

**Facile Conversion of
 $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][1\text{-Et-CB}_{11}\text{F}_{11}]$ into the
 Nonclassical Rhodium(I) Carbonyl
 $[\text{Rh}(\text{CO})_4][1\text{-Et-CB}_{11}\text{F}_{11}]$**

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Nonclassical metal carbonyls are most simply defined as those exhibiting $\nu(\text{CO})_{\text{ave}} > 2143 \text{ cm}^{-1}$.¹ Their recent study has led to new insights into $\text{M}-\text{C}\equiv\text{O}$ bonding^{1c,2} and to catalysts for organic transformations.³ Although few in number (ca. 250 are known as of this writing), they include metals from all regions of the periodic table.^{1,4} We report the isolation, vibrational spectra, and structures of crystalline $1\text{-Et-CB}_{11}\text{F}_{11}^-$ salts of the $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ and $\text{Rh}(\text{CO})_4^+$ cations and the facile conversion of $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ to $\text{Rh}(\text{CO})_4^+$ under a CO atmosphere. The lability of the π -arene ligand, noted previously for $(\eta^6\text{-C}_6\text{Me}_6)\text{Rh}(\text{CO})_2^+$ in the presence of donor solvents such as acetone,⁵ should allow $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ to become a valuable synthon for models of the important gem-dicarbonyl surface species $\text{Rh}^+(\text{CO})_2/\text{Al}_2\text{O}_3$.⁶ The $\text{Rh}(\text{CO})_4^+$ cation, with $\nu(\text{CO})_{\text{ave}} = 2167 \text{ cm}^{-1}$, is the first isolable nonclassical rhodium carbonyl complex. It was recently generated in a Ne/CO matrix, along with $\text{Rh}(\text{CO})^+$, $\text{Rh}(\text{CO})_2^+$, and $\text{Rh}(\text{CO})_3^+$, in an important study by Zhou and Andrews.⁷

In 1982, Valderrama and Oro reported that the reaction of $[\text{RhCl}(\text{CO})_2]_2$ with AgPF_6 in acetone containing hexamethylbenzene produced a mixture containing $(\eta^6\text{-C}_6\text{Me}_6)\text{Rh}(\text{CO})_2^+$ and $\text{Rh}(\text{CO})_2(\text{acetone})_2^+$.⁵ The crystalline solid $[(\eta^6\text{-C}_6\text{Me}_6)\text{Rh}(\text{CO})_2][\text{PF}_6]$ was obtained, but its structure has not been reported. We now report that treatment of $[\text{RhCl}(\text{CO})_2]_2$ with $\text{Ag}(\text{C}_6\text{H}_6)(\text{Y})^8$ ($\text{Y}^- = 1\text{-Et-CB}_{11}\text{F}_{11}^-$) in dichloromethane under a nitrogen atmosphere resulted in the precipitation of AgCl and the formation

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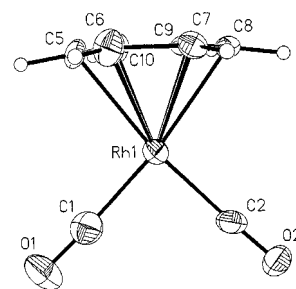
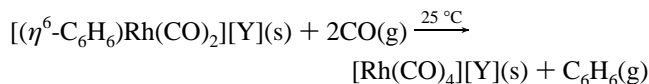


Figure 1. The structure of one of the two nearly identical $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ cations in $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][1\text{-Et-CB}_{11}\text{F}_{11}]$ (50% ellipsoids except for hydrogen atoms (arbitrary size)). Selected interatomic distances (Å) and angles (deg): $\text{Rh1}-\text{C1}$, 1.874(9); $\text{Rh1}-\text{C2}$, 1.895(9); $\text{C1}-\text{Rh}-\text{C2}$, 89.3(4); $\text{C1}-\text{O1}$, 1.134(9); $\text{C2}-\text{O2}$, 1.116(9); $\text{Rh1}-\text{C}-\text{O}$, 177.8(8) and 177.9(7); $\text{Rh1}-\text{C5}$, 2.270(7); $\text{Rh1}-\text{C6}$, 2.364(8); $\text{Rh1}-\text{C7}$, 2.343(7); $\text{Rh1}-\text{C8}$, 2.263(7); $\text{Rh1}-\text{C9}$, 2.337(7); $\text{Rh1}-\text{C10}$, 2.335(7).

