

Carbon Dioxide Coordination Chemistry. 5. The Preparation and Structure of $\text{Rh}(\eta^1\text{-CO}_2)(\text{Cl})(\text{diars})_2^1$

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There is much current activity exploring the interaction of carbon dioxide with transition-metal systems,² stimulated in large measure by interest in developing carbon dioxide as a potential alternate carbon source for petrochemicals. This communication presents the preparation and structure of a CO_2 complex with unprecedented η^1 M-CO₂ bonding and no metal-oxygen interactions, its relationship to some other 1:1 adducts, and its significance in the "chemicals from CO₂" quest.

The reaction of $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4^3$ with 4 equiv of *o*-phenylenebis(dimethylarsine) (diars) in THF affords the golden $[\text{Rh}(\text{diars})_2]\text{Cl}$ complex.⁴ This complex readily forms 18-electron species such as $[\text{Rh}(\text{diars})_2(\text{CO})]\text{Cl}$. Upon pressuring an acetonitrile solution of this complex to 5 psig with reagent grade carbon dioxide, light tan crystals of $\text{Rh}(\text{diars})_2(\text{Cl})(\text{CO}_2)$ deposit within hours.⁴ The complex displays new IR bands at 1610 (s) and 1210 (s) cm^{-1} . The same (noncrystalline) adduct can be formed from acetone solution or diethyl ether suspension of $[\text{Rh}(\text{diars})_2]\text{Cl}$ upon exposure to CO₂.

The structure of the CO₂ adduct,⁵ as determined by single-crystal X-ray analysis, is shown in the figure. The precursor⁶ consists of a Rh(I) complexed to two diars ligands in a square-planar arrangement and is ionic with the Rh atoms well separated (>7.0 Å) from the chloride ions. On complexation with CO₂, there is little change in the Rh-As framework (the average Rh-As distance increases 0.020 (1) Å), and the resulting coordination about the Rh is essentially octahedral, with the η^1 -bonded CO₂ ligand trans to the chloride. The resulting geometry about the Rh-CO₂ fragment is similar to that typically found in rhodium acyl derivatives.^{7,8} In these compounds, the Rh-C distances range from 1.97 to 2.04 Å, the Rh-C-O angles range from 112° to 125°, and the C-O distances range from 1.18 to 1.21 Å. In the present η^1 -CO₂ complex, the Rh-C(1) distance is 2.05 (2) Å, the Rh-C-O

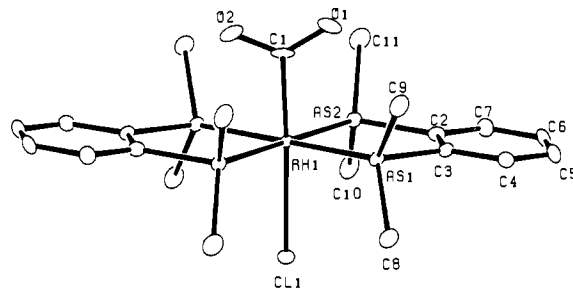
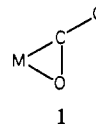


Figure 1. View of the $\text{RhAs}_4\text{C}_{20}\text{H}_{32}\text{Cl-CO}_2$ adduct shown with 25% thermal ellipsoids.

angles are each 116 (1)°, and the C-O distances are 1.20 (2) and 1.25 (2) Å. In addition, these values are like those observed in the recently reported cobalt-potassium CO₂ complex.⁹ Although in the latter the CO₂ is formally η^3 bound, the O-C-O angle of 132° is similar to the 126 (2)° observed here. It is interesting to observe that a structural determination of an η^2 niobium CO₂ complex shows essentially the same CO₂ geometry.¹⁰ In the present complex, the CO₂, Rh, and Cl atoms are planar within experimental error and perpendicular to the plane of the diars ligands. The O-C-O plane is rotated by 4° from an exact bisecting of the diars ligands in an orientation that minimizes the nonbonding repulsions with the methyl groups. This small rotation may be due to the intermolecular interaction of the oxygens with hydrogens on nearby phenyl groups. It is possible that these intra- and intermolecular C-H...O interactions influence the η^1 (rather than η^2) geometry observed here. The Rh-Cl distance, 2.635 (4) Å, is longer than the average Rh-Cl distance (2.4) of a series of related structures (range 2.2-2.6 Å),⁸ indicating a rather weak Rh-Cl bond here. In fact, the wide variation of these distances attests to the influence of steric and electronic factors on these values.¹¹ Also, a substantial trans influence of the CO₂ ligand on this bond is not unexpected.

