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Synthesis, Characterization, and Reactivity of the Meridional Isomers of Triphenylmethylphosphonium Triiodotricarbonylruthenate(II) and Triphenylmethylphosphonium Hexaiodotetracarbonyldiruthenate(II)

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The synthesis, characterization, and reactivity of the triphenylmethylphosphonium salts of several anionic ruthenium iodo carbonyl complexes are described. These complexes included the facial and meridional isomers of $[Ru(CO)_3I_3]^-$, and the dimeric dianion $[Ru_2(CO)_4I_6]^{2-}$. The two $[Ru(CO)_3I_3]^-$ isomers were characterized by their infrared spectra and by the ^{13}C NMR spectra of ^{13}CO-enriched samples of these compounds. The dimeric dianion $[Ru_2(CO)_4I_6]^{2-}$, which was generated by heating the facial isomer under Ar, was characterized by X-ray crystallography and was found to have S_2 symmetry. $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ crystallizes in the triclinic space group $P\bar{1}$-C_i^1 (No. 2) with $a = 9.794$ (4) Å, $b = 11.158$ (4) Å, $c = 11.710$ (5) Å, $\alpha = 85.01$ (3)°, $\beta = 93.70$ (3)°, $\gamma = 93.70$ (3)°, and $Z = 1$. Least-squares refinement led to a value for the conventional R index (on F) of 0.045 for 4810 independent absorption-corrected reflections having $2\theta(\text{Mo K}\alpha) < 55°$ and $I > 3\sigma(I)$. The meridional isomer of $[Ru(CO)_3I_3]^-$ was generated by adding carbon monoxide to the dimeric dianion $[Ru_2(CO)_4I_6]^{2-}$ at atmospheric pressure. The meridional isomer of $[Ru(CO)_3I_3]^-$ could be used to regenerate the dimeric dianion $[Ru_2(CO)_4I_6]^{2-}$ by heating the complex under Ar in the presence of excess iodide, or it could be used to regenerate the facial isomer by heating the complex under a carbon monoxide atmosphere.

The literature contains several reports on the chemistry of the halo carbonyl complexes of ruthenium.[1-5] Among these reports are studies regarding the anionic ruthenium halo carbonyl complexes, which include the reported synthesis of $CsRu(CO)_3I_3$ and $Cs_2Ru(CO)_2I_4$ salts.[3-5] Although the stereochemistry of these complexes was not discussed, the structure of the $CsRu(CO)_3I_3$ salt was assumed to be the facial isomer.[6a] Since the earlier descriptions of these complexes, the facial isomer of $[Ru(CO)_3I_3]^-$ has been observed in several ruthenium-catalyzed reactions that utilize synthesis gas and iodine compounds.[6-8] To date, these two anions are the only completely documented anionic ruthenium iodo carbonyl complexes.[9]

In this investigation, two previously undocumented anionic ruthenium iodo carbonyl complexes have been isolated and characterized. The facial isomer of $[Ru(CO)_3I_3]^-$ can be decarbonylated to form a dimeric hexaiodotetracarbonyldiruthenium complex, whose structure was ultimately resolved by X-ray crystallography. Subsequent carbonylation of this complex yields the meridional isomer of $[Ru(CO)_3I_3]^-$.[9] The synthesis and spectroscopic characterization of these complexes are described in this paper. Some chemical transformation of the meridional isomer will also be discussed.

Experimental Section

Infrared measurements were obtained by using a Perkin-Elmer 283B infrared spectrometer with an attached data station. ^{13}C NMR spectra were obtained by using a Bruker FT-NMR spectrometer. Conductivity measurements were obtained by using a Radiometer conductivity meter, Model COM83. The 90% carbon-13-enriched carbon monoxide was obtained from Mound Facility, Monsanto Research Corp., Miamisburg, OH.

Synthesis of $[Ru(CO)_3I_2]_2$. $[Ru(CO)_3I_2]_2$ was synthesized via a modification of a published procedure.[3-5] To a solution of 1.501 g (2.35 mmol) of $Ru_3(CO)_{12}$ in 2.7 L of toluene at room temperature was added 2.04 g (8.03 mmol) of iodine. The mixture was stirred overnight in an open vessel in a hood. The solvent was decanted from the solid residue, and then the residue was dissolved in 1.50 L of methylene chloride. The solution was filtered and then reduced in volume to about 400 mL on a rotary evaporator. Hexane (about 400 mL) was added to the remaining solution and the solvent mixture was slowly removed on a rotary evaporator. An orange powder formed (1.45 g). Repeating the solution–precipitation procedure on the remaining solids yielded another 0.83 g for a total of 2.28 g (74% yield) of $[Ru(CO)_3I_2]_2$.

Synthesis of $[Ph_3PMe][\textit{fac}\text{-}Ru(CO)_3I_3]$ from $[Ru(CO)_3I_2]_2$. To a magnetically stirred slurry of 1.876 g (2.14 mmol) of $[Ru(CO)_3I_2]_2$ in 75 mL of methanol was added 1.91 g (4.73 mmol) of solid $[Ph_3PMe]I$. Within 0.5 h at room temperature, the mixture became a red solution. Infrared analysis showed observable bands at 2097 (s) and 2027 (s) cm^{-1}. The solution was reduced in volume to about 30 mL and chilled overnight in a refrigerator (5–10 °C). The crude crystals were filtered and recrystallized from methanol to give 2.512 g (70%) of dark orange crystals. Anal. Calcd for $C_{22}H_{18}O_3RuI_3P$: C, 31.34; H, 2.15; Ru, 12.0; I, 45.15. Found: C, 31.12; H, 2.07; Ru, 12.4; I, 45.38. IR (KBr): 2102 (s), 2034 (s) cm^{-1}. IR (MeOH or THF): 2097 (s), 2027 (s) cm^{-1}. Molar conductivity (2 mM in CH_3NO): 72 $\Omega^{-1}\ cm^2\ mol^{-1}$.

