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CLEAVAGE OF DICHLOROMETHANE BY $(C_5Me_5)Ir(CO)_2/[Re(CO)_4Br]_2$. STRUCTURE OF $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+$ $[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ $(x = \sim 1.5)$

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Summary

Reaction of $(C_5Me_5)Ir(CO)_2$, $[Re(CO)_4Br]_2$, and CH_2Cl_2 at 60°C for 5 d gave $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+$ $[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ $(x = \sim 1.5)$ (**1**). The all-chloro analogue of **2**, **1**, was also synthesized. The structure of **1** was established by conventional crystallographic techniques: monoclinic, space group $P2_1/n$, a 17.841(2), b 17.576(2), c 19.994(3) Å, β 116.32(1)°, $Z = 8$; $R_F = 0.031$, $R_{wF} = 0.034$ for 3685 observed reflections with $I > 2.3\sigma(I)$ and $2\theta < 40°$. The structure consists of two independent $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+$ cations and $[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ $(x = \sim 1.5)$ anions. (The Cl and Br atoms in the anions are disordered.) The Ir–C(chloromethyl) distances are 2.07(3) and 2.11(2) Å. Spectroscopic properties of **1** and **2** are also reported.

Introduction

We have recently reported the synthesis of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$, a complex with an unbridged, donor–acceptor metal–metal bond [1]. In an extension of this study, we attempted the preparation of $(\eta^5\text{-}C_5Me_5)(OC)_2IrRe(CO)_4Br$ by the reaction of $Cp^{\star}Ir(CO)_2$ ($Cp^{\star} = \eta^5\text{-}C_5Me_5$) with $[Re(CO)_4Br]_2$ in CH_2Cl_2. This reaction, however, yielded the ionic compound $[Cp^{\star}Ir(CO)_2(CH_2Cl)]^+[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re(CO)_6]^-$ $(x = \sim 1.5)$ (**1**) instead of the desired product. In this paper we report the details of the synthesis of this unusual product along with an X-ray diffraction determination of its crystal structure.

Experimental

General synthetic procedures and instrumentation were identical to those used in the synthesis of $Cp^{\star}(OC)_2IrW(CO)_5$ [1]. The $Cp^{\star}Ir(CO)_2$ used in this study was sublimed (60°C, < 0.02 mmHg to a probe at −78°C) and then recrystallized from hexane. This purification was found to be essential in order to obtain good yields of

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the products. The rhenium compounds, $Re(CO)_5Cl$ and $[Re(CO)_4Br]_2$, were prepared by a minor modification of the literature methods [2] and were recrystallized from CH_2Cl_2/hexane before use. The ^{13}CO enriched sample of 1 was prepared from enriched $Re(CO)_5Br$ which in turn was prepared by heating a hexane solution of unenriched $Re(CO)_5Br$ at 80 °C under ^{13}CO(~2 atm; 90% ^{13}C) for 4 d [3].

Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ *(x = ~1.5) (1)*

A round-bottom flask (fitted with a Teflon valve) containing Cp*Ir $(CO)_2$ (0.050 g, 0.13 mmol), $[Re(CO)_4Br]_2$ (0.100 g, 0.13 mmol), and CH_2Cl_2 (10 ml) was evacuated at −196 °C and the solution degassed with two freeze-pump-thaw cycles. The sealed vessel was heated at 60 °C for 5 d. The CO produced in the reaction was removed twice during this period. (The rate of the reaction is dependent on whether the CO is removed from the sealed vessel.) An infrared spectrum of the red solution after the 5 d showed carbonyl bands attributable to the product and only traces of other compounds; there was no apparent decomposition. The reaction solution was filtered through Celite to a Schlenk flask; addition of hexane (10 ml) precipitated the product as off-white crystals. An infrared spectrum indicated that this crude product was pure. Several recrystallizations from CH_2Cl_2/hexane gave the analytical sample of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+$ $[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ as colorless, air-stable crystals (The crystal used in the X-ray structural determination was grown from CH_2Cl_2/hexane.) ν(CO): 2117m, 2080m, 2022vs, 1916vs cm^{-1}; (CH_2Cl_2 soln.); ^1H NMR ($CDCl_3$) δ 2.35(s), 4.14(s) (ratio 7.75/1; calcd 7.5/1) $^{13}C\{^1H\}$NMR (CH_2Cl_2/CD_2Cl_2, 4/1, RT) δ 8.62 (CH_2Cl) 9.7 (CCH_3) 108.2 (CCH_3) 159.3 (IrCO) 193 (ReCO; quadrupole broadened). (The assignment of the CH_2Cl and CH_3 ^{13}C signals was confirmed by multiplicity sorting.) MS (FAB ion source at 75 °C, sulfolane solution, xenon carrier) m/e 433 $(M)^+$ (where M denotes the cation), $(M - n\text{CO})^+$, $n = 1,2$. Found: C, 19.81, 20.07; H, 1.41, 1.48 (samples from different preparations). $C_{19}H_{17}O_8Cl_2Br_2Re_2Ir$ calcd.: C, 19.53; H, 1.47%; $C_{19}H_{17}O_8Cl_{2.5}Br_{1.5}Re_2Ir$ calcd.: C, 19.91; H, 1.49%. A ^{13}CO-enriched sample was prepared similarly from ^{13}CO-enriched $[Re(CO)_4Br]_2$.

