 1563 (br) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.6−7.0 (Ph), 4.81 (Cp), 0.48, 0.34 ($SiMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 140−130 (Ph), 92.42 (Cp), 0.52,−0.073 ($SiMe_2$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 19.83; $^{29}Si\{^1H$, DEPT$\}$ NMR (C_6D_6) δ 1.54. $Cp(PPh_3)(NO)ReCO_2Re(CO)(NO)(PPh_3)(OSiMe_2Ph)$ (**3a**): IR (THF) ν(CO) 1972, ν(NO) 1703, 1683, $\nu(OCO)_{asym}$ 1287, $\upsilon(OCO)_{asym}$ 1248 cm^{-1}; ^1H NMR δ 8.0−7.0 (Ph), 4.86 (Cp, major), 0.68, 0.41 ($SiMe_2$), 4.79 (Cp, minor), 0.47, 0.34 ($SiMe_2$); $^{13}C\{^1H\}$ NMR δ 145−130 (Ph), 93.16 (Cp, major), 3.25 ($SiMe_2$, 2 degenerate absorptions by HMQC), 92.72 (Cp, minor), 3.41, 2.85 ($SiMe_2$, verified by HMQC); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 21.51, 15.28 (major), 20.41, 17.69 (minor); $^{29}Si\{^1H$, DEPT$\}$ NMR δ −4.01 (major), −5.28 (minor).

(6) Cavanaugh, M. D.; Tetrick, S. M.; Masi, C. J.; Cutler, A. R. *J. Organomet. Chem.* **1997**, *538*, 41.

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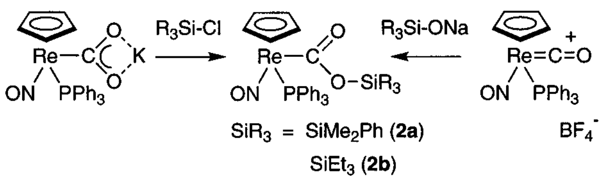
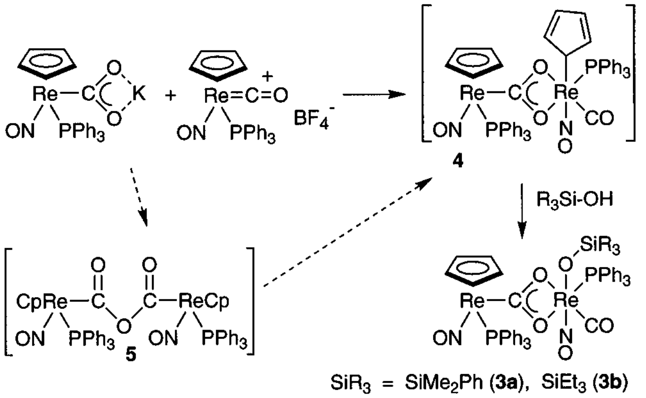
Scheme 2



Scheme 3



presence of traces of moisture (vide infra), which is in contrast with the relative ease of handling Cp*(CO)(NO)ReCO$_2$SiR$_3$.[6] By silanizing all glassware used, we procured 10:1 mixtures of **2** (30−48% NMR spectroscopic yields) and **3**. Compounds **2a** and **2b** displayed single ^{31}P and ^{29}Si NMR spectral resonances; their ^{1}H and ^{13}C NMR spectra revealed single Cp resonances plus two absorptions each for the diastereotopic methyl (**2a**) or methylene hydrogens (**2b**).[5] The presence of the silyl ester ligand on these products is consistent with their medium-intensity IR ν(C=O) absorptions at 1563 cm^{-1} (CH$_2$Cl$_2$), analogous to the 1593 cm^{-1} (THF) acyl absorption for Cp(PPh$_3$)(NO)ReCO$_2$CH$_3$.[8]

