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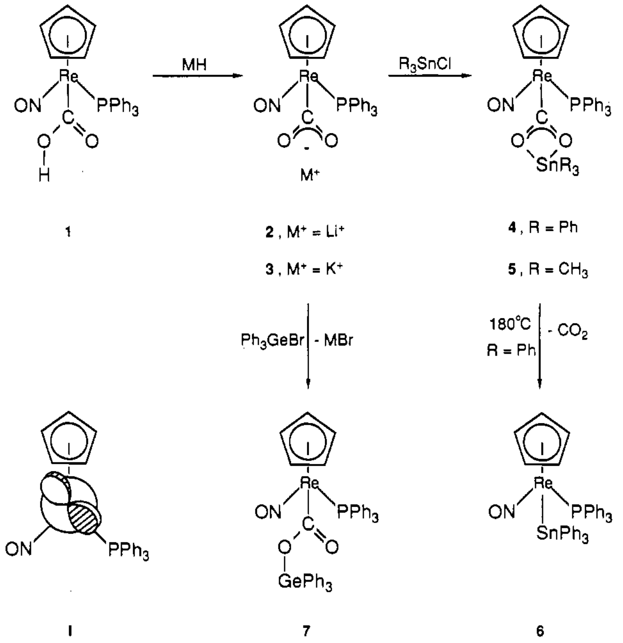
Communications

Synthesis, Structure, and Reactivity of Transition-Metal/Main-Group-Metal Bridging Carboxylate Complexes of the Formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO_2ML_n)$ (M = Li, K, Ge, Sn, Pb)

Sir:

Metal–CO_2 complexes have attracted attention from both fundamental and applied viewpoints.[1] First, CO_2 is an abundant C_1 molecule that serves as nature's photosynthetic building block. Second, CO_2 exhibits a variety of binding modes to metals.[1-6] Third, the reactivity of metal–CO_2 complexes should provide insight regarding CO_2 activation and the design of new catalytic reactions.[7] We have previously described the synthesis of the rhenium "carboxylic acid" $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$ (**1**),[8] in which a CO_2 moiety spans a transition metal and a hydrogen atom. In this communication, we report the elaboration of **1** to rhenium/main-group-metal bridging CO_2 or carboxylate complexes of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO_2ML_n)$.[1d] An added impetus for this study was the possibility that subsequent decarboxylation might provide a convenient entry to complexes with transition-metal–main-group-metal bonds.

Scheme I. Representative Syntheses and Reactions of Rhenium/Main-Group-Metal Bridging Carboxylate Complexes



Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$ (**1**)[8] with LiH and KH (THF, 25 °C) gave, after workup, the rhenium/alkali-metal CO_2 complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(\overline{\cdots O)\cdots O}Li)$ (**2**) and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(\overline{\cdots O)\cdots O}K)$ (**3**) as orange air-sensitive powders in 85–90% yields (Scheme I).[9] Complexes **2** and **3** showed IR ν_{OCO} bands (cm^{-1}, thin film) of 1435 and 1405 (ν_{asym}) and 1248 and 1239 (ν_{sym}). The ν_{asym} and the $\Delta\nu$ ($\nu_{asym} - \nu_{sym}$) values are considerably lower than those found in **1** (ν_{asym} 1551 cm^{-1}, ν_{sym} 1117 cm^{-1}) or the "methyl ester" $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(=O)-OCH_3)$ (ν_{asym} 1584 cm^{-1}, ν_{sym} 1042 cm^{-1}).[8,10] In accord with extensive literature precedent,[3b,11] these

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data are used to assign the bidentate carboxylate (or $\mu(\eta^1\text{-}C{:}\eta^2\text{-}O,O')$) binding mode.

Similar transition-metal/alkali-metal or transition-metal/alkaline-earth-metal CO_2 complexes have been previously isolated and studied by Cooper,[2] Cutler,[3] and Sutton.[4,5] However, no structural data have been reported to date. We were unable to obtain crystals of **2** or **3** suitable for X-ray analysis, so derivatization with group 14 metals was attempted. We first turned our attention to tin because of the extensive interest in, and structural studies on, tin *organo*carboxylates.[12]

Reaction of **3** with Ph_3SnCl (1.1 equiv, THF, −78 °C) and workup gave the air- and water-stable rhenium/triphenyltin CO_2 complex $(\eta^5\text{-}C_5H_5)Re(NO)PPh_3)(C(\overline{\cdots O)\cdots O}SnPh_3)$ (**4**) in 86% yield (Scheme I). The IR ν_{OCO} bands (1395, 1188 cm^{-1}) indicated a bidentate carboxylate binding mode, and the ^{119}Sn NMR chemical shift (−167.1 ppm, d, $J_{^{119}Sn-^{31}P}$ = 4.6 Hz) was upfield from that normally found for tetracoordinate tin.[12f] Yellow prisms of **4** were obtained from CH_2Cl_2/hexanes, and X-ray data were collected as described in the supplementary material. The molecular structure of **4** is given in Figure 1.

