acetonitrile N atom is significantly bent away from 180°, whilst the sequence N(1)–C(10)–C(11) is linear.

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Structure of Bis(1,5-cyclooctadiene)rhodium(I) Hexacarbonyl-tri-μ-chloro-dirhenate(I)

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Abstract. $[Rh(C_8H_{12})_2]^+ \cdot [Re_2(CO)_6Cl_3]^-$, $M_r = 966 \cdot 07$, monoclinic, $P2/n$ (non-standard setting of $P2/c$, No. 13), $a = 11 \cdot 221$ (3), $b = 7 \cdot 018$ (2), $c = 16 \cdot 562$ (6) Å, $\beta = 91 \cdot 30$ (3)°, $V = 1303 \cdot 9$ (7) Å^3, $Z = 2$, $D_m = 2 \cdot 30$ (10), $D_x = 2 \cdot 46$ g cm^{-3}, λ(Mo $K\alpha$) = $0 \cdot 71073$ Å, $\mu = 107 \cdot 45$ cm^{-1}, $F(000) = 900$, $T = 297$ K. Final $R_F = 0 \cdot 053$ for 2448 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$. The crystal structure of the title compound consists of $(C_8H_{12})_2Rh^+$ cations and $(CO)_3$-$ReCl_3Re(CO)_3^-$ anions. The 1,5-cyclooctadiene ligands are chelated to the Rh atom. The coordination about rhodium is square planar and the olefin midpoint distances are $2 \cdot 128$ (13) and $2 \cdot 131$ (14) Å. The Re atoms display pseudo-octahedral coordination bridged by the three Cl atoms. The carbonyl groups occupy the non-bridging positions about the Re atom, Re—Cl = $2 \cdot 506$ (3) and $2 \cdot 524$ (3) Å, Re—Re = $3 \cdot 380$ (1) Å, Re—C$_{av}$ = $1 \cdot 89$ (1) Å.

Introduction. In conjunction with a study of potential catalytic properties of bimetallic compounds the title compound was synthesized and found to function in a limited manner as a hydrogenation, isomerization or polymerization catalyst for certain cyclic poly-

olefins. To gain a better understanding of their catalytic properties we have been studying the structures of these bimetallic ionic compounds and report here the synthesis and structure of the title compound.

Experimental. $[Rh(C_8H_{12})_2]^+ \cdot [Re_2(CO)_6Cl_3]^-$ was prepared by the addition of $0 \cdot 100$ g ($0 \cdot 203$ mmol) of $[Rh(C_8H_{12})Cl]_2$ to $0 \cdot 30$ ml ($0 \cdot 250$ mmol) of 1,5-cyclooctadiene and $0 \cdot 300$ g ($0 \cdot 420$ mmol) of $[Re(CO)_4Cl]_2$ in 20 ml of dichloromethane. D_m measured pycnometrically in water. The red solution was stirred for 24 h and upon evaporation dark-red diamond-shaped prismatic crystals separated from the mixture. Crystal size $0 \cdot 23 \times 0 \cdot 24 \times 0 \cdot 04$ mm, ω–2θ scan with a maximum 2θ value of $57 \cdot 5°$ ($h = 0$ to ± 15, $k = 0$ to ± 9, $l = -22$ to 21) on a Picker four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections (400, 040, 006) monitored every sixty reflections, showed small random variations ($2 \cdot 5$, $5 \cdot 0$ and $1 \cdot 7\%$ respectively). Twelve non-collinear reflections were measured and their setting angles were fitted by a least-squares program to give the orientation matrix and cell dimension constants. Data were corrected for Lorentz and polarization effects. The compound has a linear absorption coefficient $\mu = $

107·45 cm^{-1} for Mo $K\alpha$ and the intensity data were corrected for absorption effects by the method of Templeton & Templeton (1973), max./min. correction = 0·65/0·11. 15 533 reflections were measured and after averaging 2448 were unique $[F_o^2 > 3\sigma(F_o^2)]$. The space group was $P2/n$ (systematic absences: $h0l$, $h + l$ = odd). Scattering factors, including anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were carried out using a locally written program (Baenziger, 1975). Illustrations were drawn by use of *ORTEP* (Johnson, 1965). The structure was solved by the Patterson method which provided the locations of the Rh, Re and Cl atoms. All other non-H atoms were positioned by Fourier synthesis methods. The final solution utilized a full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms, and a common isotropic temperature factor for H atoms which were placed in geometrically calculated positions (C—H = 0·95 Å).

