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# REACTIONS OF COORDINATED MOLECULES

## XXV *. THE PREPARATION OF SEVERAL BIS[(HYDROXY)(METHYL)]CARBENOID COMPLEXES OF RHENIUM

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## Summary

When the rhenium(I) complexes, $XRe(CO)_5$ (where X is Cl, Br or I), are treated with two molar-equivalents of methyllithium, dianionic complexes of the type, *fac*-$(OC)_3(X)Re[C(CH_3)O]_2^{2-}$, are formed. The diprotonation of these dianions with HX affords the neutral, bis-carbenoid complexes, *fac*-$(OC)_3(X)$-$Re[C(CH_3)(OH)]_2$. When X is methyl, the reaction with methyllithium gives only a monoanion. The iodo, bis-carbenoid complex decomposes in solution with the elimination of acetaldehyde and with the formation of the known dimeric complex, $[Re(CO)_4I]_2$. The X-ray molecular structure determination of this dimeric complex is reported. The $^{13}C$ NMR data of the chloro and bromo biscarbenoid complexes are also presented.

## Introduction

This report completes our recent study comparing the electronic similarities between acetyl and halide ligands in organometallic, metalate chemistry. The rhena-acetylacetonate anion, *cis*-$(OC)_4Re(CH_3CO)_2^-$, has been prepared, and it forms the neutral, rhena-acetylacetone molecule, [*cis*-$(OC)_4Re(CH_3CO)_2$]H, upon protonation [2]. The triacetylrhenate dianion, *fac*-$(OC)_3Re(CH_3CO)_3^{2-}$, has been prepared also, and it acts as a vicinal, bifurcated ligand when it is coordinated to metal ions or to a boron halide or boron alkoxide moiety [1,3,4]. The diprotonated form of the triacetylrhenate complex has been prepared, but it is thermally unstable at room temperature [1].

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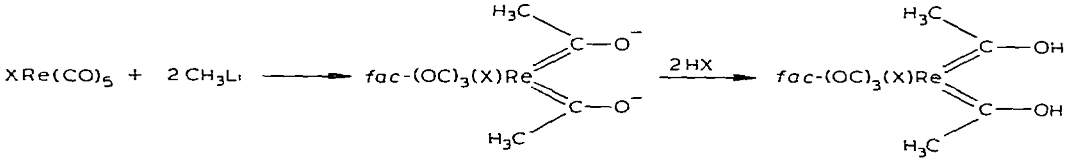
* For Part XXIV see ref. 1.

We reported recently the preparation of the acetyl (and formyl) halo-rhenate anions, *cis*-$(OC)_4(X)Re[C(CH_3)O]^-$, where X is Cl, Br or I, and the isolation of the neutral protonation products, *cis*-$(OC)_4(X)Re[C(CH_3)(OH)]$, [5]. These hydroxycarbenoid complexes are formal derivatives of the rhena-acetylacetone molecule in which one of the acetyl ligands is replaced by a halide ligand.

We now report the preparation and characterization of the dianionic complexes, *fac*-$(OC)_3(X)Re(CH_3CO)_2{}^{2-}$, where X is Cl, Br or I, and the neutral, diprotonated complexes, *fac*-$(OC)_3(X)Re[C(CH_3)(OH)]$. These anionic complexes are halo derivatives of the triacetyltricarbonylrhenate complex, and the neutral complexes are the first examples of mononuclear, bis[(hydroxy)(alkyl) carbenoid] complexes.

## Results and discussion

The addition of two molar-equivalents of methyllithium to a THF solution of $ClRe(CO)_5$, $BrRe(CO)_5$ or $IRe(CO)_5$ at −78°C affords the corresponding diacetylhalorhenate dianions. These complexes are protonated with the corresponding acid, HX, to form the halo, bis[(hydroxy)(methyl)carbenoid] complexes I—III, as shown below.



(I : X = Cl ;
II : X = Br ;
III : X = I )

The addition of the methyllithium can be followed easily by IR. The first equivalent of methyllithium forms the monoanions, *cis*-$(OC)_4(X)Re[C(CH_3)O]^-$, and then the second equivalent of methyllithium affords the dianionic complexes. The terminal carbonyl stretching band pattern indicates that the *facial* isomer is formed. This three-band pattern for the dianions appears at 1975m, 1880s and 1840s $cm^{-1}$ which represents an average frequency shift to lower energy of ca. 120 and 50 $cm^{-1}$ when compared to the carbonyl bands of the $XRe(CO)_5$ complexes and the intermediate monoanion complexes, respectively.