Compounds **3a** and **3b** also were synthesized independently by combining Cp(PPh$_3$)(NO)ReCO$_2$K and Cp(PPh$_3$)(NO)(CO)ReBF$_4$[8b] in THF, followed by treatment with PhMe$_2$SiOH or Et$_3$SiOH,[6] respectively (Scheme 3). The resulting mustard yellow solids after recrystallization from benzene-pentane (1:3) were characterized as analytically pure Cp(PPh$_3$)(NO)ReCO$_2$Re(CO)(NO)(PPh$_3$)(OSiR$_3$) (SiR$_3$ = SiMe$_2$Ph (**3a**), SiEt$_3$ (**3b**)), in 78−80% yields. Both **3a** and **3b** crystallize or precipitate as a mixture of two diastereomers in 1:1 to 1:2 ratios, as established by multinuclear NMR spectroscopy. The diastereomeric ratio of these isolated complexes was invariant with time and handling; exchange between the diastereomers for **3a** was not detected by ^{1}H NMR EXSY experiments. IR spectra of these compounds exhibit medium-intensity ν(OCO)$_{\mathrm{asym}}$ and ν(OCO)$_{\mathrm{sym}}$ bands at 1287 and 1248 cm^{-1} (THF), albeit with an very small $\Delta\nu = \nu(\mathrm{OCO})_{\mathrm{asym}} - \nu(\mathrm{OCO})_{\mathrm{sym}}$ value of 39 cm^{-1}.[9]

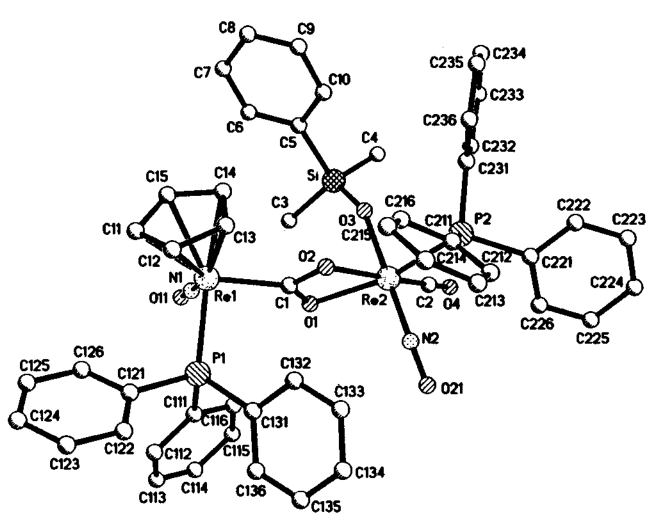
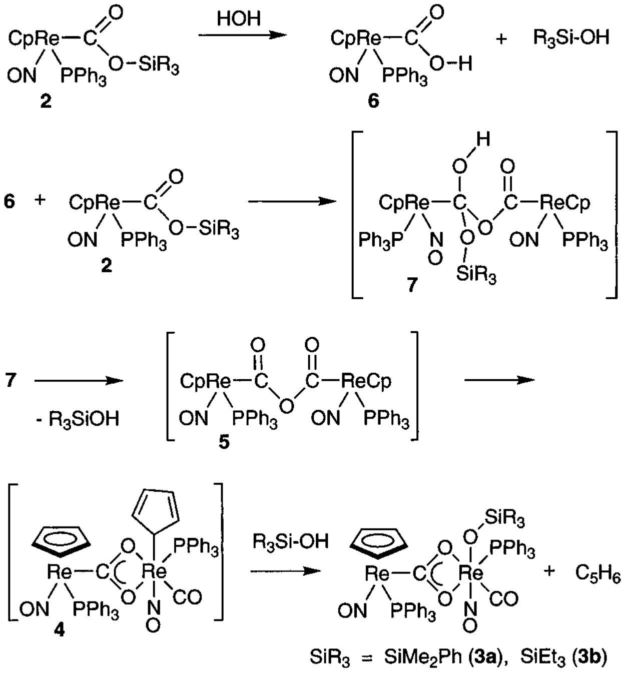


Figure 1. Ball and stick view of Cp(PPh$_3$)(NO)ReCO$_2$Re(CO)(NO)(PPh$_3$)(SiMe$_2$Ph) (**3a**). Selected interatomic distances (Å) and angles (deg): Re(1)−C(1) = 2.063(5), C(1)−O(1) = 1.306(5), C(1)−O(2) = 1.302(5), Re(2)−O(1) = 2.153(3), Re(2)−O(2) = 2.104(3), Re(2)−O(3) = 1.979(3), O(3)−Si = 1.609(4); O(1)−C(1)−O(2) = 112.0(4), O(1)−Re(2)−O(2) = 61.04(13), O(3)−Re(2)−N(2) = 178.1(2), C(2)−Re(2)−P(2) = 92.9(2), O(2)−Re(2)−P(2) = 97.60(10), C(2)−Re(2)−O(1) = 107.8(2), C(1)−Re(1)−P(1) = 92.05(13), N(1)−Re(1)−C(1) = 93.5(2), P(1)−Re(1)−Re(2)−N(2) = −12.32(15), Re(1)−O(1)−O(2) and Re(2)−O(1)−O(2) = 9.2(1), Re(2)−O(1)−O(2) and C(1)−O(1)−O(2) = 6.7(7), Re(1)−O(1)−O(2) and C(1)−O(1)−O(2) = 2.5(6).