Preparation of $[(\eta\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+[(\mu\text{-}Cl)_3Re_2(CO)_6]^-$

A 100 ml, round-bottom flask (with a Teflon valve) containing Cp*$Ir(CO)_2$ (0.027 g, 0.069 mmol), $Re(CO)_5Cl$ (0.050 g, 0.14 mmol), and CH_2Cl_2 (20 ml) was evacuated at −196 °C and the solution degassed with three freeze-pump-thaw cycles. The sealed flask was placed in an oil-bath at 100 °C for 42 h. Twice during this time the flask was cooled and a sample removed so as to monitor the course of the reaction by infrared spectroscopy. The flask was re-evacuated and the solution degassed before the flask was returned to the oil bath. After the reaction was complete as indicated by infrared spectroscopy, the flask was cooled and the yellow solution was transferred to a Schlenk flask. Hexane (20 ml) was then added and the solution allowed to stand overnight at −15 °C whereupon the product, $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+[(\mu\text{-}Cl)_3Re_2(CO)_6]^-$ (0.057 g, 76%) was obtained as pale yellow crystals that were pure by infrared spectroscopy (carbonyl region). The analytical sample was obtained as colorless crystals by recrystallization from CH_2Cl_2/hexane. ν(CO): 2118m, 2081m, 2024vs, 1916vs cm^{-1} (CH_2Cl_2 soln.); ^1H, $^{13}C\{^1H\}$ NMR and mass spectra were essentially the same as those obtained for 1. Found: C, 21.21; H, 1.49. $C_{19}H_{17}O_8Cl_4Re_2Ir$ calcd.: C, 21.14; H, 1.59%.

X-Ray structure determination of 1

A single colorless crystal was chosen and sealed in a thin-walled glass capillary which was mounted on the diffractometer. Crystal data are given in Table 1. The intensities of an independent data set were measured as outlined in Table 2. Absorption corrections [4] were applied (T range 0.136–0.243).

The structure was solved by use of MULTAN [5,6]. At this stage it was apparent that there were two independent cations and anions in the unit cell. Furthermore, there was scrambling of the Cl and Br atoms at all halogen sites in the anions, so they were regarded as Br atoms with reduced occupancies which were refined in the least-squares analysis. Examination of cation **2** revealed two peaks (one with an electron density of a Cl atom and the other with an electron density comparable with that of a C atom) midway between Ir(2) and the C_5Me_5 ring. This suggested

TABLE 1

CRYSTAL DATA FOR $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+$ $[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ ($x = \sim 1.5$) AT 18°C

$C_{19}H_{17}Br_{1.5}Cl_{2.5}IrO_8Re_2$
Crystal system: monoclinic
Space group: $P2_1/n$ [a]
a 17.841(2) Å
b 17.576(2) Å
c 19.994(3) Å
β 116.32(1)°
V 5619.4 Å^3
$FW = 1144.43$
$Z = 8$
ρ_{obs} [b] 2.63 g cm^{-3}
ρ_{calc} 2.705 g cm^{-3}
μ 158.14 cm^{-1}

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[a] Non-standard form of $P2_1/c$. Equivalent positions (x,y,z), $(\bar{x},\bar{y},\bar{z})$ $(\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$, $(\frac{1}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z)$. [b] By flotation in $CHBr_3$/hexane.