The bis-carbenoid complexes I—III are yellow solids which are isolated in low to moderate yields. The iodo complex, III, is the least stable thermally. A carbonyl stretching band pattern which is typical of *fac*-$(OC)_3M$ moieties is observed at 2060m, 2000s and 1916s $cm^{-1}$ in hexane solution. This shift of the carbonyl bands to higher energy upon protonation of the dianions is as expected. The $^1H$ NMR spectra of I—III in $CDCl_3$ show singlets at $\delta$ 2.95 ± 0.05 ppm for the two equivalent methyl groups and singlets at $\delta$ 14.94—13.54 ppm for the two equivalent hydroxyl protons. The position of the hydroxyl proton resonance appears to follow the trend of the electronegativity of the halogen atom with the hydroxyl proton resonance of the chloro complex appearing at lowest field. In contrast to the bis-carbenoid complexes, the hydroxyl proton resonances of the analogous mono-carbenoid halo complexes of rhenium or manganese are not observed due to hydrogen bonding [5,6]; however, the hydroxyl proton resonance of the (hydroxy)(methyl)carbenoid complex, $(OC)_5W[C(OH)(CH_3)]$, appears at $\delta$ 11.68 ppm.

The $^{13}C$ NMR spectra of the chloro and bromo complexes, I and II, were recorded in $CDCl_3$ solution. The carbonyl- and carbenoid-carbon resonances of I are shifted ca. 1 ppm to lower field than the corresponding resonances of II which is consistent with the greater electronegativity of the chlorine atom. The $C_s$ molecular symmetry is reflected in the $^{13}C$ NMR spectra, also. The carbenoid-carbon resonances appear at $\delta$ 322.3 and 320.7 ppm for I and II, respectively, and the very low-field position of these resonances is a diagnostic indication of the formation of this type of complex. The corresponding resonance of the (hydroxy)(methyl)carbenoid complex, $(CO)_5W[C(OH)(CH_3)]$, appears at $\delta$ 334.4 ppm [7], while the acyl carbon resonances of the rhena-acetylacetone molecule and acetylpentacarbonylrhenium appear at $\delta$ 297.9 and 244.7 ppm, respectively, [8]. Corrected values for the $^{13}C$ NMR resonances of $CH_3C(O)Re(CO)_5$, which were published previously [8], are provided here in $\delta$: $CH_3$ (57.5); *trans* CO (181.2); *cis*-CO (183.1); acyl (244.7).

Presumably, the successful substitution of an acetyl ligand by a halide ligand in these metalate complexes is due to the ability of both types of ligands to reduce the amount of electron density on the metal atom. To test this hypothesis, $CH_3Re(CO)_5$ was treated with two molar-equivalents of methyllithium under the same reaction conditions, but only the monoanion, *cis*-$(OC)_4(CH_3)Re[C(CH_3)O]^-$, was formed. This anion had carbonyl stretching bands at 2060w, 1935(br)vs and 1892s $cm^{-1}$ and an acyl C—O band at 1542m $cm^{-1}$ in THF solution. The acetyl and rhenium methyl groups have proton resonances which appear at $\delta$ 2.31 and —0.53 ppm, respectively, in THF solution. As anticipated, the methyl group destabilizes an increase in the electron density which is localized on the rhenium atom, thus preventing the formation of the dianion.

The thermal decomposition of solutions of the iodo complex III was sufficiently rapid to preclude the recording of the $^{13}C$ NMR spectrum. This decomposition was followed by $^1H$ and $^{13}C$ NMR and IR in both chloroform and benzene solutions. The reaction products were acetaldehyde and a small amount of a yellow crystalline material which was contaminated with a black powder. The yield of acetaldehyde was determined from the comparative integration of the $^1H$ NMR methyl resonance of the acetyladehyde produced from the reaction and from the additions of known amounts of acetaldehyde to the sample solution. A 0.12 mmol sample of III produced 0.22 mmol of acetaldehyde indicating that both (hydroxy)(methyl)carbenoid ligands were eliminated as acetaldehyde. This elimination parallels that observed for $(OC)_5W[C(OH)(CH_3)]$ and $C_5H_5(OC)_2Re[C(OH)(CH_3)]$, [9,10].