Synthesis of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ from $[Ru(CO)_3I_2]_2$. To a 250-mL single-necked, round-bottom flask were added 1.997 g (2.28 mmol) of solid $[Ru(CO)_3I_2]_2$, 35.63 g (88.1 mmol) of solid $[Ph_3PMe]I$, and 125 mL of methanol. The mixture was stirred until it became completely homogeneous. (An infrared spectrum at this point showed bands of 2097 (s) and 2027 (s) cm^{-1}, corresponding to the formation of *fac*-$[Ru(CO)_3I_3]^-$.)

The mixture was heated at reflux for 5 days while being purged with argon. Methanol was added as needed to maintain the solvent level. Throughout this period, the reaction was monitored by infrared analysis. The peaks at 2097 and 2027 cm^{-1} were gradually replaced by peaks at 2033 (s), 1970 (s, br), and 1996 (s) cm^{-1}.[10]

The compound was isolated by removing the solvent in vacuo and adding dry tetrahydrofuran (THF, about 150 mL) to the residue. A yellowish precipitate, primarily composed of $[Ph_3PMe]I$, formed quickly. The THF solution containing the product was decanted, and the solid residue was slurried and filtered three times with THF (about 100 mL) to remove any remaining soluble complex. The THF solutions were combined, and the solvent was removed in vacuo to yield a gummy red-orange residue, which was dissolved in about 50 mL of methanol and cooled in a refrigerator (5–10 °C). Over several days, three crops of crystals totaling 2.396 g (65% yield) were obtained from the same solution. Anal. Calcd for $C_{42}H_{36}O_4Ru_2I_6P_2$: C, 30.94; H, 2.23; Ru, 12.4. Found: C, 30.98; H, 2.18; Ru, 12.5. IR (MeOH or THF): 2033 (s),

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(9) The bis(triphenylphosphine)nitrogen(1+) salt of *mer*-$Ru(CO)_3I_3^-$ appears as an entry in a table reporting ^{99}Ru nuclear magnetic resonance shifts. The compound, which is reported to have been synthesized by B. D. Dombek, is presented without any reference to synthetic methodology and without any characterization. See: Dykstra, R. W.; Harrison, A. M. *J. Magn. Reson.* **1982**, *46*, 338.

(10) The intensity of the peak at 1996 cm^{-1}, which is due to an impurity, is inversely dependent on the amount of $[Ph_3PMe]I$. The high level of iodide salt used in this synthesis is intended to minimize the amount of this impurity.

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Table I. Crystallographic Parameters for $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$

space group	$P\bar{1}-C_i^1$
a, Å	9.794 (4)
b, Å	11.158 (4)
c, Å	11.710 (5)
α, deg	85.01 (3)
β, deg	103.35 (3)
γ, deg	93.70 (3)
V, Å^3	1239.0 (9)
d_{calcd}, g/cm^3	2.185
Z	1
fw	1630.3
cryst size, mm	0.12 × 0.62 × 0.72
μ(Mo $K\alpha$), cm^{-1}	44.0
radiation; rel transmission factors	Mo $K\bar{\alpha}$, λ = 0.71073 Å; 0.206–1.000
diffractometer	Nicolet
monochromator	graphite
method	ω scan
scan range, deg	1.00
data collecn range (2θ), deg speed; deg/min	3.0–43.0; 8.0 43.0–55.0, 4.0
bkgd time	0.5 of net scan time
stds	6 every 300 reflecns
2θ limits	3.0–55.0
no. of unique data	5695
no. of data with $\lvert F_o^2\rvert > 3\sigma\lvert F_o^2\rvert$	4810
$R_1{}^a$	0.045
$R_2{}^a$	0.054
no. of variables	257
largest shift/error, σ_p	0.01
goodness of fit	3.05
temp, °C	20 ± 1

[a] See ref 11.

1969 (s) cm^{-1}. IR (KBr): 2041 (s), 1961 (s) cm^{-1}. IR (CH_3NO_2): 2045 (s); 1981 (s). Far-IR (solid): 213 (vs), 198 (m), 177 (m), 158 (m), 132 (m) cm^{-1}. Raman solid, 100–900 cm^{-1}): 109 (m), 132 (vs), 151 (m), 174 (s) cm^{-1}. FABMS: clusters of peaks with the largest peak in each cluster at m/e 539 ($Ru(CO)_2I_3$), 511 ($Ru(CO)I_3$), 482 (RuI_3), 413 ($Ru(CO)_2I_2$) 384 ($Ru(CO)I_2$), 357 (RuI_2), 285 ($Ru(CO)_2I$), 259 (Ru(CO)I), 127 (I). Molar conductivity (2 mM in CH_3NO_2): 71 Ω^{-1} cm^2 mol^{-1}.

X-ray Crystallographic Structure Determination of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$. Crystals of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ that were acceptable for X-ray analysis were obtained by recrystallization of the complex from nitromethane. The X-ray analysis was performed by Crystalytics Co., Lincoln, NE.

