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Synthesis and Characterization of Rhenium Metallocarboxylates

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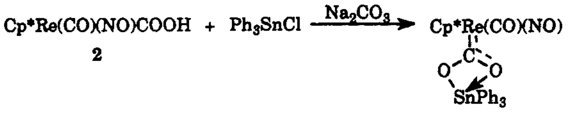
*Summary: Reactions of a new metallocarboxylic acid, Cp*Re(CO)(NO)COOH (2), with Ph_3SnCl and $Re(CO)_4(PPh_3)(F–BF_3)$ have provided the corresponding CO_2-bridged complexes $Cp^*Re(CO)(NO)(CO_2)SnPh_3$ (3) and $Cp^*Re(CO)(NO)(CO_2)Re(CO)_3(PPh_3)$ (4), which have been structurally characterized. Complexes 3 and 4 exhibit different types of μ_2-η^3 bonding of the bridging CO_2 ligand which can be correlated with the IR and ^{13}C NMR spectral properties of the compounds.*

There is much current interest in finding ways to activate carbon dioxide and to use it as a building block for organic synthesis.[1] The possibility that bifunctional systems,[2] having a basic center to bind the carboxyl carbon and an acidic one to bind one or both oxygens, might be effective in activating CO_2 has prompted interest in the synthesis and characterization of such compounds.[3]

In bimetallic complexes there is the possibility for different coordination modes of a bridging CO_2 ligand. In addition to the simple μ_2-η^2 type involving coordination of the carboxyl carbon to one center and coordination of a single oxygen to the second center, we[3t] previously suggested, on the basis of spectral data, that there are two distinct types of μ_2-η^3 complexes. Particularly with transition-metal bimetallic complexes, structural data are sparse. We now report the structural characterizations of two μ_2-η^3 complexes derived from the same metallocarboxylic acid, Cp*Re(CO)(NO)COOH (Cp* = η^5-C_5Me_5; 2), and comparisons of their spectral properties which support our previous suggestion.

Treatment of $Cp^*Re(CO)_2(NO)^+BF_4^-$ (1)[4] with 1 equiv of aqueous KOH afforded the acid 2 as an orange powder, which has been characterized by spectral data and elemental analysis.[5] Reaction of 2 with Ph_3SnCl in the presence of Na_2CO_3 (eq 1) afforded a product whose properties were in agreement with its formulation as the μ_2-η^3-CO_2-bridged complex $Cp^*Re(CO)(NO)(CO_2)SnPh_3$ (3). Compound 3 has been characterized by X-ray crystallography,[7] which confirms the μ_2-η^3 binding of the CO_2 ligand (see Figure 1). As with other tin derivatives of metallocarboxylates,[3k,p,w] binding of the carboxyl oxygens to carbon and to the tin atom is unsymmetrical.



2

3

(1)

$$Cp^*Re(CO)(NO)COOH + Ph_3SnCl \xrightarrow{Na_2CO_3} Cp^*Re(CO)(NO)(CO_2)SnPh_3 \quad (1)$$

Reaction of 2 with 1 equiv of $Re(CO)_4(PPh_3)(F–BF_3)$[8] in the presence of Na_2CO_3 (eq 2) afforded orange crystals of a product whose properties[9] again indicated μ_2-η^3 coordination of the bridging CO_2 ligand. Differences in the DRIFTS data for the ν_{OCO} absorptions, 1429 and 1174

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[5] To 0.550 g (1.11 mmol) of 1 in 5 mL of water was added 0.063 g (1.11 mmol) of KOH. The reaction mixture was stirred for 0.5 h, and an orange precipitate was collected by filtration. The precipitate was washed with 3 mL of water and vacuum-dried to give 0.450 g (95% yield) of Cp*Re(CO)(NO)COOH, mp 129–131 °C dec. Anal. Calcd for $C_{12}H_{16}NO_4Re$: C, 33.96; H, 3.80. Found: C, 33.88; H, 3.80. IR (Nujol): 1950 (s), 1690 (s), 1590 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 2.13 (s), 9.21 (s, br). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 10.28 (s), 105.31 (s), 194.95 (s), 206.94 (s).

[6] To a mixture of **2** (0.200 g, 0.470 mmol) and Na_2CO_3 (0.055 g, 0.470 mmol) in CH_2Cl_2 (ca. 10 mL) was added Ph_3SnCl (0.180 g, 0.470 mmol) dissolved in 5 mL of CH_2Cl_2. This mixture was then stirred for 3 h, filtered, and concentrated to dryness under vacuum, leaving an oil. The residue was extracted with 2 × 5 mL of ether. The ether extracts were combined and evaporated to dryness, leaving the crude product as an orange solid (0.234 g, 64% yield). The solid was recrystallized from CH_2Cl_2/pentane (1:1, v/v) to give orange crystals, mp 160–162 °C. Anal. Calcd for $C_{30}H_{30}NO_4ReSn$: C, 46.59; H, 3.91. Found: C, 46.53; H, 3.92. IR ν_{CO} (Nujol): 1970 cm^{-1}. DRIFTS ν_{OCO} (KCl): 1429 (m), 1174 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 2.09 (s), 7.40–7.71 (m). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 10.31 (s), 105.26 (s), 128.74 (s), 129.48 (s), 137.16 (s), 142.39 (s), 201.13 (s), 206.94 (s).