The solid products could not be identified unambiguously using the normal methods, so a single-crystal X-ray structural determination of the yellow solid was performed. This product was identified as the well-known dimer, $[Re(CO)_4I]_2$. The black solid is presumed to be a rhenium iodide species which was not identified.

The ORTEP diagram of $[Re(CO)_4I]_2$ is shown in Figure 1. The unit cell and

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS [a] (WITH ESD'S) FOR $[Re(CO)_4I]_2$

| Atom | $x$ | $y$ | $z$ | $B_{11}$ or $B$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Re(1) | 0.60686 (7) | 0.12977 (5) | 0.31594 (5) | 1.76 (3) | 1.91 (3) | 2.41 (3) | −0.00 (3) | 0.23 (3) | −0.00 (3) |
| Re(2) | 0.16713 (7) | 0.13003 (6) | 0.21042 (5) | 1.73 (3) | 1.94 (3) | 2.31 (3) | 0.08 (3) | 0.02 (3) | 0.02 (3) |
| I(1) | 0.38495 (12) | 0.00862 (10) | 0.34912 (10) | 2.13 (5) | 2.44 (5) | 3.47 (6) | 0.06 (4) | 0.21 (4) | 1.18 (5) |
| I(2) | 0.38714 (12) | 0.25358 (10) | 0.17974 (10) | 2.40 (5) | 2.16 (5) | 3.62 (6) | −0.12 (4) | 0.15 (4) | 0.97 (5) |
| C(1) | 0.7515 (21) | 0.2095 (17) | 0.2883 (16) | 3.18 (34) | | | | | |
| C(2) | 0.6050 (22) | 0.2264 (17) | 0.4383 (17) | 3.43 (36) | | | | | |
| C(3) | 0.7489 (20) | 0.0388 (15) | 0.4086 (15) | 2.67 (30) | | | | | |
| C(4) | 0.6049 (22) | 0.0358 (17) | 0.1896 (17) | 3.21 (35) | | | | | |
| C(5) | 0.1786 (24) | 0.0334 (18) | 0.0926 (18) | 3.66 (39) | | | | | |
| C(6) | 0.0255 (22) | 0.2170 (17) | 0.1168 (16) | 3.20 (34) | | | | | |
| C(7) | 0.0252 (23) | 0.0426 (17) | 0.2391 (17) | 3.29 (35) | | | | | |
| C(8) | 0.1635 (22) | 0.2277 (17) | 0.3328 (17) | 3.39 (36) | | | | | |
| O(1) | 0.8352 (18) | 0.2726 (14) | 0.2748 (14) | 4.94 (34) | | | | | |
| O(2) | 0.6114 (18) | 0.2790 (14) | 0.5076 (14) | 4.86 (34) | | | | | |
| O(3) | 0.8365 (18) | −0.0185 (13) | 0.4673 (13) | 4.25 (30) | | | | | |
| O(4) | 0.5973 (18) | −0.0132 (14) | 0.1175 (13) | 4.49 (32) | | | | | |
| O(5) | 0.1825 (21) | −0.0233 (15) | 0.0235 (16) | 5.61 (39) | | | | | |
| O(6) | −0.0569 (20) | 0.2714 (14) | 0.0531 (15) | 5.35 (37) | | | | | |
| O(7) | −0.0530 (19) | −0.0154 (14) | 0.2580 (14) | 4.67 (33) | | | | | |
| O(8) | 0.1686 (19) | 0.2809 (15) | 0.4019 (15) | 5.19 (36) | | | | | |

[a] The anisotropic temperature factors are of the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