Scheme 4



An X-ray crystallographic structure determination of **3a** confirmed the presence of the Re$_2$(μ_2-η^3-CO$_2$) bridging carboxylate (Figure 1).[10] Re(1) on the pseudooctahedral Cp(PPh$_3$)(NO)Re moiety[11] connects to the carboxylate carbon, and the carboxylate oxygens chelate Re(2) in a facial array with the silanolate ligand. Remaining ligands on Re(2) include PPh$_3$ and CO trans to the metallocarboxylate O's and NO trans to the silanolate. The μ-η^1(C(Re$_1$)):η^2(O,O′(Re$_2$)) carboxylate ligand on **3** has Re−C = 2.063(5) Å, which, although relatively short for a μ_2-η^3-CO$_2$ bimetallocarboxylate,[7,9] is reasonable for an acyl complex Cp(PPh$_3$)(NO)ReCOR.[11b] The sym-

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(7) Senn, D. R.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Inorg. Chem.* **1987**, *26*, 2737.

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(9) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063.

metrical chelation of the carboxylate oxygens to Re(2) resembles that observed in Gibson's Cp*(CO)(NO)Re(CO_2)Re(PPh_3)$(CO)_3$,[12] although unsymmetrical chelation was noted for Gladysz's Cp(PPh_3)(NO)ReCO_2-SnPh_3.[7] Solid-state structural data also have been reported for several examples of Cp*(CO)(NO)Re(CO_2)ML_x (L_x = Mo$(CO)_2$Cp, ZrClCp_2, WCp_2^+, SnMe_3, and SnPh_3) as well as for Cp(CO)(PPh_3)Fe(CO_2)Re$(CO)_3$-[P(OEt_3)].[9]

A plausible pathway for the synthesis of **3** from Cp(PPh_3)(NO)ReCO_2K and Cp(PPh_3)(NO)(CO)ReBF_4 also appears in Scheme 3. The key intermediate postulated in this reaction is **4**, which results from an $\eta^5-\eta^1$ Cp ring shift[13] commensurate with O,O′-chelation of the rhenium carboxylate group. Examples of Cp ligand slippage have been documented for other Re(I) compounds.[13b−g] The silanol present presumably traps **4**, with or without ionization of the η^1-Cp as Cp^-,[13c] and provides **3** plus C_5H_6 (which also was detected, 85%). We have no information at present on the (nonobligatory) intermediacy of the metalloanhydride **5**.[14] A similar Fp-based metalloanhydride was postulated by Cooper and Lee during their studies on the reaction between Cp$(CO)_2$FeCO_2Na and FpCOBF_4.[14d]

The rearrangement of **2** to **3** also could entail transience of intermediates **4** and **5** (Scheme 4). This rearrangement could be initiated by adventitious water, hydrolyzing **2** to the rhenium acid Cp(PPh_3)(NO)ReCO_2H (**6**)[15] and silanol.[16] Subsequent addition of **6** to **2**, perhaps via the depicted tetrahedral intermediate **7**,[17] then provides **5** plus more silanol. Rearrangement of **5** to **4** followed by "silanolysis" yields the observed **3**. In support of this mechanism, treatment of **2b** with either 1.0 equiv of **6** or 0.5 equiv of water gave 93% **3b**, as quantified by ^1H NMR spectroscopy.[18]

Most examples of bimetallic μ-CO_2 complexes have resulted from metalation of either metal−CO_2 adducts or metallocarboxylic acids with the appropriate metal electrophile, usually under carefully controlled reaction conditions.[9] The clean transformation of rhenium silyl esters **2** to the $Re_2(\mu_2\text{-}\eta^3\text{-}CO_2)$ compounds **3**, in contrast, represents a mechanistically unique example of degradation of a metallocarboxylic derivative into a stable bimetallic μ-CO_2 complex.[19] Studies in progress address (a) the metallocarboxylate ligand promoted $\eta^5-\eta^1$ Cp ring slippage and (b) the intermediacy of the putative metalloanhydride **5** during the transformation of **2** to **3**.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Science, and from the National Science Foundation (Grant CHE-9108591) is gratefully acknowledged.