[7] Crystal data for **3**: $C_{30}H_{30}NO_4ReSn$, M_r = 773.47, monoclinic, $P2_1/a$, a = 19.644(8) Å, b = 11.819(9) Å, c = 12.171(8) Å, β = 100.16(5)°, V = 2781(3) Å^3, Z = 4, D_c = 1.85 g/cm^3. Data were collected on an Enraf-Nonius CAD4 diffractometer using the ω–2θ scan technique to a maximum 2θ = 54°. The structure was refined using full-matrix least squares to final agreement factors $R(F)$ = 0.053 and $R_w(F)$ = 0.068 for 5339 observed reflections ($I > 3\sigma(I)$) and 335 parameters. All computations were performed using the Texsan package (Molecular Structure Corp.).

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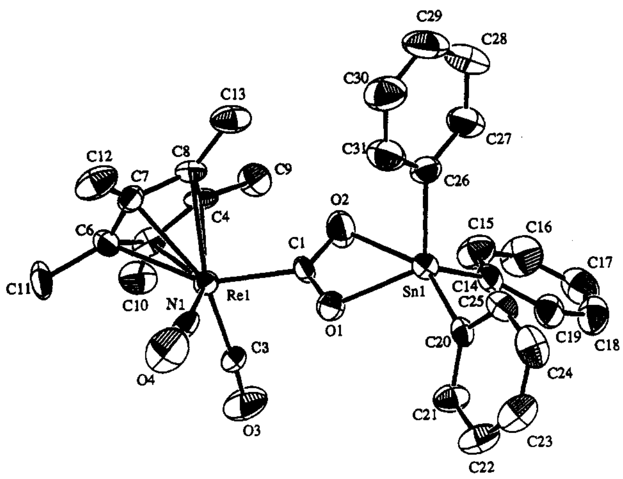
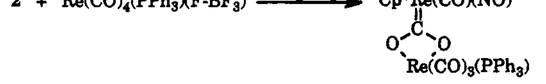


Figure 1. ORTEP drawing of **3** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Re–C(1), 2.100(9); C(1)–O(1), 1.322(9); C(1)–O(2), 1.24(1); O(1)–Sn, 2.092(3); O(2)–Sn, 2.399(1); O(1)–C(1)–O(2), 114.6(7); Re–C(1)–O(1), 119.4(6); Re–C(1)–O(2), 126.0(6); O(1)–Sn–O(2), 56.79(5).



$$\mathbf{2} + Re(CO)_4(PPh_3)(F\text{-}BF_3) \xrightarrow{Na_2CO_3} Cp^*Re(CO)(NO)(=\!C\{O\}_2)Re(CO)_3(PPh_3) \quad (2)$$

4

cm^{-1} in the tin complex **3** and 1437 and 1282 cm^{-1} in the homobimetallic compound **4**, as well as differences in the chemical shift positions of the carboxyl carbons in the two compounds (a singlet at 201.13 ppm in **3** and a doublet at 219.17 ppm in **4**) suggested different bonding modes for the CO_2 ligand in these compounds as noted before for iron metallocarboxylates.[3t] Thus, an unsymmetrical structure (previously described as type B[3t]) was suggested for **3**, whereas a symmetrical (type A) structure (as shown in eq 2) was suggested for compound **4**. An X-ray structure determination of **4**[10] and comparisons of the bonding characteristics of the CO_2 ligand in this compound with those in **3** confirmed the differences in structural types (see Figure 2).

It is interesting to note that a μ_2-η^2 complex is not observed as a precursor to **4**. With the μ_2-η^2 complex CpFe(CO)(PPh$_3$)(CO$_2$)Re(CO)$_4$(PPh$_3$), thermolysis at 85 °C for several hours was required to accomplish the μ_2-η^2 to μ_2-η^3 conversion.[3t] In the present case, facile conversion to the μ_2-η^3 complex is apparently greatly enhanced by the strongly electron-donating Cp* ligand.