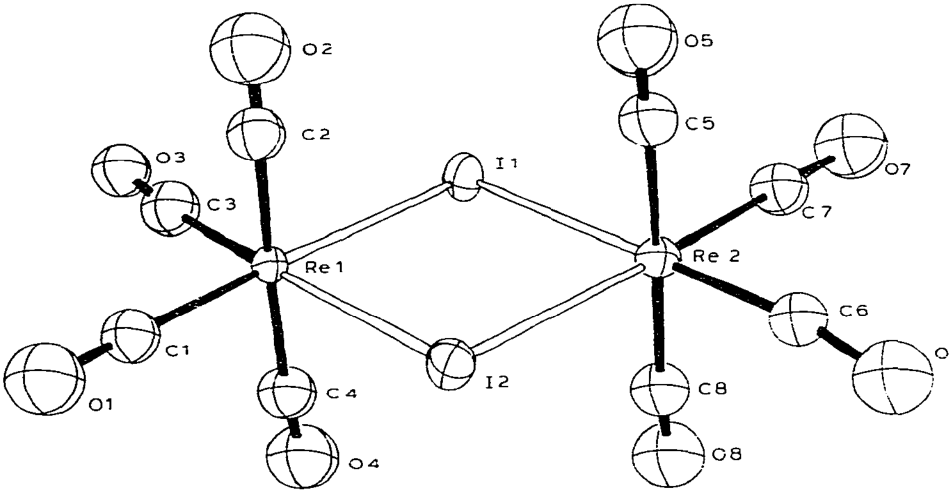


Fig. 1. An ORTEP view of $[Re(CO)_4I]_2$ showing the atomic numbering scheme. The sizes and shapes of the atoms are determined by their final thermal parameters and their perspective view.

atomic positional parameters indicate that this solid is isomorphous with $[Mn(CO)_4Br]_2$, although a different origin was choosen in reporting the structure of the manganese dimer [11]. The atomic positional parameters for the heavy atoms of the Mn and Re halide dimers agree to within 0.018 fractional-coordinate units or better. The atomic positional and thermal parameters for $[Re(CO)_4I]_2$ are shown in Table 1.

The molecular structure of $[Re(CO)_4I]_2$ has idealized $D_{2h}$ symmetry. The atoms Re(1), Re(2), I(1) and I(2) are nearly coplanar (Plane I, maximum atomic deviation is 0.012 Å), and this plane is essentially a horizontal molecular mirror plane since the atoms C(1), C(3), C(6) and C(7) are nearly in this plane [(maximum atomic deviation from Plane I for these atoms is −0.09 Å for C(1)]. The plane defined by Re(1), Re(2), C(4) and C(5) (Plane II, maximum atomic deviation is 0.018 Å) is essentially a vertical molecular mirror plane since the difference between the atomic displacements from this plane for the pairs of atoms I(1) and I(2), C(1) and C(3) and C(6) and C(7) are only 0.001, 0.13 and 0.03 Å, respectively. The acute dihedral angle between Planes I and II is 89.0° which is also quite consistent with the nearly $D_{2h}$ molecular symmetry.

A selected listing of bond distances and angles is provided in Table 2. The two iodine atoms act as essentially symmetrical doubly bridging ligands between the Re atoms where the average Re—I distance is 2.820 Å. The average value of the I—Re—I angles is 83.18°. There is nearly octahedral coordination geometry about the Re atoms, although the Re—C distances to the carbonyl ligands which are *trans* to the iodine atoms are slightly shorter than the Re—C distances to the axial carbonyl ligands. The average values of the Re—C distances to the equatorial and axial carbonyl ligands are 1.91 Å and 2.00 Å, respectively. This *trans* effect due to the iodine atoms is expected since the high polarizability of the iodine atoms increases the Re—C $d_\pi$—$p_\pi$ bonding to the equatorial carbonyl ligands. The average values of the carbonyl C—O dis-

TABLE 2

SELECTED BOND DISTANCES AND ANGLES IN $[Re(CO)_4I]_2$ WITH ESTIMATED STANDARD DEVIATIONS OF THE LEAST SIGNIFICANT DIGIT IN PARENTHESES

| Distances (Å) | | Angles (°) | |
|---|---|---|---|
| Re(1)—I(1) | 2.827 (2) | I(1)—Re(1)—I(2) | 82.93 (4) |
| Re(1)—I(2) | 2.826 (2) | I(1)—Re(2)—I(2) | 83.41 (4) |
| Re(2)—I(1) | 2.813 (2) | Re(1)—I(1)—Re(2) | 96.82 (4) |
| Re(2)—I(2) | 2.814 (2) | Re(1)—I(2)—Re(2) | 96.82 (4) |
| Re(1)—C(1) | 1.88 (3) | C(1)—Re(1)—I(1) | 177.8 (6) |
| Re(1)—C(2) | 2.00 (3) | C(3)—Re(1)—I(2) | 176.7 (6) |
| Re(1)—C(3) | 1.93 (2) | C(2)—Re(1)—C(4) | 178.2 (8) |
| Re(1)—C(4) | 2.02 (3) | C(1)—Re(1)—C(3) | 87.4 (9) |
| Re(2)—C(5) | 1.98 (3) | C(2)—Re(1)—I(1) | 89.0 (7) |
| Re(2)—C(6) | 1.90 (2) | C(2)—Re(1)—I(2) | 89.7 (6) |
| Re(2)—C(7) | 1.92 (3) | C(4)—Re(1)—I(1) | 91.1 (7) |
| Re(2)—C(8) | 2.02 (3) | C(4)—Re(1)—I(2) | 88.6 (6) |
| C(1)—O(1) | 1.20 (3) | C(6)—Re(2)—I(1) | 177.5 (7) |
| C(2)—O(2) | 1.10 (3) | C(7)—Re(2)—I(2) | 176.5 (6) |
| C(3)—O(3) | 1.20 (2) | C(5)—Re(2)—C(8) | 177.8 (9) |
| C(4)—O(4) | 1.11 (3) | C(6)—Re(2)—C(7) | 89.1 (9) |
| C(5)—O(5) | 1.16 (3) | C(5)—Re(2)—I(1) | 88.4 (6) |
| C(6)—O(6) | 1.19 (3) | C(5)—Re(2)—I(2) | 88.4 (7) |
| C(7)—O(7) | 1.14 (3) | C(8)—Re(2)—I(1) | 89.8 (6) |
| C(8)—O(8) | 1.11 (3) | C(8)—Re(2)—I(2) | 90.2 (7) |