of a yellow-orange solution,⁹ which upon cooling to $-18 \text{ }^\circ\text{C}$ yielded crystals of $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][\text{Y}]$ suitable for diffraction. The structure of one of the two virtually identical $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ cations present in the asymmetric unit is shown in Figure 1.¹⁰ The $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ cations have idealized C_{2v} symmetry. The structure of the Y^- anion is normal.¹¹ There are no $\text{Rh}\cdots\text{F}$ contacts shorter than 3.6 \AA and no $\text{C}\cdots\text{F}$ or $\text{O}\cdots\text{F}$ contacts shorter than 2.9 \AA . The two equal-intensity $\nu(\text{CO})$ bands observed at $2115 (\text{A}_1)$ and $2065 (\text{B}_2) \text{ cm}^{-1}$ for $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][\text{Y}]$ are consistent with the $\sim 90^\circ \text{ C}-\text{Rh}-\text{C}$ angle for the two $\text{Rh}(\text{CO})_2$ moieties.

Whether $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ or $(\eta^6\text{-C}_6\text{Me}_6)\text{Rh}(\text{CO})_2^+$ undergo photoassisted loss of CO and subsequent alkane activation, similar to $\text{Rh}^+(\text{CO})_2/\text{Al}_2\text{O}_3$, $\text{CpRh}(\text{CO})_2$, and $\text{Cp}^*\text{Rh}(\text{CO})_2$,^{6,12} remains to be seen. Unlike $\text{Rh}^+(\text{CO})_2/\text{Al}_2\text{O}_3$, $\text{CpRh}(\text{CO})_2$, and $\text{Cp}^*\text{Rh}(\text{CO})_2$, $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][\text{Y}]$ reacted with 1 atm of CO in the solid state, resulting in the loss of the η^6 -benzene ligand and the formation of $[\text{Rh}(\text{CO})_4][\text{Y}]$, containing the $\text{Rh}(\text{CO})_4^+$ cation, according to the following equation:



This unexpected reaction was monitored by attenuated total reflectance (ATR) FTIR spectroscopy. When a thin film of $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][\text{Y}]$ was deposited by evaporation from a dichloromethane solution on the silicon crystal of an ASI SiComp ATR-FTIR probe and treated with 1 atm of CO, the bands at 2115 , 2065 , and 3108 cm^{-1} disappeared and were replaced by a single band at 2138 cm^{-1} . The 3108 cm^{-1} band is assigned to one or more $\nu(\text{CH})$ normal modes of the η^6 -benzene ligand; the 2138 cm^{-1} band is the $\text{E}_u \nu(\text{CO})$ band of $\text{Rh}(\text{CO})_4^+$ (see below). The reaction proceeded over several hours at 1 atm of CO; it was considerably faster at elevated pressure.

The crystalline compound $[\text{Rh}(\text{CO})_4][\text{Y}]$ was independently prepared by treating $[\text{RhCl}(\text{CO})_2]_2$ with benzene-free AgY^8 in

(9) See Supporting Information for additional details.

(10) $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][1\text{-Et-CB}_{11}\text{F}_{11}]$: monoclinic, $P2_1/c$, $a = 25.1687(5) \text{ \AA}$, $b = 10.5913(1) \text{ \AA}$, $c = 16.1831(3) \text{ \AA}$, $\beta = 102.621(1)^\circ$, $V = 4209.7(1) \text{ \AA}^3$, $Z = 8$. Data were collected at $-102(2)^\circ\text{C}$ on a Siemens SMART System with Mo K α radiation to $2\theta_{\text{max}} = 56.54^\circ$, giving 9921 unique reflections; the structure was solved by direct methods (Sheldrick, G. M. SHELXTL, v. 5.03, 1994) with full-matrix least-squares refinement on F^2 , yielding $R_1 = 0.068$ ($I > 2\sigma(I)$), $wR_2 = 0.150$ (all data).