TABLE 2

DATA COLLECTION AND REFINEMENT

Diffractometer:	Enraf–Nonius CAD4F
Radiation:	Mo-K_α, graphite monochromator
λ of radiation:	0.70930 Å (α_1); 0.71359 Å (α_2)
Scan mode:	Coupled $\omega - 2\theta$
Scan width:	0.25° in ω. Also corrected for $\alpha_1 - \alpha_2$ dispersion
Scan speeds:	2.0–0.37° min^{-1} in ω
Background:	scan extended by 25% on each side
2θ range:	0–40°
Size of crystal:	0.12×0.12×0.25 mm
Total no. reflections:	5220
Reflections with $I > 2.3\sigma(I)$:	3685
No. variables:	361

Final $R_F = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.031$
Final $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma F_o^2]^{1/2} = 0.034$
$GOF = [\Sigma w(|F_o| - |F_c|)^2/(\text{no. observations} - \text{no. variables})]^{1/2} = 1.06$
$w = 1/[(\sigma(F_o))^2 + 0.0004F_o^2]$

that cation 2 was disordered. The occupancy of Ir(2) was, therefore, reduced to 0.85 and two Ir atoms of occupancies 0.10 (Ir(3)) and 0.05 (Ir(4)) were placed at the sites of the residual peaks *. These three occupancies were refined in the resulting least-squares analysis and constrained to a total of 1.0.

Idealized positions for the hydrogen atoms were calculated geometrically and were included in the full-matrix least-squares refinement as fixed-atom contributors. The Ir (except Ir(3) and Ir(4)), Re, Br, and Cl atoms were refined with anisotropic temperature factors while the O and C atoms were kept isotropic. An extinction parameter [7] was introduced. The refinement converged at $R_F = 0.031$ with all shift-to-error ratios < 0.01 in the final cycle. All features in a final difference map were of magnitude $< 0.8(2)$ e Å^{-3}. Neutral-atom scattering factors with anomalous dispersion corrections were used [8]. Computer programs were run on a VAX 11/750 computer [6].

Results and discussion

Reaction of $Cp^{\star}Ir(CO)_2$, $[Re(CO)_4Br]_2$, and CH_2Cl_2 at 60 °C over a period of 5 d resulted in the formation of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+$ $[(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ ($x = \sim 1.5$) (**1**). No intermediate species in the reaction were detected by infrared spectroscopy. Compound **1** crystallized from CH_2Cl_2/hexane as air-stable, colorless crystals which were insoluble in non-polar organic solvents. The all chloro analogue of **1**, $[(\eta^5\text{-}C_5Me_5)Ir(CO_2)(CH_2Cl)]^+$ $[(\mu\text{-}Cl)_3Re_2(CO)_6]^-$ (**2**), was similarly synthesized at 100 °C with a correspondingly shorter reaction period (the yield was 76%).

Crystal structure of 1

The structure of **1** was determined by conventional X-ray diffraction techniques. Crystal data, data collection and refinement, interatomic distances and angles, and fractional coordinates for non-hydrogen atoms are given in Tables 1–4, respectively. The unit cell consists of two ion pairs. An atomic thermal ellipsoid plot of the non-disordered cation and one anion are shown in Figs. 1 and 2 respectively which also gives the labelling scheme employed. (The numbering schemes for the second cation and anion are analogous to those shown for the first cation in Fig. 1 and anion in Fig. 2.) The structure reveals that CH_2Cl_2 has been cleaved into the fragments CH_2Cl and Cl, the first of which is bonded to the iridium atom and the second incorporated into the binuclear rhenium anion.

The cation exists in two conformational forms in the solid-state, one with the Cl atom of the CH_2Cl group directed away from the plane of the $Cp^{\star}$ ring (Fig. 1), the other where the C–Cl bond is approximately parallel to this plane. The Ir–C(chloromethyl) bond lengths of 2.11(2) and 2.07(3) Å may be compared to the value of 2.09(2) Å found for the Pt–C bond in $Pt(CH_2I)(I)(PPh_3)_2$ [9]. The average Ir–C($Cp^{\star}$) distances for **1** are slightly contracted with respect to the Ir^{I} compounds $Cp^{\star}Ir(CO)_2$ [10] and $Cp^{\star}(OC)_2IrW(CO)_5$ [1] (2.23 vs. 2.26 and 2.27 Å, respectively) although the differences are not significant. These distances are longer than those in

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[*] Since the iridium sites form an approximate equilateral triangle displaced towards the $Cp^{\star}$ of the cation it is difficult to rationalize this disorder without invoking some change of composition. This is clearly not a fully satisfactory situation.