Crystal data and data collection parameters are given in Table I. X-ray diffraction intensity data (5695 independent reflections having 2θ(Mo $K\bar{\alpha}$) < 55° (the equivalent of 1.0 limiting Cu $K\bar{\alpha}$ spheres)) were collected on a computer-controlled four-circle Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo $K\bar{\alpha}$ radiation and full (1.00° wide) π scans. The intensity data were corrected empirically for absorption effects with use of Ψ scans for seven intense reflections having 2θ between 12.8 and 41.2° (the relative transmission factors ranged from 0.206 to 1.000).

The Ru and three I atoms were located with use of "direct methods" techniques (SHELXTL). Counting-statistics-weighted isotropic full-matrix least-squares refinement of the structural parameters for the Ru and I atoms converged to R_1(unweighted, based on F)[11] = 0.228 and R_2(weighted, based on F)[11] = 0.315 for 2561 independent absorption-corrected reflections having 2θ(Mo $K\bar{\alpha}$) < 43° and $I > 3\sigma(I)$. Positions for the remaining 24 non-hydrogen atoms of the asymmetric unit appeared in a difference Fourier synthesis calculated at this point. Cycles of counting-statistics-weighted cascade block-diagonal least-squares refinement that utilized anisotropic thermal parameters for all non-hydrogen atoms gave R_1 = 0.046 and R_2 = 0.059 for 2561 independent reflections. Positions for the phenyl ring hydrogen atoms of the $[Ph_3PMe]^+$ cation were calculated at this point (assuming sp^2 hydridization of the carbon atoms and a C–H bond length of 0.96 Å) and fixed in subsequent least-squares cycles. The methyl group of the cation was refined as a rigid rotor with sp^3-hydridized geometry and a C–H bond length of 0.96 Å. Each hydrogen atom was included in the final structure factor calculations with an isotropic thermal parameter fixed at 1.2 times the value of the equivalent isotropic thermal parameter for the carbon atom to which it is covalently bonded.

The final[12] cycles of cascade block-diagonal least-squares refinement, which utilized anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for all hydrogen atoms, gave R_1 = 0.045 and R_2 = 0.054 for 4810 absorption-corrected reflections having 2θ(Mo $K\bar{\alpha}$) < 55° and $I > 3\sigma(I)$.

All structure factor calculations employed recent tabulations of atomic form factors,[13a] anomalous dispersion corrections[13b] to the scattering factors of the Ru, I, and P atoms, and a least-squares refinable extinction correction.[14] These calculations were performed on a Data General Eclipse S-200 or S-230 computer equipped with 128K of 16-bit words, a floating point processor for 32- and 64-bit arithmetic, and versions of the EXTL and SHELXTL interactive crystallographic software package as modified at Crystalytics Co.

Synthesis of $[Ph_3PMe]$[*mer*-$Ru(CO)_3I_3$]: Carbonylation of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$. To a 25-mL round-bottom flask were added 202 mg (0.248 mmol) of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ and 20 mL of THF. For 3.5 h carbon monoxide was bubbled through the magnetically stirred solution. Over the course of the reaction, the original heterogeneous mixture is converted to an orange solution whose infrared spectrum contains bands at 2112 (w), 2041 (vs), 2012 (s), and 1984 (w) cm^{-1}.

The product was isolated and purified by removing the THF in vacuo and dissolving the residue in methanol. Crystallization from methanol yielded 96.2 mg (46%) of pure $[Ph_3PMe]$[*mer*-$Ru(CO)_3I_3$]. Further attempts at crystallization only led to the isolation of a red oil. Anal. Calcd for $C_{22}H_{18}O_3RuI_3P$: C, 31.34; H, 2.15; Ru, 12.0; I, 45.15. Found: C, 31.33; H, 2.17; Ru, 12.1; I, 44.79. IR (MeOH or THF): 2112 (w), 2041 (vs), 2012 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.45–8.05 (m, 5 H), 3.13 (d, J = 13 Hz).

Synthesis and ^{13}C NMR Spectrum of ^{13}CO-Enriched $[Ru(CO)_3I_2]_2$. To a 3-oz Fischer–Porter bottle equipped with a stir bar and containing 1.018 g (1.16 mmol) of $[Ru(CO)_3I_2]_2$ was added 65 mL of THF. The Fischer–Porter bottle was closed and pressurized to 80 psi with 90% ^{13}C-enriched CO. The solution was stirred for 28 h and then depressurized. The solution was then stirred for 30 h under a slow purge of argon to completely decarbonylate any $Ru(CO)_4I_2$ present in the reaction mixture. The solvent was removed in vacuo, and a ^{13}C NMR spectrum in CD_2Cl_2 (with Cr(acac)$_3$ added) was recorded. ^{13}C NMR: δ 195.0, 184.1, 181.8, 177.8, 177.0.[15]

Synthesis and ^{13}C NMR Spectrum of ^{13}CO-Enriched $[Ph_3PMe]$[*fac*-$Ru(CO)_3I_3$]. To a mixture of 310 mg (0.35 mmol) of ^{13}CO-enriched $[Ru(CO)_3I_2]_2$ and 4.4 mL of methanol was added 315 mg (0.77 mmol) of $[Ph_3PMe]I$. The mixture was stirred for 2.5 h at room temperature and then placed in a refrigerator (5–10 °C). After 3 days, yellow crystals had formed. These crystals were isolated and dissolved in CD_2Cl_2. After addition of a small amount of Cr(acac)$_3$, a ^{13}C NMR spectrum was recorded. ^{13}C NMR: δ 187.3 (s).