The bonding to tin in **4** is unusual. As previously noted by Holmes, the structures of most monomeric triaryltin organocarboxylates can be derived by distorting the C=O oxygen of a hypothetical structure containing tetrahedral tin toward a tetrahedral face opposite to one aryl group.[12b–e] The result can be considered a distorted trigonal bipyramid with the "C=O" oxygen and unique aryl group in axial positions. However, the axial tin–oxygen bond typically remains 0.7–0.8 Å longer than the equatorial tin–oxygen bond.[12c,e] Complex **4** is unique in having *nearly equal* tin–oxygen bond lengths (2.257 (7), 2.175 (7) Å). This small difference can likely be ascribed to the asymmetric steric environment about rhenium. Further, the sum of the equatorial bond angles in **4** is 351.2° (C11, C31, O2), considerably closer to that of an idealized trigonal bipyramid (360°) than in triaryltin organocarboxylates (333–341°).[12b–e] Also, the tin is displaced only 0.364 Å from the plane of the equatorial atoms, in contrast to 0.543–0.693 Å in triaryltin organocarboxylates. Finally, the O1–C6–O2 plane makes a 5 (1)° angle with the N–Re bond. This orientation is analogous to that of formyl and acyl ligands in complexes of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$[13] and maximizes overlap of the rhenium fragment HOMO shown in I (Scheme I) with the acceptor orbital on C_α.

The reaction of **3** and Me_3SnCl (1.1 equiv, THF, −78 °C) gave the rhenium/trimethyltin CO_2 complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(\overline{\cdots O)\cdots O}SnMe_3)$ (**5**, 95%). Complex **4** was also synthesized directly from **1** and $(Ph_3Sn)_2O$ (0.5 equiv, THF, 25 °C; 95%). When **4** was heated, it cleanly decarboxylated (Scheme I; <10 min, 180 °C, solid; 20 h, 140 °C, xylenes) to the rhenium-tin complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SnPh_3)$ (**6**, >98%). The structure of **6** was confirmed by an independent, NMR-monitored synthesis from the "anion"[14] $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ and Ph_3SnCl (1.0 equiv, THF, −78 °C).

The synthesis of other rhenium/group 14 metal bridging CO_2 complexes was attempted. First, reaction of **3** and Ph_3GeBr (25 °C, THF) gave the rhenium/germanium CO_2 complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(=O)-OGePh_3)$ (**7**) in 52% yield after CH_2Cl_2/hexanes recrystallization. IR data (ν_{OCO} 1545, 1048 cm^{-1}) indicated a monodentate carboxylate binding mode.[12] An analogous reaction of **3** and Ph_3PbCl gave a (33 ± 2):(67 ± 2) mixture of the rhenium/lead CO_2 complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(\overline{\cdots O)\cdots O}PbPh_3)$ (**8**; ν_{OCO} 1425, 1184 cm^{-1}) and the rhenium-lead complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PbPh_3)$ (**9**). The latter compound crystallized as orange prisms from CH_2Cl_2/hexanes. When the reaction of **3** and Ph_3PbCl was conducted at −78 °C and worked up at 0 °C, pure **8** was isolated. Facile decarboxylation to **9** occurred in C_6H_6 at room temperature (<48 h).

In summary, we have shown that rhenium/main-group-metal bridging CO_2 complexes derived from **1** are easily synthesized. Both bidentate and monodentate carboxylate binding modes are observed, with the symmetrical bidentate binding to tin in **4** being unprecedented. Clean thermal decarboxylation occurs when the main-group metal is tin or lead, providing convenient routes to