TABLE 3

SELECTED DISTANCES (Å) AND ANGLES (°) FOR **1** [a,b]

	n = 1	*n* = 2		*n* = 1	*n* = 2
Ir(*n*)–C(*n*1)	1.82(2)	1.80(3)	Ir(*n*)–C(*n*5)	2.23(2)	2.21(2)
Ir(*n*)–C(*n*2)	1.88(2)	1.85(3)	Ir(*n*)–C(*n*6)	2.25(2)	2.21(2)
Ir(*n*)–C(*n*3)	2.11(2)	2.07(3)	Ir(*n*)–C(*n*7)	2.23(2)	2.23(2)
C(*n*1)–O(*n*1)	1.18(2)	1.19(3)	Ir(*n*)–C(*n*8)	2.26(2)	2.22(2)
C(*n*2)–O(*n*2)	1.16(2)	1.18(3)	Ir(*n*)–C(*n*9)	2.21(2)	2.18(2)
C(*n*3)–Cl(*n*3)	1.80(2)	1.79(3)			
Re(*n*1)–X(*n*1)	2.639(2)	2.637(2)	Re(*n*2)–X(*n*1)	2.630(2)	2.637(2)
Re(*n*1)–X(*n*2)	2.642(2)	2.560(3)	Re(*n*2)–X(*n*2)	2.619(2)	2.564(3)
Re(*n*1)–X(*n*3)	2.574(3)	2.560(3)	Re(*n*2)–X(*n*3)	2.590(3)	2.585(3)
Re(*n*1)–C(*n*11)	1.83(2)	1.82(2)	Re(*n*2)–C(*n*21)	1.86(2)	1.81(2)
Re(*n*1)–C(*n*12)	1.86(2)	1.85(2)	Re(*n*2)–C(*n*22)	1.80(2)	1.90(2)
Re(*n*1)–C(*n*13)	1.83(2)	1.87(2)	Re(*n*2)–C(*n*23)	1.81(2)	1.86(2)
C(*n*11)–O(*n*11)	1.20(2)	1.20(2)	C(*n*21)–O(*n*21)	1.18(3)	1.23(2)
C(*n*12)–O(*n*12)	1.19(2)	1.18(2)	C(*n*22)–O(*n*22)	1.21(3)	1.15(3)
C(*n*13)–O(*n*13)	1.20(2)	1.19(3)	C(*n*23)–O(*n*23)	1.22(2)	1.18(3)
Re(*n*1) ··· Re(*n*2)	3.428(1)	3.390(1)			
Cp(*n*)–Ir(*n*)–C(*n*1)	126.2	129.1	C(*n*1)–Ir(*n*)–C(*n*2)	93.7(8)	91.2(12)
Cp(*n*)–Ir(*n*)–C(*n*2)	127.0	125.5	C(*n*1)–Ir(*n*)–C(*n*3)	89.2(7)	87.6(11)
Cp(*n*)–Ir(*n*)–C(*n*3)	120.8	123.2	C(*n*2)–Ir(*n*)–C(*n*3)	88.8(7)	87.8(11)
Ir(*n*)–C(*n*1)–O(*n*1)	174 (2)	167 (2)	Ir(*n*)–C(*n*3)–Cl(*n*3)	116.3(9)	114.6(13)
Ir(*n*)–C(*n*2)–O(*n*2)	174 (2)	169 (2)			
X(*n*1)–Re(*n*1)–X(*n*2)	81.42(7)	81.93(8)	X(*n*1)–Re(*n*2)–X(*n*2)	82.03(8)	81.83(8)
X(*n*1)–Re(*n*1)–X(*n*3)	81.54(9)	82.11(8)	X(*n*1)–Re(*n*2)–X(*n*3)	81.40(8)	81.64(8)
X(*n*2)–Re(*n*1)–X(*n*3)	81.87(9)	81.95(10)	X(*n*2)–Re(*n*2)–X(*n*3)	82.01(9)	81.38(10)
Re(*n*1)–X(*n*1)–Re(*n*2)	81.16(7)	80.00(6)	Re(*n*1)–X(*n*3)–Re(*n*2)	83.17(9)	82.43(9)
Re(*n*1)–X(*n*2)–Re(*n*2)	81.32(7)	82.84(9)			

[a] Cp(*n*) is the centroid of atoms C(*n*5)–C(*n*9): Cp(1) = 0.0792, 0.5194, 0.2539; Cp(2) = 0.8938, 0.0684, 0.3031. [b] Within the disordered cation **2** Ir(2) ··· Ir(3) 1.41(1) Å; Ir(2) ··· Ir(4) 1.19(2) Å; Ir(3) ··· Ir(4) 1.16(2) Å.

the Ir^{III} compounds $[Cp^{\star}Ir(X)_2]_2$ (average Ir–C: X = Cl, 2.132; X = Br, 2.148; X = I, 2.172 Å) [11]. However, these distances are known to be sensitive to the nature of the ligands *trans* to the Cp* ring [12].