Synthesis and ^{13}C NMR Spectrum of ^{13}CO-Enriched $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$. To a solution of 5.11 g (12.65 mmol) of $[Ph_3PMe]I$ in 26 mL of methanol was added 0.59 g of ^{13}CO-enriched $[Ru(CO)_3I_2]_2$. The solution was heated at reflux for 5.5 days under an argon purge. Methanol was added to maintain volume.

After the reaction was complete, the solution was reduced in volume to about 10 mL. The solution was quickly added to 500 mL of THF in one portion. Precipitated $[Ph_3PMe]I$ was removed by filtration, and the filtrate was reduced in vacuo to a volume of about 200–250 mL. The solution was refiltered to remove more $[Ph_3PMe]I$. Then the filtrate was evaporated to dryness and about 10 mL of methanol was added. The mixture was warmed gently and then cooled to give dark red crystals. The crystals were washed with 2 mL of CD_2Cl_2. Although the compound was not very soluble in CD_2Cl_2, a solution of sufficient concentration to obtain a ^{13}C NMR spectrum was obtained by stirring the crystals in 4 mL of CD_2Cl_2 for 1 h. The ^{13}C NMR spectrum was recorded in the presence of a small quantity of Cr(acac)$_3$ and displayed a single peak at δ 197.8.

Synthesis and ^{13}C NMR Spectrum of ^{13}CO-Enriched $[Ph_3PMe]$[*mer*-$Ru(CO)_3I_3$]. To a 3-oz Fischer–Porter bottle were added 370 mg (0.421

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(11) The R values are defined as $R_1 = \sum\lVert F_0\rvert - \lvert F_c\rVert/\sum\lvert F_0\rvert$ and $R_2 = [\sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_0\rvert^2]^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(\lvert F_0\rvert - K\lvert F_c\rvert)^2$, where K is the scale factor. The weighing scheme uses $w = 1/\sigma_F{}^2$; for weights derived from counting statistics, $\sigma_F = \{[\sigma(F_0)]^2 + (0.01\lvert F_3\rvert)_2\}^{-1/2}$.

(12) See paragraph at the end of the paper regarding supplementary material.

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

(14) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(15) $[Ru(CO)_3I_2]_2$ has been reported to exist as two isomers, which accounts for the complex ^{13}C NMR spectrum. See ref 1.

mmol) of ^{13}CO-enriched $[Ph_0PMe]_2[Ru_2(CO)_4I_6]$ and 30 mL of THF. A stir bar was added to the Fischer–Porter bottle, and the bottle was then closed. The Fischer–Porter bottle was pressurized to 80 psi with 90% ^{13}CO-enriched CO. The initially heterogeneous mixture turned homogeneous in about 15–20 min. The mixture was stirred for 2–5 h, and then the bottle was vented.[16] The THF was removed in vacuo and the residue dissolved in CD_2Cl_2. The ^{13}C NMR spectrum showed two signals, a triplet with relative signal intensities of 1:1:1 centered at δ 187.5 and a quintet with relative signal intensities of 2:4:5:4:2 centered at δ 191.4. The relative intensity for the two sets of peaks was about 2:1, respectively (J_{C-C} = 5 Hz).

Conversion of *mer*-$[Ru(CO)_3I_3]^-$ to *fac*-$[Ru(CO)_3I_3]^-$. To a 3-oz Fischer–Porter bottle containing a stir bar and 103 mg (0.126 mmol) of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ was added 10 mL of THF. The bottle was sealed and pressurized to 80 psi with CO. The mixture was stirred for 3 h, and the CO was vented. An infrared spectrum of the mixture displayed bands at 2112 (w), 2041 (vs), and 2012 (s) cm^{-1}, characteristic of *mer*-$[Ru(CO)_3I_3]^-$.

The Fischer–Porter bottle was repressurized to 30 psi with CO and heated for 16 h at 80 °C. The bottle was cooled and the pressure vented. The infrared spectrum of the resultant solution displayed only two strong bands. These bands, at 2098 and 2027 cm^{-1}, indicate a quantitative conversion to *fac*-$[Ru(CO)_3I_3]^-$.

Decarbonylation of *mer*-$[Ru(CO)_3I_3]^-$ to $[Ru_2(CO)_4I_6]^{2-}$. Carbon monoxide was bubbled for 20 min through a mixture of 80 mg (0.098 mmol) of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ in 8 mL of THF. Infrared examination of the solution displayed bands at 2112 (w), 2041 (vs), 2012 (s), and 1984 (w) cm^{-1}, indicative of the meridional isomer of $[Ru(CO)_3I_3]^-$. (The peak at 1984 cm^{-1} represents an impurity that usually is removed during purification.) To this solution was added 55 mg of anhydrous LiI (0.387 mmol). The solution was heated at reflux for 1.5 h. After the solution cooled, an infrared spectrum was recorded. Very strong bands was observed at 2033 and 1971 cm^{-1}, characteristic of the dimeric ruthenium complex $[Ru_2(CO)_4I_6]^{2-}$. A weak peak at 2097 cm^{-1} was also observed, which indicates that some of the *mer*-$[Ru(CO)_3I_3]^-$ isomerized to *fac*-$[Ru(CO)_3I_3]^-$.