The counteranion in $[\text{Rh}(\text{diars})_2]\text{Cl}$ may be replaced by other anions via metathesis. While the iodide forms a 1:1 CO₂ adduct, the tetraphenylborate does not. This is consistent with the observed covalent halide binding in $\text{Rh}(\text{CO}_2)(\text{Cl})(\text{diars})_2$. Of the remaining $[\text{ML}_4]\text{X}$ (M = Rh, Ir; L = PMe_3 , dmpe/2, depe/2, diars/2; X = Cl, I) complexes examined, all form 1:1 M-CO₂ adducts,¹² displaying the characteristic strong infrared bands at ~1600 (ν_{CO_2} , asym) and ~1200 (ν_{CO_2} , sym) cm^{-1} , indicating analogous η^1 M-CO₂ binding.

In contrast to these η^1 M-CO₂ adducts, the other structurally characterized CO₂ complexes each contain C- and O-bound CO₂. $\text{Ni}(\text{CO})_2(\text{PCy}_3)_2^{13}$ and $\text{Nb}(\text{C}_5\text{H}_4\text{Me})_2(\text{CH}_2\text{SiMe}_3)(\text{CO}_2)^{10}$ contain η^2 -CO₂ (1). Floriani's $\text{M}[\text{Co}(\text{salen})]$ complexes form 1:1 Co-CO₂



adducts with Co-C bonds and strong M...O interactions (M = alkali metal).⁹ A series of carbonyl clusters containing CO₂ with osmium atoms bonded to all three CO₂ atoms have been reported,¹⁴ as well as Beck et. al's recent μ_3 -CO₂ bridged $[(\text{CO})_5\text{Re}(\text{CO}_2)]$

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(5) $\text{RhAs}_4\text{ClO}_2\text{C}_{21}\text{H}_{32}$; $M_w = 754.528$; monoclinic; space group $P2_1/n$; $a = 8.935$ (3), $b = 9.304$ (3), $c = 15.648$ (5) Å; $\beta = 100.16$ (4)°; temp = -100 °C; $V = 1280.4$; $D_{\text{calc}} = 1.957$ g/cm³ for $Z = 2$; crystal flat hexagonal plate with faces $\pm [101, 0.029; 001, 0.117; 110, 0.122$ mm]; 2416 reflections corrected for Lp and absorption (Gaussian grid $8 \times 8 \times 8$); final $R = 0.039$, $R_w = 0.036$ for 215 independent variables. All hydrogen atoms were refined isotropically. The Rh atom lies on a crystallographic inversion center requiring a superposition of the chloride and CO₂ ligands. Further discussion of this disorder along with a contour map of the region is included in the supplementary material. An examination of the final difference map shows no large residuals in this area.

(6) $\text{RhAs}_4\text{C}_{20}\text{H}_{32}\text{Cl} \cdot 2\text{CH}_3\text{CN}$; $M_w = 792.625$; monoclinic; space group $P2_1/n$; $a = 17.988$ (3), $b = 6.395$ (1), $c = 14.004$ (2) Å; $\beta = 111.91$ (1)°; temp = -100 °C; $V = 1494.6$; $D_{\text{calc}} = 1.71$ g/cm³ for $Z = 2$; plate with faces $\pm [101, 0.10; 010, 0.15]; 100, 0.125; 102, 0.125; 2326$ reflections corrected for Lp and absorption (Gaussian grid $8 \times 8 \times 8$), final $R = 0.024$, $R_w = 0.033$ for 224 independent variables.