There are also two independent anions in the unit cell. The values obtained for the halide occupancies suggest that each anion is predominantly, if not completely, a composite of $[(\mu\text{-Cl})_2(\mu\text{-Br})Re_2(CO)_6]^-$ and $[(\mu\text{-Cl})(\mu\text{-Br})_2Re_2(CO)_6]^-$ and, furthermore, that the Cl and Br atoms are unequally distributed over all the halide sites. The thermal parameters are remarkably small and isotropic; the final electron density difference map was generally flat in these areas which confirms that our simple, single atom site model for the bridging groups in the anion is satisfactory. The anions exhibit slightly different overall compositions but both have confacial bis-octahedral structures. The nonbonding Re ··· Re separations (3.390(1) and 3.428(2) Å) are different from what would be expected from the variation in composition alone, which may indicate that this distance is sensitive to packing forces. Distances of 3.34 [13] and 3.375(1) Å (**1**) [14] have previously been reported for the trichloro anion and 3.46 Å for the tribromo analogue [13]. The fact that the Cl/Br ratio in the anions of **1** was calculated to be greater than 1/2 suggests that

(Continued on p. 262)

TABLE 4

FINAL ATOMIC COORDINATES FOR THE NON-HYDROGEN ATOMS OF 1

Atom	x	y	z	B_{eq}/B
Re(11)	0.28187(4)	0.29503(4)	0.99895(4)	3.92(4) [a]
Re(12)	0.46124(5)	0.19204(4)	1.04517(4)	3.98(4) [a]
X(11) [b]	0.41909(14)	0.28484(13)	1.12602(13)	5.00(14) [a]
X(12) [b]	0.39294(15)	0.29897(14)	0.94513(14)	5.02(16) [a]
X(13) [b]	0.30663(19)	0.15088(17)	0.99765(17)	4.95(21) [a]
C(111)	0.1910(12)	0.2940(11)	0.9072(11)	5.3(4)
O(111)	0.1332(8)	0.2948(8)	0.8463(8)	6.9(3)
C(112)	0.2109(12)	0.2880(10)	1.0441(10)	5.3(4)
O(112)	0.1652(8)	0.2798(7)	1.0723(7)	6.8(3)
C(113)	0.2743(12)	0.3986(11)	1.0023(11)	5.4(5)
O(113)	0.2693(8)	0.4662(8)	1.0040(8)	7.1(3)
C(121)	0.4823(12)	0.1258(12)	0.9826(12)	6.4(5)
O(121)	0.4931(9)	0.0835(8)	0.9423(8)	7.5(4)
C(122)	0.5028(12)	0.1220(11)	1.1183(11)	5.5(5)
O(122)	0.5364(8)	0.0774(8)	1.1692(8)	6.9(3)
C(123)	0.5649(12)	0.2311(11)	1.0752(10)	5.3(4)
O(123)	0.6348(9)	0.2562(8)	1.0938(8)	7.5(4)
Re(21)	0.71723(4)	0.78957(4)	0.52071(4)	3.42(4) [a]
Re(22)	0.56068(4)	0.66683(4)	0.49664(4)	3.91(4) [a]
X(21) [b]	0.55490(12)	0.81340(11)	0.46646(12)	4.38(13) [a]
X(22) [b]	0.69004(18)	0.70860(17)	0.61413(16)	4.85(19) [a]
X(23) [b]	0.66775(18)	0.66837(17)	0.44214(17)	5.26(20) [a]
C(211)	0.8269(12)	0.7629(10)	0.5560(10)	4.9(4)
O(211)	0.8990(9)	0.7448(8)	0.5794(7)	6.9(3)
C(212)	0.7266(11)	0.8451(10)	0.4459(10)	4.8(4)
O(212)	0.7293(8)	0.8817(8)	0.3974(8)	6.7(3)
C(213)	0.7471(11)	0.8727(11)	0.5858(11)	5.1(4)
O(213)	0.7653(8)	0.9233(8)	0.6287(8)	7.1(4)
C(221)	0.5804(11)	0.5671(11)	0.5214(10)	5.1(4)
O(221)	0.5983(8)	0.5004(8)	0.5391(7)	6.4(3)
C(222)	0.4674(12)	0.6414(11)	0.4056(11)	5.5(5)
O(222)	0.4130(9)	0.6250(8)	0.3491(8)	7.1(3)
C(223)	0.4902(12)	0.6722(11)	0.5423(11)	6.0(5)
O(223)	0.4451(9)	0.6754(8)	0.5710(8)	7.9(4)
Ir(1)	0.13550(4)	0.45594(4)	0.21499(4)	3.18(4) [a]
C(11)	0.1267(12)	0.4592(11)	0.1207(11)	5.7(5)
O(11)	0.1130(8)	0.4625(8)	0.0575(8)	6.9(3)
C(12)	0.1426(12)	0.3490(11)	0.2205(11)	5.6(5)
O(12)	0.1397(8)	0.2831(8)	0.2241(7)	6.1(3)
C(13)	0.2667(10)	0.4603(10)	0.2574(9)	4.3(4)
Cl(13)	0.3128(3)	0.3955(3)	0.2161(3)	6.0(3) [a]
C(15)	0.1438(10)	0.5559(10)	0.2870(9)	4.0(4)
C(151)	0.2161(11)	0.6047(10)	0.3296(10)	5.3(5)
C(16)	0.0806(10)	0.5713(9)	0.2154(9)	4.0(4)
C(161)	0.0748(11)	0.6394(11)	0.1675(11)	5.6(5)
C(17)	0.0169(10)	0.5142(9)	0.1967(9)	3.7(4)
C(171)	−0.0688(11)	0.5150(10)	0.1270(10)	5.2(4)
C(18)	0.0369(10)	0.4658(9)	0.2565(9)	3.5(4)
C(181)	−0.0138(11)	0.4016(10)	0.2648(10)	5.3(4)
C(19)	0.1179(9)	0.4899(9)	0.3137(9)	3.3(3)
C(191)	0.1621(11)	0.4560(10)	0.3920(10)	5.0(4)
Ir(2) [c]	0.86280(5)	0.00843(5)	0.21846(5)	4.14(6) [a]
Ir(3) [c]	0.8511(6)	0.0014(6)	0.2835(6)	2.9(4)