The function minimized was $\sum w(\Delta F)^2$ where $w = 1/\sigma^2$ and σ is the estimated standard deviation of F_{obs}, final $R = 0·053$, $wR = 0·059$, goodness of fit = 3·98. A final ΔF map showed no peaks greater than

Table 1. *Positional parameters for the symmetrically unique non-H atoms in bis(1,5-cyclooctadiene)-rhodium(I) tri-μ-chlorohexacarbonyldirhenate(I)*

$$B_{iso} = 1/3(B_{22}) + (B_{11} + B_{33} + 2B_{13}\cos\beta)/3\sin^2\beta.$$

	x	y	z	$B_{iso}(\text{Å}^2)$
Rh	0·5000	0·5000	0·0000	3·9
C(1)	0·6868 (10)	0·585 (3)	−0·0154 (7)	7·7
C(2)	0·6447 (12)	0·707 (2)	0·0360 (13)	8·4
C(3)	0·6491 (7)	0·721 (5)	0·1199 (17)	13·9
C(4)	0·614 (3)	0·565 (4)	0·1676 (9)	15·0
C(5)	0·5484 (10)	0·404 (3)	0·1234 (7)	6·4
C(6)	0·5959 (16)	0·279 (2)	0·0755 (9)	7·9
C(7)	0·709 (2)	0·250 (4)	0·0512 (10)	14·1
C(8)	0·7667 (10)	0·421 (3)	0·0122 (13)	9·8
Re	0·12539 (3)	−0·0133 (6)	0·19075 (2)	3·7
Cl(1)	0·2500	0·2538 (5)	0·2500	4·4
Cl(2)	0·3316 (2)	−0·1374 (4)	0·1697 (1)	4·7
C(9)	0·0457 (10)	−0·239 (2)	0·1535 (6)	6·4
C(10)	0·1050 (9)	0·091 (2)	0·0858 (6)	5·4
C(11)	−0·0265 (10)	0·079 (2)	0·2132 (6)	6·2
O(9)	−0·0001 (1)	−0·3816 (17)	0·1363 (5)	8·5
O(10)	0·0891 (8)	0·1491 (18)	0·0212 (5)	8·6
O(11)	−0·1208 (6)	0·146 (2)	0·2258 (5)	9·6
M(1,2)*	0·6658	0·646	0·0103	
M(5,6)*	0·5722	0·342	0·0994	

* M is the midpoint of the olefin bonds in the C_8H_{12} ligand.

0·85 of the value of a hydrogen peak for distances greater than 0·83 Å from the metal atoms.

Discussion. The numbering scheme for the cation is shown in Fig. 1 and for the anion in Fig. 2. Final positional and thermal parameters are listed in Table 1.* Bond lengths and angles are given in Table 2.

The compound consists of $(1,5\text{-}C_8H_{12})_2Rh^+$ cations possessing an inversion center and $(CO)_3$-$ReCl_3Re(CO)_3^-$ anions, possessing twofold symmetry. The coordination of rhodium is essentially square planar with each of the 1,5-cyclooctadiene molecules chelated to the metal. The distances from the rhodium to the midpoints of the olefin bonds are 2·128 (13) and 2·131 (14) Å. The rhodium cation is the same as that prepared previously (Green, Kuc & Taylor, 1970, 1971; Green & Parker, 1974; Uson, Oro, Claver & Garralda, 1976; Schrock & Osborn, 1971) and the configuration conforms to the predictions based on semi-empirical molecular orbital calculations (Rösch & Hoffmann, 1974).