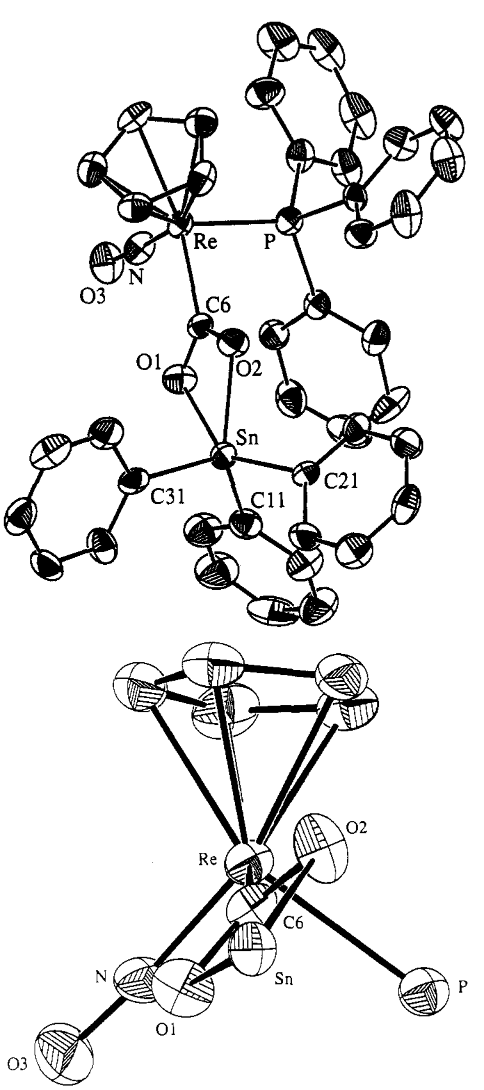

Figure 1. Two views of the structure of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(\overline{\cdots O)\cdots O}SnPh_3)$ (**4**). The bottom view omits the phenyl rings. Selected bond lengths (Å) and angles (deg) are as follows: Re–C6, 2.058 (9); C6–O1, 1.269 (11); C6–O2, 1.313 (11); Sn–O1, 2.257 (7); Sn–O2, 2.175 (7); Sn–C11, 2.142 (10); Sn–C21, 2.162 (10); Sn–C31, 2.117 (10); Re–N, 1.751 (7); Re–P, 2.355 (3); N–O3, 1.200 (10); C6–O1–Sn, 93.7 (6); O1–Sn–O2, 57.8 (2); Sn–O2–C6, 96.3 (5); O2–C6–O1, 112.2 (8); O1–Sn–C11, 88.2 (3); O1–Sn–C21, 144.4 (3); O1–Sn–C31, 99.7 (3); O2–Sn–C11, 132.2 (3); O2–Sn–C21, 90.8 (3); O2–Sn–C31, 104.1 (3); C11–Sn–C21, 104.5 (4); C11–Sn–C31, 114.9 (4); C21–Sn–C31, 104.4 (4); Re–C6–O1, 123.9 (7); Re–C6–O2, 123.8 (6); Re–N–O3, 175.4 (7); N–Re–P, 93.7 (3); N–Re–C6, 94.2 (4); P–Re–C6, 87.7 (3).

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heterobimetallic complexes. Additional chemical and physical properties will be detailed in our full paper.

Acknowledgment. We thank the Department of Energy for support of this research. NMR spectrometers utilized were provided by NSF and DOD instrumentation grants.

Supplementary Material Available: A listing of the data in ref 9, details of the X-ray data collection and structural refinement of **4**, tables of crystallographic data, atomic coordinates, bond lengths, bond and torsion angles, and anisotropic thermal parameters, and a figure showing the numbering of atoms in **4** (16 pages); a listing of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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Donor–Acceptor Metal–Metal Bonding Instead of Metathesis with Vaska's Compound and the Silver(I) Salt of the Weakly Coordinating Anion $B_{11}CH_{12}^-$

Sir:

While exploring the candidacy of the unusually stable carborane anion $B_{11}CH_{12}^-$ for a role as the least coordinating anion,[1] we have obtained an unexpected result when a seemingly straightforward halide abstraction reaction was attempted with Vaska's compound, $IrCl(CO)(PPh_3)_2$. Silver salt metathesis is a widely preferred method of halide ion abstraction from labile coordination compounds, and the formation of the perchlorato analogue of Vaska's compound is a typical example:[2]

$$IrCl(CO)(PPh_3)_2 + AgClO_4 \xrightarrow{\text{benzene}} Ir(OClO_3)(CO)(PPh_3)_2 + AgCl(s)$$

In contrast, when a toluene solution of $IrCl(CO)(PPh_3)_2$ is treated with the silver carborane salt $Ag[B_{11}CH_{12}]$,[3] there is no precipitate of AgCl. This obviously has important implications for the mechanism of the metathesis reaction. However, a slight lemon to orange color change is discernable and product workup and elemental analysis indicated 1:1 adduct formation.[4] The IR spectrum showed an increase in ν(CO) from 1950 to 1990 cm^{-1} (KBr), indicating a decrease of electron density on iridium. Recrystallization from fluorobenzene gave yellow single crystals of a hemisolvate, whose X-ray structure has been determined.[5]