Results and Discussion

The facial isomer of the triphenylmethylphosphonium salt of triiodotricarbonylruthenate(II) was readily obtained by adding 1.1 equiv of $[Ph_3PMe]I$ to $[Ru(CO)_3I_2]_2$ in methanol at room temperature. The product, $[Ph_3PMe][Ru(CO)_3I_3]$, was isolated as analytically pure yellow-orange crystals in 70% yield. The infrared bands at 2097 (s) and 2026 (s) cm^{-1} and the presence of a single peak in the ^{13}C NMR spectrum of a ^{13}CO-enriched sample (vide infra) indicated that this complex was the facial isomer. Although the earlier structural assignment was based solely on infrared data, this complex has been reported previously in the iodine-promoted homologation of organic oxygenates with synthesis gas using ruthenium catalysts[6-8] and was correctly identified as the facial isomer.[6a]

When a methanolic solution of $[Ph_3PMe]$[*fac*-$Ru(CO)_3I_3$] and 25 equiv of $[Ph_3PMe]I$[10] were heated at reflux for 5 days under an argon purge (to remove CO), the infrared bands attributable to *fac*-$[Ru(CO)_3I_3]^-$ gradually disappeared and were replaced by infrared bands of about equal intensity at 2033 (s) and 1969 (s, br) cm^{-1}. These experimental conditions were expected to yield $[Ph_3PMe]_2[Ru(CO)_2I_4]$, and indeed, the infrared bands were similar to those reported for the previously isolated cesium salt, $Cs_2Ru(CO)_2I_4$.[3-5] However, the elemental analysis indicated that the compound had to be formulated as $[Ph_3PMe][Ru(CO)_2I_3]$.

The compound was further characterized by the ^{13}C NMR spectrum of a ^{13}CO-enriched sample and by mass spectrometry. The ^{13}C NMR spectrum of a ^{13}C-labeled sample (vide infra) displayed a single peak. Field desorption (FD) mass spectrometry showed the presence of Ph_3PMe^+, whereas fast-atom bombardment (FAB) mass spectroscopic techniques revealed the heaviest particles to be a cluster of masses[17] whose largest peak was at *m/e* 539. The peak at *m/e* 539 would be characteristic of a $[Ru(CO)_2I_3]^-$ anion. The remaining lower mass peaks in the FAB-generated mass spectrum correspond to the expected ligand losses.

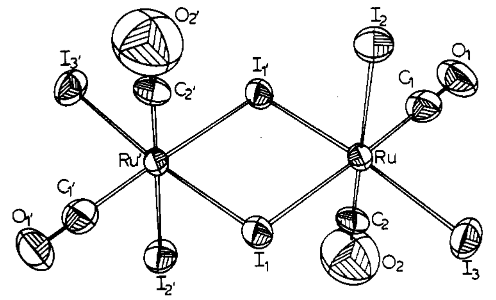

Figure 1. ORTEP representation of the dimeric dianion $[Ru_2(CO)_4I_6]^{2-}$. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Atoms labeled with a prime (′) are related to those without a prime by the crystallographic inversion center at $^1/_2$, 0, 0.

Table II. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$[a]

atom type[b]	fractional coordinates			equiv isotropic thermal parameter, B, ×10 Å^2[c]
	10^4x	10^4y	10^4z	
		Anion		
Ru	3352 (1)	500 (1)	575 (1)	24 (1)
I_1	5863 (1)	1542 (1)	156 (1)	31 (1)
I_2	4598 (1)	−163 (1)	2900 (1)	48 (1)
I_3	2585 (1)	2635 (1)	1092 (1)	42 (1)
O_1	790 (6)	−650 (7)	1182 (6)	63 (2)
O_2	1949 (6)	1196 (5)	−1912 (4)	122 (2)
C_1	1699 (8)	−236 (7)	953 (7)	42 (2)
C_2	2508 (7)	929 (6)	−957 (5)	31 (2)
		Cation		
P	2275 (2)	3504 (2)	4654 (2)	28 (1)
C_{a1}	2858 (7)	4296 (6)	5962 (5)	27 (2)
C_{a2}	2800 (7)	5544 (6)	5945 (7)	35 (2)
C_{a3}	3254 (8)	6118 (7)	6978 (7)	44 (2)
C_{a4}	3748 (9)	5451 (8)	8028 (7)	45 (2)
C_{a5}	3814 (8)	4227 (7)	8048 (7)	41 (2)
C_{a6}	3388 (8)	3631 (6)	7026 (6)	35 (2)
C_{b1}	765 (7)	2542 (6)	4757 (6)	30 (2)
C_{b2}	134 (7)	2567 (6)	5696 (6)	33 (2)
C_{b3}	−1064 (9)	1840 (7)	5757 (8)	48 (2)
C_{b4}	−1632 (10)	1097 (7)	4861 (8)	53 (3)
C_{b5}	−997 (12)	1066 (8)	3935 (9)	64 (3)
C_{b6}	206 (11)	1789 (7)	3866 (7)	50 (3)
C_{c1}	1835 (7)	4567 (6)	3410 (5)	29 (2)
C_{c2}	462 (8)	4661 (7)	2766 (6)	38 (2)
C_{c3}	168 (9)	5489 (7)	1780 (7)	46 (2)
C_{c4}	1187 (10)	6219 (7)	1475 (7)	51 (3)
C_{c5}	2567 (11)	6119 (8)	2086 (8)	56 (3)
C_{c6}	2895 (8)	5302 (7)	3059 (7)	45 (2)
C_{d1}	3669 (9)	2608 (8)	4510 (7)	48 (2)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 1 and 2. [c] This is one-third of the trace of the orthogonalized B_{ij} tensor.