TABLE 4 (continued)

Atom	x	y	z	B_{eq}/B
Ir(4) [c]	0.8472(10)	0.0574(13)	0.2513(11)	3.6(8)
C(21)	0.9189(17)	−0.0102(15)	0.1643(15)	9.8(7)
O(21)	0.9695(12)	−0.0221(11)	0.1418(11)	12.3(6)
C(22)	0.7628(17)	0.0158(15)	0.1327(15)	9.4(7)
O(22)	0.6944(12)	0.0259(10)	0.0851(11)	11.1(5)
C(23)	0.8418(16)	−0.1076(15)	0.2170(14)	10.0(7)
Cl(23)	0.7447(6)	−0.1331(4)	0.2173(4)	13.2(7) [a]
C(25)	0.8983(13)	0.0096(11)	0.3392(13)	5.6(5)
C(251)	0.9122(14)	−0.0512(14)	0.3945(13)	8.1(6)
C(26)	0.9645(13)	0.0441(11)	0.3269(11)	5.7(5)
C(261)	1.0505(18)	0.0220(16)	0.3603(16)	11.0(8)
C(27)	0.9291(12)	0.1122(11)	0.2809(11)	5.2(4)
C(271)	0.9797(16)	0.1674(15)	0.2644(15)	10.4(8)
C(28)	0.8492(12)	0.1184(14)	0.2665(11)	5.6(5)
C(281)	0.7939(15)	0.1830(14)	0.2303(14)	9.1(7)
C(29)	0.8281(14)	0.0553(14)	0.3018(13)	6.9(5)
C(291)	0.7450(14)	0.0436(13)	0.3092(12)	7.8(6)

[a] B_{eq} is the arithmetic mean of the principal axes of the atomic thermal ellipsoid. [b] Halogen sites in the anions were treated as bromine atoms with partial occupancies. The final refined values for the occupancies are given below. The percent Cl and percent Br at each site were calculated from these occupancies and are given in square brackets.

		Cl Br			Cl Br
X(11)	0.854(6)	[28%, 72%]	X(21)	0.869(5)	[25%, 75%]
X(12)	0.800(6)	[39%, 61%]	X(22)	0.639(5)	[70%, 30%]
X(13)	0.640(6)	[70%, 30%]	X(23)	0.662(6)	[66%, 34%]

The proportion of Cl/Br in the anions obtained by this method is 2.98/3.02. [c] The final refined occupancies for the Ir atoms in cation 2 are: Ir(2) 0.882(3); Ir(3) 0.073(3); Ir(4) 0.044(4).

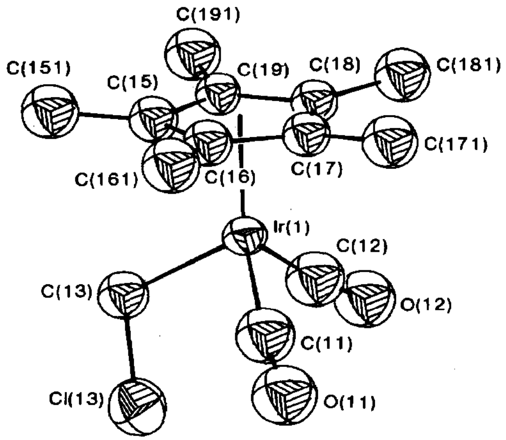


Fig. 1. Atomic thermal ellipsoid diagram (with the numbering scheme) of one of the cations of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+[\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ ($x = \sim 1.5$). Hydrogen atoms have been omitted.