tances and the Re—C—O angles of 1.15 Å and 176°, respectively, are very reasonable values for terminally coordinated carbonyl ligands. The nonbonded Re—Re distance is 4.218(2) Å.

## Experimental

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25°C unless stated otherwise. Solvents were distilled from Na/K alloy before use. The halopentacarbonylrhenium complexes were prepared by literature methods [5,12], while methyllithium (Ventron Corp.) and all other reagents were purchased.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer in 0.10 mm sodium chloride cavity cells using the solvents as a reference and polystyrene film as a calibration standard. NMR spectra were recorded on a Jeol MH-100 spectrometer (proton) and a Jeol FX90Q Fourier transform spectrometer (carbon) using TMS as an internal reference. For $^{13}C$ NMR spectra, $Cr(acac)_3$ was added to the sample solution to facilitate relaxation and a pulse angle of 90° was used. Mass spectra were recorded on a LKB 9000 spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc. Knoxville, Tennessee.

### *Preparation of the fac-*$(OC)_3(X)Re[C(CH_3)(OH)]_2$ *complexes (I—III)*

*General procedure.* To a stirred solution of 0.22—0.30 g of the appropriate halopentacarbonylrhenium complex in 20 ml of THF [65 ml for $ClRe(CO)_5$] at —78°C was added dropwise two molar equivalents of methyllithium (low-halide MeLi for the chloro and iodo complexes) as an ether solution. As the temperature was increased gradually to 0° C, the colorless solution turned yellow. After stirring for 1 h, the solvent was removed under reduced pressure and the dianionic complex was dissolved in 20 ml of ether (30 ml for the chloro complex) and then cooled to 0° C. To this solution was added dropwise 2.5 molar equivalents of the appropriate anhydrous hydrohalic acid (aqueous HI solution for the iodo complex) as an ether solution. A white precipitate formed upon stirring the reaction mixture as the temperature was gradually increased to 25° C over a 30 min period. The ether was removed under reduced pressure, and the residue was extracted with 10 ml hexane (15 ml of chloro complex) and then filtered. The yellow solution was then concentrated to approximately half volume. The yellow complexes crystallized from this solution when kept at —20° C for 16 h. Specific data for each reaction are given below.

*fac-*$(OC)_3(Cl)Re[C(CH_3)(OH)]_2$ *(I).* Using 0.30 g (0.82 mmol) of $ClRe(CO)_5$ afforded 116 mg (0.29 mmol, 36%) of I as yellow crystals: m.p. 78—79° C; IR (hexane) $\nu$(CO) 2060m, 2000s, 1916s $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\tau$ 7.09 (singlet, 3, $CH_3$), —4.94 (singlet, I, OH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 46.9 ($CH_3$), 192.5 (CO *trans* to Cl), 194.6 (CO's *cis* to Cl), 322.3 ppm (COHMe); Mass spectra (calcd for $C_7H_8{}^{37}ClO_5{}^{187}Re$: $M^+$, *m/e* 396) possesses the correct three-peak isotopic pattern for the parent ions at *m/e* 392, 294 and 396 (*P*, 55%) and for subsequent fragmentation ions. Anal. Calcd. for $C_7H_8ClO_5Re$: C, 21.35; H, 2.05; Cl, 9.00. Found: C, 21.09; H, 1.97; Cl, 9.23%.