These spectroscopic data indicated that the complex contained a pair of equivalent carbonyls (based upon the ^{13}C NMR spectra) and that these carbonyl ligands were cis and were at about a 90° angle (on the basis of the infrared data). Further, the mass spectra appeared to indicate the presence of a monomeric ruthenium species.

However, an X-ray crystallographic study revealed that the anion is dimeric (Figure 1) with S_2 symmetry and contains a pair of nonequivalent cis carbonyl ligands about each ruthenium atom.[18]

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(16) This procedure was first performed by using unenriched $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ and was shown to give $[Ph_3PMe]$[*mer*-$Ru(CO)_3I_3$]. The procedure, which conserves valuable ^{13}CO, is also described in the two subsequent experimental procedures.

(17) The clusters of masses in the mass spectrum are typical for ruthenium compounds because of the large number of ruthenium isotopes.

(18) The structure determined by this X-ray crystallographic study is contrary to that assigned to the analogous iodine-bridged ruthenium complex $[Ru_2(CO)_2(t\text{-}Bu_2PH)_2I_6]^{2-}$. The present X-ray structural analysis of $[Ru_2(CO)_4I_6]^{2-}$ places the earlier assignment of this complex in question. See: Schumann, H.; Opitz, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 38.

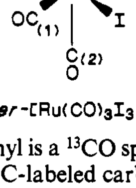
The complex is composed of discrete $[Ru_2(CO)_4I_6]^{2-}$ dimers (Figure 1) and $[Ph_3PMe]^+$ cations.[12] Final atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms are given with estimated standard deviations in Tables II and III,[12] respectively. Idealized coordinates generated for the phenyl ring hydrogen atoms and the rigid-rotor methyl hydrogens of the $[Ph_3PMe]^+$ cation are given in Table IV.[12] Bond lengths and angles for the anion and the cation are given in Tables V and VI,[12] respectively.

The structure as determined by X-ray crystallography was consistent with the infrared data but required a reinterpretation of the ^{13}C NMR data. A plausible explanation for the observation of a single ^{13}C NMR signal is that the carbonyl ligands are rapidly interconverted via an undefined mechanism.[19] The low solubility of the complex in noncoordinating solvents such as methylene chloride or chloroform precluded a rigorous temperature-dependence study.

When $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ was dissolved in THF and CO bubbled through the solution at room temperature for 2 h (or when the solution was stirred under 30 psi of CO), *fac*-$[Ru(CO)_3I_3]^-$ was not regenerated. Instead, a new compound was observed with IR bands at 2112 (w), 2041 (vs), and 2012 (s) cm^{-1}. The elemental analysis indicated the formulation to be consistent with $[Ph_3PMe][Ru(CO)_3I_3]$. These two pieces of data were consistent with the meridional isomer of $[Ru(CO)_3I_3]^-$. The structure of this new compound was ultimately determined by ^{13}C NMR spectroscopy.

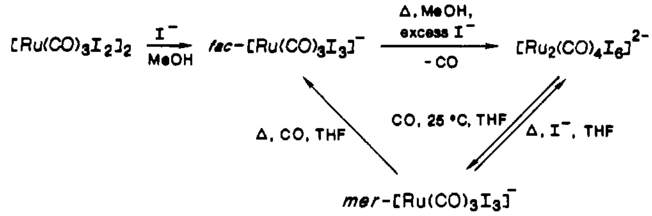
A ^{13}CO-enriched sample of this new compound was generated from $[Ru(CO)_3I_2]_2$ by treating unlabeled $[Ru(CO)_3I_2]_2$ at 80 psi with a quantity of ^{13}CO that was sufficient to exchange about 50% of the CO on ruthenium if exchange was complete. The resultant ^{13}CO-enriched $Ru(CO)_4I_2$ was allowed to decarbonylate to generate a ^{13}C-labeled sample of $[Ru(CO)_3I_2]_2$. Enriched samples of the facial isomer of $[Ru(CO)_3I_3]^-$ and of the dianion $[Ru_2(CO)_4I_6]^{2-}$ were generated from the enriched dimer by the same methods used for the unenriched materials. The ^{13}C NMR spectrum of the facial isomer of $[Ru(CO)_3I_3]^-$ displayed a single peak at 187.3 ppm, and the ^{13}C NMR spectrum of $[Ru_2(CO)_4I_6]^{2-}$ showed a single peak at 197.8 ppm. (These results were discussed earlier.)