Supporting Information Available: Text giving spectroscopic and characterization data for all compounds and tables of crystallographic parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles and figures giving additional views of **3a** (22 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for **3a**: $C_{51}H_{46}N_2O_6P_2Re_2Si\cdot 0.5C_6H_6$, $M_r = 1284.38$, triclinic, $P\bar{1}$ (No. 2); $a = 9.1251(5)$ Å, $b = 14.4101(8)$ Å, $c = 19.8446(9)$ Å; $\alpha = 85.392(4)$, $\beta = 87.004(4)$, $\gamma = 81.382(4)°$, $V = 2541.3$ Å^3; $Z = 2$; $D_c = 1.678$ g/cm^3; yellow prism (0.06 × 0.16 × 0.48 mm); 9720 reflections (7996 independent); 198 K; Siemens P4 diffractometer (ω-2θ scan, $3.4 \leq 2\theta \leq 48°$). The full-matrix least-squares refinement was based on 7996 reflections ($I > 2\sigma(I)$) and 604 parameters and converged with $R = 0.0282$ ($R_w = 0.0642$). Data were processed using the SHELXTL version 5.03 package (Siemens). Only the diastereomer depicted was observed in the crystal examined.

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(12) Gibson, D. H.; Mehta, J. M.; Ming, Y.; Richardson, J. F.; Mashuta, M. S. *Organometallics* **1994**, *13*, 1070.

(13) (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* **1983**, *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*, 1, 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.

(14) Considerably more evidence is available for the transience of η^2(C,C′) metalloanhydride intermediates involving a single metal center, L_xMC(O)OC(O),[14a−c] as oppposed to those involving a bridging metalloanhydride ligand:[14d] (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) Pinkes, J. R.; Masi, C. J.; Chiulli, R.; Steffey, B. D.; Cutler, A. R. *Inorg. Chem.* **1997**, *36*, 70. (d) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1467.

(15) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(16) (a) Analogous alcoholysis reactions occur for Cp*(CO)(NO)-ReCO_2SiR_3.[6] (b) Related transesterification reactions of metallocarboxylic acids and esters[16d−e] are well-known. (c) Treatment of Cp(PPh_3)(NO)ReCO_2H with 4 equiv of methanol in $CDCl_3$ promptly yielded a 3:2 mixture of Cp(PPh_3)(NO)ReCO_2CH_3 and starting acid, as determined by NMR spectroscopy. (d) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139. (e) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

(17) In the transformation of Cp(PPh_3)(NO)ReCO_2CH_3 to other acyl complexes Cp(PPh_3)(NO)ReCOR, stronger nucleophiles (e.g., RMgCl) presumably add to a rhenium alkoxycarbonyl ligand via tetrahedral intermediates. (a) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. C.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.

(18) The frequently discussed mechanism for transesterification of metallocarboxylic acids and esters L_xMCO_2R involves metal-assisted ionization[19] to L_xMCO$^+$ and then association of the exchanging alcohol, an overall S_N1 process.[16d,e] We disfavor involvement of this pathway in the conversion of Cp(PPh_3)(NO)ReCO_2H and **2** to **3** for two reasons. (1) Ionization of **2** or Cp(PPh_3)(NO)ReCO_2H to Cp(PPh_3)(NO)ReCO$^+$ and OSiR_3^- or OH^-, respectively, was not detected in dry THF, CH_2Cl_2, or dimethylformamide. (2) No reaction took place between Cp(PPh_3)(NO)ReCO_2H and Cp(PPh_3)(NO)ReCO$^+$ in the presence of 1 equiv of lutidine (which does not independently react with Cp(PPh_3)(NO)ReCO$^+$). These observations were the result of IR spectral monitoring of reactions involving 1 equiv of potential base for at least 2 h.

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(20) In a formally related degradation, Cp(NO)(CO)ReC(=O)OCH_2-CH_2Mo$(CO)_3$Cp extrudes CO plus ethylene and leaves the μ-η^1(C(Re)):η^2(O,O′(Mo)) bimetallocarboxylate Cp(NO)(CO)ReCO_2Mo$(CO)_2$Cp: Gibson, D. H.; Franco, J. O.; Mehta, J. M.; Harris, M. T.; Ding, Y.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1995**, *14*, 5073.