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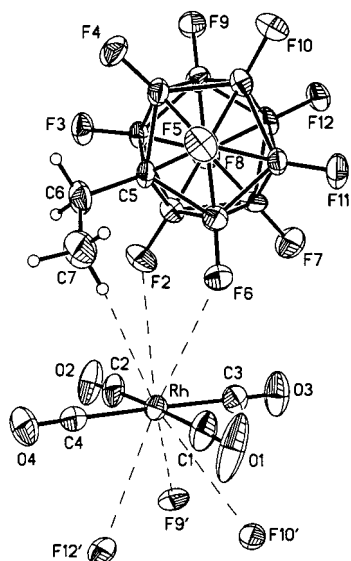


Figure 2. Structure of $[\text{Rh}(\text{CO})_4][1\text{-Et-CB}_{11}\text{F}_{11}]$, showing one $\text{Rh}(\text{CO})_4^+$ cation and the two carborane anions that weakly interact with it (50% ellipsoids except for hydrogen atoms (arbitrary size)). Selected interatomic distances (\AA) and angles (deg): Rh–C1, 1.947(6); Rh–C2, 1.949(6); Rh–C3, 1.958(6); Rh–C4, 1.951(6); C–Rh–C, 88.8(2)–90.9(2), 177.3(3), and 178.9(2); C–O, 1.109(7)–1.124(7); Rh–C–O, 177.3(5)–178.8(5); Rh \cdots H7C, 3.21; Rh \cdots F2, 3.588(9); Rh \cdots F6, 3.234(9); Rh \cdots F9', 3.420(9); Rh \cdots F10', 3.399(9); Rh \cdots F12', 3.220(9).

dichloromethane under a nitrogen atmosphere, removing AgCl by filtration, and treating the yellow-orange filtrate with 1 atm of CO .⁹ The structure of this salt is shown in Figure 2.¹³ The $\text{Rh}(\text{CO})_4^+$ cation has idealized D_{4h} symmetry. The structure of the Y^- anion is normal.¹¹ There are no Rh \cdots F contacts shorter than 3.2 \AA and no C \cdots F or O \cdots F contacts shorter than 2.8 \AA . Interestingly, there appears to be a Rh \cdots H(C) contact of 3.21 \AA with one of the hydrogen atoms of the carborane methyl group; the possible significance of this with respect to C–H activation is under further investigation. The four Rh–CO distances range from 1.946(6) to 1.958(6) \AA , significantly longer than the distances in $(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2^+$ and more than 0.1 \AA longer than typical $\text{Rh}^{\text{I}}\text{--CO}$ distances.¹⁴ A similar lengthening was observed for the tetrahedral $\text{Cu}(\text{CO})_4^+$ cation.¹⁰ In that case, the Cu–CO distances ranged from 1.961(3) to 1.968(3) \AA , much longer than typical $\text{Cu}^{\text{I}}\text{--CO}$ distances of 1.78–1.85 \AA . Long M–CO bonds, greatly attenuated M–CO π back-bonding, and unusually high $\nu(\text{CO})$ values are the hallmarks of nonclassical metal carbonyls,^{14,15} many (but not all) of which are homoleptic noble-metal carbonyl cations such as $\text{Cu}(\text{CO})_4^+$,¹¹ $\text{Ag}(\text{CO})_2^+$,^{15c} $\text{Au}(\text{CO})_2^+$,^{15a,b}

(13) $[\text{Rh}(\text{CO})_4][1\text{-Et-CB}_{11}\text{F}_{11}]$: monoclinic, $P2_1/c$, $a = 10.634(3)$ \AA , $b = 8.853(3)$ \AA , $c = 20.918(7)$ \AA , $\beta = 94.03(2)^\circ$, $V = 1964(1)$ \AA^3 , $Z = 4$. Data were collected at $-102(2)$ $^\circ\text{C}$ on a Siemens SMART System with Mo $K\alpha$ radiation to $2\theta_{\text{max}} = 56.80^\circ$, giving 4769 unique reflections; the structure was solved by direct methods (Sheldrick, G. M. SHELXTL, v. 5.03, 1994) with full-matrix least-squares refinement on F^2 , yielding $R_1 = 0.055$ ($I > 3\sigma(I)$), $wR_2 = 0.147$ (all data).