When a Fischer–Porter bottle containing a THF solution of ^{13}C-labeled $[Ru_2(CO)_4I_6]^{2-}$ was pressurized to 80 psi with 90% ^{13}CO, the ^{13}C NMR spectrum of the isolated ruthenium complex showed a triplet with relative peak intensities of 1:1:1 at δ 187.5 and a quintet with relative peak intensities of 2:4:5:4:2 at δ 191.4, with a relative peak intensity for the two sets of peaks of about 2:1, respectively. The spectrum can be explained by examining the potential magnetic environments for the carbonyls in a highly enriched sample of the *mer*-$[Ru(CO)_3I_3]^-$ anion. There are two different types of carbonyls in this isomer. One carbonyl (the carbonyl in the iodine plane) is unique, and the other two (the carbonyls that are mutually trans) are equivalent. In the structure of the meridional isomer, these carbonyl ligands are labeled as $C_{(1)}O$ and $C_{(2)}O$ respectively:



mer-$[Ru(CO)_3I_3]^-$

Scheme I. Interconversions of the Anionic Iodo Carbonyl Complexes of Ruthenium



When the unique carbonyl is a ^{13}CO species, it can have between zero and two additional ^{13}C-labeled carbonyls coordinated to the same metal atom. The observed spectrum would be a singlet when the unique carbonyl is the only ^{13}CO present, a doublet when a second ^{13}CO is on the metal, and a triplet in the completely labeled complex. The resultant spectrum would be a composite of these three possible combinations, and therefore, a quintet. Since the relative intensities of the peaks are a function of the level of ^{13}CO incorporation, the quintet would not be expected to be a normal 1:4:6:4:1 quintet but would display distorted peak intensities, in this case a 2:4:5:4:2 pattern.

The spectrum of the mutually trans (identical) carbonyls would be anticipated to be simpler. Since the identical carbonyls are magnetically equivalent, they would not be expected to couple with each other. Therefore, only two possibilities must be considered: either the unique position is ^{13}C-labeled or it is not. If the unique position were labeled, the ^{13}C NMR spectrum would display a doublet, whereas if it were unlabeled, a singlet would be observed. The result of superimposing these two spectra would be a triplet. Again, this triplet would be expected to be distorted from a normal 1:2:1 triplet (in this case a 1:1:1 triplet) since the peak intensities are a function of the level of ^{13}CO incorporation. (The measured coupling constant for the C–C coupling was 5 Hz.)

An attempt was made at selectively labeling one of the coordination sites in *mer*-$[Ru(CO)_3I_3]^-$ with a ^{13}CO ligand. When unlabeled $[Ru_2(CO)_4I_6]^{2-}$ was treated with 90% ^{13}CO, by use of the same conditions employed previously in the conversion of labeled $[Ru_2(CO)_4I_6]^{2-}$ to labeled *mer*-$[Ru(CO)_3I_3]^-$, the ^{13}C NMR of the resultant complex still displayed a triplet with relative intensities of 7:17:7 at δ 187.5 and a quintet with relative intensities of 1:5:7:5:1 at δ 191.4 with a relative peak intensity for the two sets of peaks of about 2:1. As evidenced by the changed intensities of multiplets, the only difference between the spectra obtained with use of labeled and unlabeled $[Ru_2(CO)_4I_6]^{2-}$ was that the peaks due to carbon–carbon coupling were larger when labeled starting materials were used. The presence of some carbon–carbon splitting, even when unlabeled $[Ru_2(CO)_4I_6]^{2-}$ is used as a starting material, and the lack of selectivity indicates that there is a process that equilibrates the carbonyl ligands. This process, which may be related to the interconversion of the dimer carbonyls, is undefined.

A solution of meridional isomer can be converted to the thermodynamically more stable facial isomer by heating under a CO atmosphere. When a THF solution of *mer*-$[Ru(CO)_3I_3]^-$ was heated for 16 h at 80 °C under 30 psi of CO, the IR bands at 2112, 2042, and 2012 cm^{-1} disappeared and were replaced by strong bands at 2027 and 2098 cm^{-1}. These bands are diagnostic for the facial isomer of $[Ru(CO)_3I_3]^-$.

The meridional isomer of $[Ru(CO)_3I_3]^-$ could also be readily decarbonylated to re-form $[Ru_2(CO)_4I_6]^{2-}$. When a THF solution containing 4 equiv of LiI was heated at reflux for 1.5 h, the bands corresponding to *mer*-$[Ru(CO)_3I_3]^-$ were replaced by two new bands at 2033 and 1971 cm^{-1}. These new bands are diagnostic for $[Ru_2(CO)_4I_6]^{2-}$. There was also some *fac*-$[Ru(CO)_3I_3]^-$ present, as evidenced by a small peak at 2097 cm^{-1}. (The peak height was about 10% of the peak height for the band at 2033 cm^{-1}.) The interconversions of the anionic iodo carbonyl complexes of ruthenium are summarized in Scheme I.

Conclusion

Two previously undocumented anionic iodo carbonyl complexes of ruthenium have been isolated and characterized. The first is the dimeric species $[Ru_2(CO)_4I_6]^{2-}$, which is generated by the decarbonylation of *fac*-$[Ru(CO)_3I_3]^-$ and has S_2 symmetry. The dimeric dianion $[Ru_2(CO)_4I_6]^{2-}$ is readily converted to the me-

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(19) We speculate that the two most likely processes in the carbonyl exchange are a scission of one of the I bridges and complete dissociation to the monomer. Both processes generate coordinatively unsaturated species capable of undergoing rapid interconversion.

ridional isomer of $[Ru(CO)_3I_3]^-$ by carbonylation. The structural integrity of the meridional isomer has been determined from its infrared and ^{13}C NMR spectra. The meridional isomer of $[Ru(CO)_3I_3]^-$ can be converted by heating it under a CO atmosphere to the thermodynamically more stable facial isomer or it can be used to regenerate $[Ru_2(CO)_4I_6]^{2-}$ by heating a THF solution containing excess iodide under an argon atmosphere.