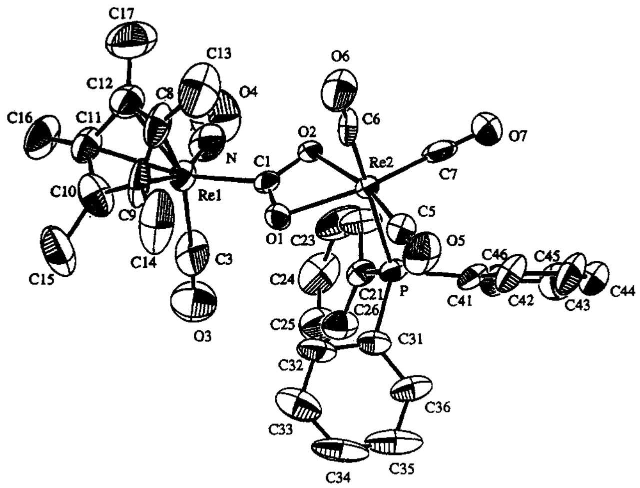


Figure 2. ORTEP drawing of **4** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)–C(1), 2.089(6); C(1)–O(1), 1.296(6); C(1)–O(2), 1.289(8); O(1)–Re(2), 2.165(4); O(2)–Re(2), 2.175(3); O(1)–C(1)–O(2), 113.2(5); Re(1)–C(1)–O(1), 122.0(4); Re(1)–C(1)–O(2), 124.8(3); O(1)–Re(2)–O(2), 59.6(1).

The differences between **3** and **4** parallel differences in structural parameters and ^{13}C chemical shifts reported by Geoffroy for cationic complexes which are closely related to **3** and **4**. Thus, the μ_2-η^3 complex Cp*Re(CO)(NO)(CO$_2$)WCp$_2$$^+BF_4$$^-$ [3n] shows highly symmetrical bonding of the bridging CO_2 and a short Re–carboxyl carbon bond (2.04(4) Å) together with a very low field carbon resonance position for the carboxyl carbon (243.1 ppm). However, another μ_2-η^3 complex, Cp*Re(CO)(NO)(CO$_2$)Ti(tmtaa)$^+$BF$_4$$^-$,[11] shows an unsymmetrically bonded CO_2 ligand and considerably longer Re–carboxyl carbon bond (2.081(9) Å) together with a much higher field carboxyl carbon ^{13}C shift (226.2 ppm). The Re–carboxyl bond length in the μ_2-η^3 complex CpRe(NO)(PPh$_3$)(CO$_2$)SnPh$_3$ is 2.058(9) Å, and the carboxyl carbon appears at δ 207.6; this system is unsymmetrical with differing C–O and O–Sn bond lengths.[3k] Angelici[12] reported the characterization of a dioxycarbene complex of rhenium several years ago; Re(CO)$_4$Br(C—OCH$_2$CH$_2$—O) shows a rhenium–carbene carbon length of 2.135(13) Å and signal at δ 224.31 for the carbene carbon. Although rhenium–alkylidene carbon bonds are shorter,[13] all rhenium oxycarbenes also show Re–carbene carbon bond lengths in excess of 2.0 Å (e.g., MnRe(CO)$_9$=C(OCH$_3$)(CH$_3$) at 2.094(7) Å).[14]

Within the series of four compounds having the fragment Cp*Re(CO)(NO)(CO$_2$) there are relationships of Re–carboxyl carbon bond length, O–C–O bond angle, carboxyl oxygen–metal bond length, and carbon chemical shift

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[9] In a glovebox, under nitrogen, **2** (0.200 g, 0.470 mmol) and Na_2CO_3 (0.025 g, 0.240 mmol) were slurried in 10 mL of CH_2Cl_2 and maintained at 0 °C. Re(CO)$_4$(PPh$_3$)(F–BF$_3$) (0.305 g, 0.470 mmol) was dissolved in 5 mL of CH_2Cl_2, chilled to 0 °C, and then added to the mixture containing **2**. The resulting mixture was stirred at 0 °C for 30 min and then warmed to room temperature and stirred for 2 h. After filtration, solvent was removed under vacuum, leaving a yellow-orange powder (0.320 g, 71% yield). Recrystallization of the crude product from ether afforded orange crystals, mp 208–210 °C dec. Anal. Calcd for $C_{33}H_{30}NO_7PRe_2$: C, 41.50; H, 3.16. Found: C, 41.61; H, 3.20. IR (CH_2Cl_2): 2020 (s), 1980 (s), 1920 (s), 1900 (s), 1710 (m) cm^{-1}. DRIFTS ν_{OCO} (KCl): 1437 (m), 1282 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 2.08 (s), 7.46 (m). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 10.44 (s), 104.80 (s), 128.82 (d, J_{PC} = 9.8 Hz), 130.86 (s), 131.55 (d, J_{PC} = 43.8 Hz), 134.68 (d, J_{PC} = 11.2 Hz), 193.19 (d, J_{PC} = 76.3 Hz), 197.23 (d, J_{PC} = 7.2 Hz), 197.67 (d, J_{PC} = 7.3 Hz), 206.37 (s), 219.17 (d, J_{PC} = 2.1 Hz). ^{31}P NMR (CD_2Cl_2, 25 °C): δ 24.43 (s). *Note*: Reactions conducted without Na_2CO_3 gave only cation **1**.