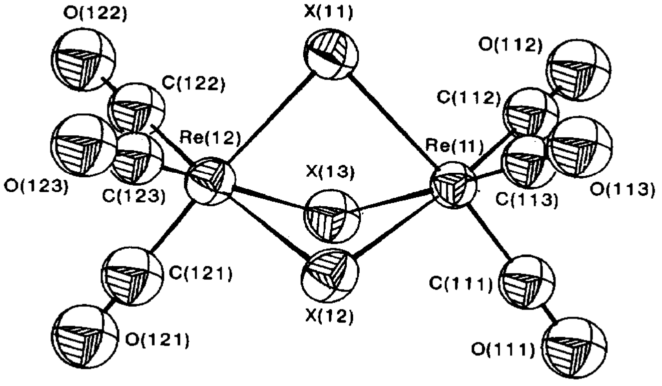


Fig. 2. Atomic thermal ellipsoid diagram (with the numbering scheme) of one of the anions of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+ [(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}Re_2(CO)_6]^-$ ($x = \sim 1.5$).

partial exchange of Br for Cl from the solvent occurred. There is some support for this from the carbon/hydrogen analyses of **1** (Experimental) (A chlorine/bromine analysis of **1** was not attempted). Recrystallization of $[(\eta^5\text{-}C_5Me_5)Rh(Br)](\mu\text{-}Br)_2$ from 1,2-dichloroethane was found to result in halogen exchange [15].

Spectroscopic properties of 1

The spectroscopic properties of **1** in solution are consistent with the structure found in the solid state. The infrared spectrum in the carbonyl region consists of four bands. The two most intense bands which are also at lower frequency (2022 and 1916 cm^{-1}) are assigned to the anion, in agreement with the literature values for the unmixed halogen-bridged anions [16]. For example, carbonyl absorptions at 2030 and 1917 cm^{-1} in CH_2Cl_2 have been reported for $[Et_4N]^+ [(\mu\text{-}Cl)_3Re_2(CO)_6]^-$. Although the anion in **1** lacks rigorous C_{3v} symmetry, no asymmetry of the two carbonyl bands attributed to this anion was detected. The other two bands in the spectrum, at 2117 and 2080 cm^{-1}, are assigned to the cation; the higher frequencies of these bands are consistent with the positive charge on the species. The ^1H NMR spectrum of **1** at ambient temperature in $CDCl_3$ shows a signal at δ 4.14 attributed to the CH_2Cl ligand. This value is within the range of values previously reported [9,17,18] for neutral chloromethyl complexes and is comparable to the value of 3.95 ppm found for this ligand in the Ir^{III} compound $Ir(CO)(PMe_3)_2(Cl)_2(CH_2Cl)$ [19]. In the $^{13}C\{^1H\}$ NMR spectrum of **1** (CH_2Cl_2/CD_2Cl_2) solution, the resonance at 8.62 ppm is assigned to the CH_2Cl group. In $(\eta^5\text{-}C_5Me_5)Co(CO)(CH_2Cl)Cl$ the corresponding resonance was observed at 42.6 ppm [18]. However, it is well known that there is a shift to higher field of the ^{13}C resonance of the coordinated carbon of a ligand when the metal is replaced by the member lower in the group [20]. The carbonyl region consists of a sharp singlet at 159.3 ppm assigned to the two Ir bound carbonyls, and a broad signal centered at 193 ppm assigned to the Re-bound carbonyls. The broadening is presumed due to interaction of the carbon atoms with the quadrupolar Re nuclei. When a ^{13}CO-enriched sample of **1** was cooled to −83°C the broad signal was resolved into two signals at 193.9 and 192.4 ppm (in an approximate ratio of 1/2). It is uncertain whether the two signals can be attributed to two types of anion present or if it reflects different halide atoms *trans* to a particular carbonyl. Although the ^{13}CO-enriched sample was prepared from unenriched $Cp^{\star}Ir(CO)_2$ and ^{13}CO-enriched $[Re(CO)_4Br]_2$, it was found that the label was distributed over all the available carbonyl sites in the compound. This observation is discussed in more detail below.