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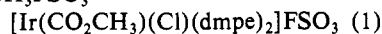
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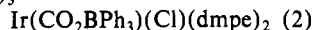
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$\text{Re}(\text{CO})_4]_2$.¹⁵ Unlike all these reports, this paper demonstrates that CO_2 can be bound η^1 to various rhodium and iridium complexes leaving the oxygens sterically and electronically accessible. This allows such chemistry as methyl cation addition (1)¹ (which $\text{Ir}(\text{CO})_2(\text{Cl})(\text{dmpe})_2 + \text{CH}_3\text{FSO}_3 \rightarrow$



does not occur in Floriani's system⁹) and Lewis acid binding (2)^{12c} $\text{Ir}(\text{CO})_2(\text{Cl})(\text{dmpe})_2 + \text{B}(\text{C}_6\text{H}_5)_3 \rightarrow$



to complexed CO_2 . The reaction between the iridium-carbon dioxide complex and methyl triflate (1)¹ is consistent with a CO_2 structure with nucleophilic oxygen atoms. Preliminary theoretical calculations on this structure also indicate that the CO_2 ligand has significant electronegative character¹⁶ at the oxygen atoms. All of these observations are consistent with the metalcarboxylate structure. This reaction chemistry is hopefully an important, novel addition to the "chemicals from CO_2 " quest.

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Registry No. $[\text{Rh}(\text{diars})_2]\text{Cl}$, 38337-86-9; $\text{Rh}(\text{diars})_2(\text{Cl})(\text{CO}_2)$, 83853-75-2; CO_2 , 124-38-9.

Supplementary Material Available: A listing of fractional coordinates, thermal parameters, and all bond lengths and angles (35 pages). Ordering information is given on any current masthead page.

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Effects of Electron Correlation on the Energies of 2-Norbornyl Cation Structures. Evaluation of the Nonclassical Stabilization Energy

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The solid-state ^{13}C NMR spectrum of the 2-norbornyl cation at 5 K provides the latest evidence for the symmetrically bridged, nonclassical structure.¹ The ESCA spectrum,² the ^{13}C and ^1H chemical shifts,³ and the perturbation isotope effects⁴ all suggest

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Table I. Energy Differences (kcal/mol)

theoretical levels	2-norbornyl cations, C_1 vs. C_8 forms ^a		
	STO-3G geom- etries	4-21P geom- etries	2-norbornyl vs. 2-propyl, eq 1 ^b
Hartree-Fock			
4-21P	+0.4	-0.2 ^c	-13.8
6-31G	-1.0	-0.8	-11.0
4-21P+5d		+0.6	-16.0
electron correlated			
MP2/4-21P	+7.9	+2.2	-23.0
MP2/6-31G	+7.5	+2.1	-20.2
MP2/4-21P+5d		+2.4	-24.8

^a Positive values indicate the symmetrically bridged (C_8) 2-norbornyl cation to be more stable than the partially bridged C_1 form.

^b In all cases, energies for the symmetrically bridged C_8 2-norbornyl cation were employed. ^c Identical with ref 13.

that the 2-norbornyl cation has a bridged structure in stable ion media.⁵

In the gas phase, experimental determinations by several groups⁶ have shown that the *secondary* 2-norbornyl cation is thermodynamically much more stable than all comparable secondary aliphatic acyclic and cyclic cations and rivals *tertiary* carbocations in this respect.^{7,8} This evidence, while indirect, supports the nonclassical structural assignment for the 2-norbornyl cation: the multicenter bonding associated with the bridged structure accounts for the energy lowering.

Quantitative theoretical methods provide independent means of determining both structures and energies. Earlier calculations on the 2-norbornyl cation,⁹⁻¹³ while notable, were not definitive since electron correlation corrections, known from studies of smaller carbocations to favor bridged structures,¹⁴ were not included explicitly. In this communication we report the results of our calculations including such correlation corrections.

Using previous 4-21P¹³ (and in some cases STO-3G¹²) optimized geometries, we have now performed single-point calculations including electron correlation corrections at the second-order Møller-Plesset (MP2) perturbation level¹⁵ using three different basis sets, viz., 4-21P¹³, 6-31G¹⁶, and the 4-21P basis augmented by a set of five d-type polarization functions on each carbon.¹⁷

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