Neither the meridional isomer of $[Ru(CO)_3I_3]^-$ nor its precursor, $[Ru_2(CO)_4I_6]^{2-}$, have been completely documented in prior literature. Thus this report represents the first completely documented syntheses of these ruthenium halo carbonyl complexes.

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Registry No. $[Ru(CO)_3I_2]_2$, 32423-80-6; $[Ph_3PMe]$[*fac*-$Ru(CO)_3I_3$], 104092-01-5; $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$, 104153-54-0; $[Ph_3PMe]$[*mer*-$Ru(CO)_3I_3$], 104092-02-6; $Ru_3(CO)_{12}$, 15243-33-1; iodine, 7553-56-2.

Supplementary Material Available: Crystal structure analysis report for $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$, Table III (anisotropic thermal parameters for non-hydrogen atoms), Table IV (idealized positions for hydrogen atoms in the cation of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$), Tables V and VI (bond lengths and bond angles in the cation of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$), and Figure 2 (ORTEP drawing for the cation of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$) (14 pages); structure factor tables for the X-ray study of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ (21 pages). Ordering information is given on any current masthead page.

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Multiple Routes to the Formation of a Phosphine-Bridged Trirhodium Dihydride Cation, $[Rh_3\{\mu\text{-}(Ph_2PCH_2)_2PPh\}_2(H)_2(\mu\text{-}Cl)_2(CO)_2]^+$

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Red-orange $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (dpmp is bis((diphenylphosphino)methyl)phenylphosphine) is formed by treatment of dichloromethane solutions of $[Rh_3(\mu\text{-dpmp})_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$ or $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)Cl][BPh_4]$ with dihydrogen, by the reaction of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ with aqueous formaldehyde, paraformaldehyde, or acetaldehyde, or by treatment of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)_2Cl_4][BPh_4]$ with dihydrogen. Deep green $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)_2Cl_4][BPh_4]$ is formed by treatment of dichloromethane solutions of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ with aqueous hydrochloric acid or hydrogen chloride vapor. Spectroscopic data characterizing these complexes are reported. $[Rh_3(\mu\text{-dpmp})_2(H)_2(CO)_2(\mu\text{-}Cl)_2][BPh_4]\cdot 3CH_2Cl_2$ crystallizes in the space group $P2_1/n$ (No. 14) with $a = 14.498$ (2) Å, $b = 22.077$ (3) Å, $c = 28.353$ (3) Å, $\beta = 99.86$ (1)°, and $Z = 4$ at 130 K, $R = 0.049$, $R_w = 0.054$ for 12079 reflections with $I > 3\sigma(I)$ and 558 parameters. The complex consists of two chloro-bridged A-frame units linked side-by-side through the central rhodium. The hydrides, which were well-behaved on refinement, are primarily localized on the central rhodium; Rh(2)–H distances are 1.48 (7) and 1.55 (7) Å. Structural and ^1H NMR spectroscopic evidence suggests a semibridging interaction between these hydrides and the terminal $Rh(CO)Cl(P)_2$ units.

Introduction

We recently reported the preparation, isolation, and structural characterization of the trinuclear rhodium hydride $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (**1a**) (dpmp is bis((diphenylphosphino)methyl)phenylphosphine).[1] This was the first phosphine-bridged rhodium hydride obtained directly from dihydrogen and a precursor complex, either $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^{+\,2}$ (**2**) or $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)CO(\mu\text{-}Cl)Cl]^{+\,3}$ (**3**), and its structure showed that the dihydrogen had added to the central rhodium center within the nearly linear complex. This hydride is exceptionally stable. Here we describe its preparation by a number of routes and present details of its characterization.

Results

Preparative Chemistry. Red $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (**1a**) is readily prepared by a variety of procedures. The paths delineated here are summarized in Chart I.

Treatment of a red dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)Cl][BPh_4]$ (**3**) under 1 atm of dihydrogen for 12 h produces a lighter red solution from which red-orange crystals of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (**1a**) can be isolated by the gradual addition of ethyl ether. Isolation of the same hydride from the rose-colored tricarbonyl, $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ (**2**), requires the use of a higher pressure of dihydrogen. After 12 h under 10 atm of dihydrogen, a dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ yields **1a** in comparable yield. The formation of the dihydride **1a** from $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ is accompanied by the exchange reaction $H_2 + D_2 \rightarrow 2HD$. Thus when a sample of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ is exposed to 2 atm of a mixture of H_2 and D_2 (ratio of $H_2{:}D_2{:}HD = 42{:}55{:}3$) and the gas sampled after 35 h, significant quantities of HD have formed (new ratio, 30:41:29). Consequently, sites for multiple attachment of dihydrogen must be available, or hydride and deuteride ligands must undergo interionic exchange. Sampling of reaction mixtures by ^1H NMR spectroscopy reveals the presence of small amounts of other hydrides, which have not been produced in large enough quantity for isolation and characterization. These may be involved in the exchange process.

Dihydride **1a** is also formed when $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ is treated with aqueous formaldehyde in a two-phase reaction or with paraformaldehyde in a homogeneous reaction. The procedure using aqueous formaldehyde is probably the most convenient for the preparation of **1a**. These reactions are unusual. Formaldehyde has frequently been used as a source of a carbonyl ligand in preparative organometallic chemistry.[4] Here, however, is a case where a carbon monoxide ligand must be lost from the parent complex and formaldehyde is serving us a source of the hydride ligands. Oxidative addition of a formaldehyde C–H bond to low-valent metal ions has been shown to produce hydrido formyl

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