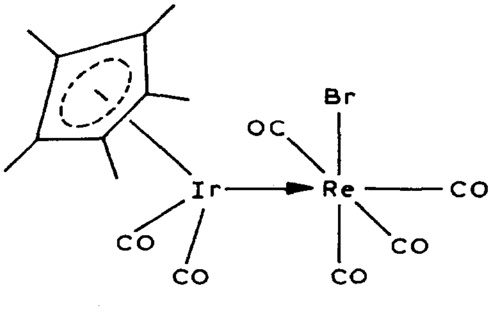
The spectroscopic properties of **2** are essentially the same as those of **1**, although the $^{13}C\{^1H\}$NMR spectrum of **2** was not investigated at low temperatures.

Comments on the mechanism of formation of 1

Cleavage of the carbon halogen bond of a methyl halide by a nucleophilic transition metal complex to give an ionic product is well established. For example, $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ itself reacts with methyl iodide to give $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_3)]^+ I^-$ [21]. However, the similar cleavage of the carbon chlorine bond in CH_2Cl_2 by an organometallic complex is only known in a few cases [22].

Labinger, Osborn and Coville found that CH_2Cl_2 oxidatively adds to *trans*-$IrCl(CO)(PMe_3)_2$ although the reaction required ultraviolet irradiation [19]. In accord with their other studies, a radical mechanism was implicated. They observed no thermal reaction between these two reagents. In contrast, the formation of **1** occurred via a thermal reaction between CH_2Cl_2 and $Cp^{\star}Ir(CO)_2$ in the presence of $[Re(CO)_4Br]_2$. The reaction between $Cp^{\star}Ir(CO)_2$ and CH_2Cl_2 in the absence of the last reagent is extremely slow * which suggests the rhenium complex plays an important role as a non-coordinating halide abstractor. Simple Lewis acids such as H^+ and Ag^+ were found to form adducts with the basic $Cp^{\star}Ir(CO)_2$ molecule. (The Lewis basicity of $CpIr(CO)(PPh_3)$ has been investigated [23].) It was also found that $[Re(CO)_4Br]_2$ readily gave $[(\mu\text{-}Cl)(\mu\text{-}Br)_2Re_2(CO)_6]^-$ when stirred with $[(Ph_3P)_2N][Cl]$ in CH_2Cl_2 at 60°C for 8 h, in an evacuated, sealed flask. The present evidence, therefore, is not inconsistent with a mechanism that proceeds by the ionic intermediate, $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)]^+ Cl^-$. This in turn could arise from the η^3-Cp* intermediate $(\eta^3\text{-}C_5Me_5)Ir(CO)_2(CH_2Cl)(Cl)$, followed by extrusion of Cl^-. Note these intermediates and the cation of **1** formally involve Ir^{III} and the $(CH_2Cl)^-$ ligand. It may, therefore, not be correct to view the carbon–chlorine cleavage as heterolytic i.e., into the fragments $(CH_2Cl)^+$ and Cl^-.

Another possibility is that the cleavage occurs by the reaction of CH_2Cl_2 with the intermediate complex **3** with an Ir–Re donor–acceptor bond.



(3)

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* The products from this latter reaction have not been identified, but it is suspected that they are the oxidative-addition derivatives $Cp^{\star}Ir(CO)(CH_2Cl)(Cl)$ and $Cp^{\star}Ir(CO)(Cl)_2$, and $[Cp^{\star}Ir(Cl)_2]_2$.

Attempts to prepare **3** by an alternate route have so far proven unsuccessful. However, preliminary results from this laboratory indicate that a complex with an Os–Re donor–acceptor bond reacts with CH_2Cl_2 under similar conditions to yield a product analogous to **1**. This reaction may proceed by initial dissociation of the Os–Re bond before reaction with CH_2Cl_2. This type of dissociation for compounds with donor–acceptor metal–metal bonds has been observed [24].

If the formation of **1** does proceed via intermediate **3**, it could account for the ^{13}CO scrambling described above. In $Cp^\star(OC)_2IrW(CO)_5$, a complex closely related to **3**, the carbonyls undergo exchange in solution at a rate which is rapid by ^{13}C NMR spectroscopy [1]. The scrambling could, however, be explained by the $[Cp^\star Ir(CO)_2(CH_2Cl)]^+$ undergoing exchange with the ^{13}CO liberated in the formation of $[(\mu\text{-}Cl)(\mu\text{-}Br)_2Re_2(CO)_6]^-$. It was observed that both the cation and anion of unenriched **1** underwent exchange with ^{13}CO when **1** was stirred in CH_2Cl_2 under 1 atm of ^{13}CO at 60°C.

Further studies on the mechanism of this reaction are planned.

Acknowledgements

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Additional Material. Atomic thermal ellipsoid views of both cations and anions of **1**; tables of, atomic coordinates for hydrogen atoms, final temperature factors and least-squares planes; and a listing of observed-calculated structure factors for **1** (38 pages) are available on request from F.W.B.E.

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