*fac-*$(CO)_3(Br)Re[C(CH_3)(OH)]_2$ *(II).* Using 0.22 g (0.54 mmol) of $BrRe(CO)_5$ afforded 57 mg (0.13 mmol, 24%) of II as yellow crystals: m.p. 80—82° C; IR (hexane) $\nu$(CO) 2060m, 2001s, 1914s $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\tau$ 7.05 (singlet, 3, $CH_3$), —4.40 (singlet, 1, OH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 47.1 ($CH_3$), 191.7 (CO *trans* to Br), 193.6 (CO's *cis* to Br), 320.7 ppm (COHMe); Mass Spectra (calcd for $C_7H_8{}^{81}BrO_5{}^{187}Re$: $M^+$, *m/e* 440) exhibited the correct three-peak isotopic pattern for the parent ions at *m/e* 436, 438 and 440 (*P*, 39%) and for subsequent fragmentation ions. Anal. Calcd for $C_7H_8BrO_5Re$: C, 19.18; H, 1.84; Br, 18.23. Found: C, 19.33; H, 1.85; Br, 18.30%.

*fac-*$(CO)_3(I)Re[C(CH_3)(OH)]_2$ *(III).* Using 0.26 g (0.57 mmol) of $IRe(CO)_5$ afforded 34 mg (0.07 mmol, 12%) of III as yellow crystals: m.p. 63—64° C; IR (hexane) $\nu$(CO) 2058m, 2000s, 1918s $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\tau$ 7.00 (singlet, 3, $CH_3$), —3.54 (singlet, 1, OH); Mass Spectrum (calcd for $C_7H_8IO_5{}^{187}Re$: $M^+$, *m/e* 487) showed the correct isotopic pattern for the parent ions at *m/e* 485 and 487 (*P*, 41%), and for subsequent fragmentation ions. Anal. Calcd for $C_7H_8IO_5Re$: C, 17.33; H, 1.67; I, 26.15. Found: C, 17.06; H, 1.58; I, 25.05%.

### *X-ray-crystallographic study of* $[Re(CO)_4I]_2$

A crystal measuring ca. 0.7 × 0.3 × 0.2 mm was examined by preliminary precession and cone-axis photographs. These photographs indicated 2/*m* Laue symmetry and revealed the systematic absences 0*k*0 for *k* odd and *h*0*l* for *l* odd which identified the space group as $P2_1/c$. The refined unit cell parameters at 20° C using 15 reflections (Mo-$K_\alpha$, $\lambda$ 0.71070 Å) are; *a* 10.077(3), *b* 12.250(3), *c* 13.172(5) Å, $\beta$ 107.83(4)°, *d* (calcd.) 3.649 $g/cm^3$, *V* 1547.8 $Å^3$ with $Z = 4$. The observed density of 3.59 $g/cm^3$ was measured by flotation using an aqueous solution of thallous formate and thallous malonate.

Intensity data were collected with Nb-filtered Mo-$K_\alpha$ radiation on a 4-circle automated Picker diffractometer. The control softwave used for the Picker FACS-I system has been reported previously [13]. All reflections out to 55° in $2\theta$ in the $\pm h\ k\ l$ quadrant were measured using a $\theta$—$2\theta$ peak top stepscan technique (5 steps in 0.32° $2\theta$). No significant loss in intensity of the monitor reflections was observed during the 70 hours of X-ray exposure. Absorption corrections were calculated with ORABS [14] using a linear absorption coefficient of 198.2 $\text{cm}^{-1}$. All 3553 symmetry independent reflections were used in the solution and refinement of the structure.

The structure was solved using the Patterson method yielding the locations of the rhenium and iodine atoms. Subsequent difference Fourier syntheses yielded the locations of the other atoms. Refinement was by full-matrix least-squares with anisotropic thermal parameters and anomalous scattering contributions for the rhenium and iodine atoms and isotropic thermal parameters for the remaining atoms. Weights were based on counting statistics with an instability factor of 2.0%. Final agreement factors of $R$ = 0.073 and $R_w = \{[\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\}^{1/2}$ = 0.083 were obtained with a maximum coordinate shift-to-error ratio of 0.08 for the final least-squares cycle. The observed and calculated structure factors, a complete list of bond distances and angles, and a selected list of calculated least-squares planes are available from the authors upon request.

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