Figure 1 shows the nature of the adduct. The iridium to silver metal–metal bond is one of the clearest illustrations to date of pure donor–acceptor metal–metal bonding. The Ir–Ag bond length (2.683 (1) Å) can be compared to the Pt–Ag distance of 2.77 Å in $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$, which is considered to indicate a quite respectable bond strength.[6] A precedent for this reaction can be found in the intramolecular Ag···Ir interaction observed in a triazenido analogue of Vaska's compound;[7] despite the entropic advantage, however, the bonding is considerably weaker (2.87 Å). While donor–acceptor adduct formation is a widely used synthetic strategy for metal–metal bond formation, the concept is frequently ambiguous when the structure of the adduct is examined.[8] Often the Lewis base donor has no obvious lone pair (e.g. $Co(CO)_4^-$ is tetrahedral), and its structural reorganization upon adduct formation is typical of a formal one- or two-electron oxidation (e.g. Co approaches a trigonal-bipyramidal geometry in $(CO)_4Co-Ag(ttas)$[9]). In the present complex the donor, iridium, scarcely changes its geometry from the planarity of the starting material. The P–Ir–P and Cl–Ir–C angles are 169.23 (4) and 173.6 (1)°, respectively, the iridium atom is displaced by only 0.16 Å from the mean plane of the donor atoms, and the metal–ligand bond lengths (see caption to Figure 1) are close to those of $IrCl(CO)(P(o\text{-tol})_3)_2$.[10] This suggests that the filled d_{z^2} orbital on iridium should be viewed in the traditional manner of a lone pair of electrons. Such a clear illustration of donor–acceptor or Lewis acid–base character in a metal–metal bond is conceptually useful in classifying the different types of metal–metal bonds. Another example can be found in the recently reported octaethylporphyrin species (OEP)Rh–In(OEP), which has a notably small rhodium atom displacement from the porphyrin plane toward the indium atom.[11] We also note the conceptual relationship between the present findings and the BF_3 and SO_2 Lewis acid adducts of Vaska's compound.[12]

In the present reaction, the choice made by the electron-deficient silver atom for iridium over chloride in adduct formation indicates that the iridium atom is the most basic site in Vaska's compound.

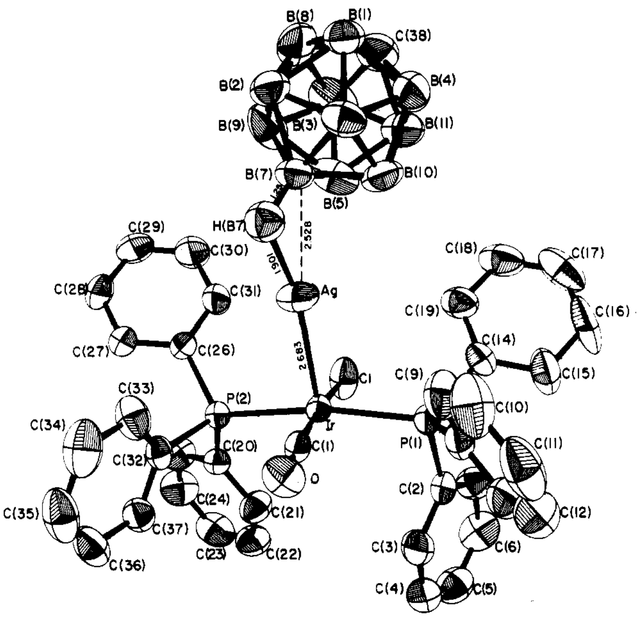

Figure 1. Computer-drawn (ORTEP2) diagram of $IrCl(CO)(PPh_3)_2 \cdot Ag(B_{11}CH_{12})$. Bond distances around silver are shown. Bond distances at iridium are Ir–P(1) = 2.341 (1) Å, Ir–P(2) = 2.346 (1) Å, Ir–Cl = 2.343 (1) Å, Ir–C(1) = 1.829 (5) Å and C(1)–O = 1.137 (5) Å. The coordinated hydrogen atom H(B7) was located with reasonable certainty in difference Fourier maps.

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[4] Anal. Calcd for the 0.5 toluene solvate $C_{41.5}H_{46}ClAgIrOP_2B_{11}$: C, 46.22; H, 4.31; P, 5.75; Cl, 3.28. Found: C, 45.95; H, 4.41; P, 5.93; Cl, 3.26.

[5] Crystal data: $IrAgClP_2C_{38}B_{11}H_{42}O \cdot 0.5C_6H_5F$, monoclinic, space group *C2/c*, $a = 37.405$ (3) Å, $b = 12.037$ (1) Å, $c = 20.672$ (2) Å, $\beta = 107.53$ (1)°, $Z = 8$. The structure was solved by direct methods (MULTAN 78) and refined by full-matrix least-squares techniques to a final $R_1 = 0.028$ and $R_2 = 0.033$ for 6757 observed reflections with $F_o > 3\sigma(F_o)$, collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation at ambient temperature (293 K). $\rho_{calcd} = 1.543$ g cm^{-1}; $\rho_{measd} = 1.54$ g cm^{-1}.

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