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$\text{Pd}(\text{CO})_4^{2+}$,^{15d} and $\text{Fe}(\text{CO})_6^{2+}$.^{15e} Despite the lack of significant π back-bonding, the M–CO bonds in these species are relatively strong because of the very polar σ bonds with a significant electrostatic contribution.^{1,2,4}

The Raman (R) and IR spectra of $[\text{Rh}(\text{CO})_4][\text{Y}]$ exhibited $\nu(\text{CO})$ bands at 2215 (R), 2176 (R), and 2138 cm^{-1} (IR). These bands are assigned to the A_{1g} , B_{2g} , and E_u C–O stretching normal modes of the square-planar $\text{Rh}(\text{CO})_4^+$ cation; they can be compared with the corresponding bands for the isoelectronic $\text{Pd}(\text{CO})_4^{2+}$ dication,^{15d} which are 2279 (R), 2263 (R), and 2248 cm^{-1} (IR). The difference in $\nu(\text{CO})_{\text{ave}}$ values for these two species, 66 cm^{-1} , is larger than the 44 cm^{-1} difference for $\text{Au}(\text{CO})_2^+/\text{Hg}(\text{CO})_2^{2+}$ ^{14a,16} but is considerably smaller than the 95 and 144 cm^{-1} differences for $\text{Re}(\text{CO})_6^+/\text{Os}(\text{CO})_6^{2+}$ ¹⁷ and $\text{Ni}(\text{CO})_4/\text{Cu}(\text{CO})_4^+$,¹¹ respectively. The IR band at 2138 cm^{-1} for d^8 $\text{Rh}(\text{CO})_4^+$ can also be compared with the IR bands for d^9 $\text{Rh}(\text{CO})_4^+$, 2019 and/or 2010 cm^{-1} ,^{7,18} and d^{10} $\text{Rh}(\text{CO})_4^-$, 1900–1906 cm^{-1} .^{7,19}

Zhou and Andrews recently reported the IR $\nu(\text{CO})$ bands for $\text{Rh}(\text{CO})_n^+$ cations in solid Ne at ca. 4 K ($n = 1\text{--}4$):⁷ $\text{Rh}(\text{CO})^+$, 2174 cm^{-1} ; $\text{Rh}(\text{CO})_2^+$, 2185 cm^{-1} ; $\text{Rh}(\text{CO})_3^+$, 2168 cm^{-1} ; $\text{Rh}(\text{CO})_4^+$, 2162 cm^{-1} . The difference between their E_u $\nu(\text{CO})$ value for $\text{Rh}(\text{CO})_4^+$, 2162 cm^{-1} , and our value, 2138 cm^{-1} , might be due to the weak Rh \cdots F and/or Rh \cdots H interactions present in solid $[\text{Rh}(\text{CO})_4][\text{Y}]$. The trend in IR $\nu(\text{CO})$ values for these d^8 cations is the opposite of the trend observed for the series of d^{10} cations $\text{Cu}(\text{CO})^+$ (2178 cm^{-1}),²⁰ $\text{Cu}(\text{CO})_2^+$ (2164 cm^{-1}),²⁰ $\text{Cu}(\text{CO})_3^+$ (2179 cm^{-1}),²⁰ and $\text{Cu}(\text{CO})_4^+$ (2183 cm^{-1})¹¹ despite the fact that all of these $\nu(\text{CO})$ values are 2160 ± 23 cm^{-1} . This trend reversal will no doubt be studied by theorists who are interested in nonclassical metal carbonyls.

Finally, the isolation of the $\text{Rh}(\text{CO})_4^+$ cation, which was only possible because of the low basicity of the superweak anion $1\text{-Et-CB}_{11}\text{F}_{11}^-$,²¹ will allow us to test the 1984 prediction of Saillard and Hoffmann that $\text{Rh}(\text{CO})_4^+$ will bind H_2 to form a $\text{Rh}(\text{CO})_4\text{-(H}_2)^+$ complex with C_{2v} symmetry.²² This and other experiments with the compounds $[(\eta^6\text{-arene})\text{Rh}(\text{CO})_2][\text{Y}]$ and $[\text{Rh}(\text{CO})_4][\text{Y}]$ and their cobalt and iridium homologues are in progress.

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Note Added in Proof: After this paper was submitted, we became aware of two reports of the generation of $\text{Rh}(\text{CO})_4^+$ in neat HSO_3F : Souma, Y.; Xu, Q. personal communication; Bach, C. Ph.D. Thesis, University of Hannover, 1999.

Supporting Information Available: Synthetic details, Figure S-1, showing the IR spectrum and two views of the structure of $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][1\text{-Et-CB}_{11}\text{F}_{11}]$, and Tables S-1 to S-10, listing crystallographic parameters and results for $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{CO})_2][1\text{-Et-CB}_{11}\text{F}_{11}]$ and $[\text{Rh}(\text{CO})_4][1\text{-Et-CB}_{11}\text{F}_{11}]$ (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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