[10] Crystal data for **4**: $C_{33}H_{30}NO_7PRe_2$, 955.98, triclinic, $P\bar{1}$, a = 11.117(3) Å, b = 16.892(4) Å, c = 10.121(3) Å, α = 104.67(2)°, β = 107.16(2)°, γ = 97.86(2)°, V = 1710.2 Å^3, Z = 2, D_c = 1.86 g/cm^3. Data were collected on an Enraf-Nonius CAD4 diffractometer using the ω–2θ scan technique to a maximum $2\theta = 50°$. The structure was refined using full-matrix least squares to final agreement factors $R(F) = 0.025$ and $R_w(F) = 0.027$ for 4252 observed reflections ($I > 3\sigma(I)$) and 398 parameters. All computations were performed using the MolEN package (Enraf-Nonius).

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[12] Miessler, G. L.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 1690.

[13] (a) Re=C in Cp*Re(NO)[P(OPh)$_3$](=CH$_2$)$^+$ is 1.898(18) Å. See: Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. (b) Re=C in CpRe(NO)(PPh$_3$)(=CHPh)$^+$ is 1.949(6) Å. See: Kiel, W. A.; Lin, G. Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

[14] Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.

which define each type. Thus, the symmetrical Re–W complex has the shortest Re–C bond length, the smallest O–C–O angle (106(3)°), and the lowest field carbon shift, while the unsymmetrical Re–Sn complex **3** has the longest Re–carboxy carbon bond length, the largest O–C–O bond angle (see Figure 1), and the highest δ value for the carboxyl carbon. However, the greatest structural differences between the two types are with the carboxyl oxygen–metal bond lengths; these differ by approximately 0.3 Å in compound **3** and just 0.01 Å in **4**. Differences between the related, but cationic, complexes prepared by Geoffroy can be described in the same way. On the basis of rhenium–carboxy carbon bond lengths, all four compounds should be cast as "carbene" complexes; yet the unsymmetrically bonded compounds, such as **3**, do constitute one class and the symmetrically bonded ones, such as **4**, constitute another. All of the bimetallic CO_2-bridged compounds which have been structurally characterized to the present time can be fitted into one of these two types. Although spectral data place the μ_2-η^3 complexes prepared by Cutler[3g,r] (and involving early transition metals bonded to the carboxyl oxygen atoms) in the unsymmetrical class, there are not yet any structural data on these compounds. The simple type B structure suggested earlier[3t] does not adequately describe compounds of the unsymmetrical type; the delocalized system shown for **3** is offered as an improvement. The dioxycarbene structure (previously type A) is retained for the symmetrical types such as **4**. There are not yet any physical data to support charge separation within compounds of this type; ν_{CO} values appear to be normal.

From these comparisons and our previous work on CO_2-bridged iron–tin[3p,s,w] and iron–rhenium complexes,[3t] it is apparent that structural differences in the complexes can be correlated with differences in their ν_{OCO} bands in DRIFTS spectra as well as in the ^{13}C chemical shifts of the bridging carboxyl carbons. It was noted previously for IR spectra of carboxylato complexes that the difference in ν_{asym} and ν_{sym} ($\Delta\nu$) is helpful in distinguishing unidentate and bidentate coordination modes, since $\Delta\nu$ for the unidentate complexes is much larger.[15] The μ_2-η^2-CO_2-bridged iron–rhenium complexes prepared by us previously[3t] showed $\Delta\nu$ approximately equal to 353 cm^{-1}. Our symmetrical μ_2-η^3 complexes[3t] showed much smaller $\Delta\nu$ values of about 188 cm^{-1}, whereas the unsymmetrical compounds showed intermediate $\Delta\nu$ values between 207[3k] and 258 cm^{-1}.[3s] With the present compounds, **3** has $\Delta\nu$ = 255 cm^{-1} and **4** shows a smaller $\Delta\nu$ (155 cm^{-1}), as expected.

Acknowledgment. Support of this work by the United States Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), Office of Energy Research, is gratefully acknowledged. The X-ray equipment was purchased with assistance from the National Science Foundation (Grant No. CHE-9016978). Support of the Molecular Structure Laboratory through the NSF/KY EPSCoR program (Grant No. EHR-9108764) is also gratefully acknowledged.

Supplementary Material Available: Tables of data collection and refinement parameters, anisotropic thermal parameters, atomic positional parameters, bond distances, bond angles, and torsional angles for **3** and **4** (34 pages). Ordering information is given on any current masthead page.

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