The anion $[Re_2(CO)_6Cl_3]^-$ is comprised of two symmetry equivalent Re atoms bridged by three Cl atoms. Three carbonyl groups are bound to each rhenium to complete the pseudo-octahedral configuration about rhenium. An analogous rhenium bromo

Fig. 1. A perspective view and numbering scheme for the $[Rh(1,5\text{-}C_8H_{12})_2]^+$ cation (*ORTEP* drawings, 25% probability ellipsoids). Primed atoms are related to those unprimed by inversion center of symmetry at the Rh atom.
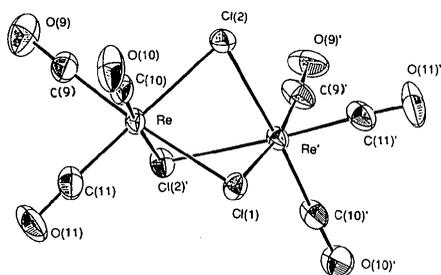
Fig. 2. A perspective view and numbering scheme for the $[Re(CO)_6Cl_3]^-$ anion (*ORTEP* drawings, 25% probability ellipsoids). Primed atoms are related to those unprimed by a twofold axis passing through Cl(1) and the midpoint of the Re–Re vector.

* Lists of temperature factor parameters, a table of calculated and observed structure factors, and a table of hydrogen atom positions and tables of non-bonded distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53505 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Rh—C(1)	2·198 (10)	C(1)—C(8)	1·524 (29)
Rh—C(2)	2·251 (13)	C(1)—C(2)	1·302 (22)
Rh—C(3)	3·005 (20)	C(2)—C(3)	1·393 (29)
Rh—C(4)	3·074 (15)	C(3)—C(4)	1·410 (40)
Rh—C(5)	2·210 (11)	C(4)—C(5)	1·528 (33)
Rh—C(6)	2·254 (14)	C(5)—C(6)	1·303 (21)
Rh—C(7)	3·037 (15)	C(6)—C(7)	1·354 (26)
Rh—C(8)	3·047 (12)	C(7)—C(8)	1·514 (31)
Rh—M(1,2)	2·128 (13)	C(n)—H(n)	0·950
Rh—M(5,6)	2·133 (14)		
Re—Cl(1)	2·524 (3)	Re—C(11)	1·867 (12)
Re—Cl(2)	2·504 (2)	C(9)—O(9)	1·158 (15)
Re—Cl(2)'	2·506 (3)	C(10)—O(10)	1·155 (12)
Re—C(9)	1·914 (13)	C(11)—O(11)	1·181 (14)
Re—C(10)	1·896 (11)	Re—Re'	3·380 (1)
M(1,2)—Rh—M(5,6)	82·5	Cl(1)—Re—Cl(2)	78·87 (8)
M(1,2)—Rh—M(5,6)'	97·5	Cl(1)—Re—Cl(2)'	78·82 (8)
M(1,2)—Rh—M(1,2)'	180	Cl(2)—Re—Cl(2)'	81·28 (7)
M(5,6)—Rh—M(5,6)'	180	Re—C(9)—O(9)	175 (1)
Re—Cl(1)—Re'	84·07 (11)	Re—C(10)—O(10)	177 (1)
Re—Cl(2)—Re'	84·83 (6)	Re—C(11)—O(11)	177 (1)

anion has been reported (Davis & Baenziger, 1977); the same D_{3h} structure has also been predicted for the manganese anion, $[Mn_2(CO)_6Cl_3]^-$ (Cihonski, Walker & Levenson, 1975). The Re—Re distance is 3·380 (1) Å, considerably longer than the distance 3·08 Å found for the metal—metal bonded di-rhenium decarbonyl (Dahl, Ishishi & Rundle, 1957; Gapotchenko, Alekseev, Kolobova, Anisimov, Ronova & Johansson, 1972). The Re atoms are bridged by three Cl atoms; however, only two of the Cl atoms are symmetry equivalent. The symmetry unique Cl atom has a Re—Cl bond length of

2·524 (3) Å which is statistically longer than the two nearly identical distances found for the symmetry related pair, 2·504 (2) and 2·506 (3) Å. The variation of 2·524 *vs* 2·505 Å may be due to solid-state packing forces since the Re—Cl distances reported previously (Davis & Baenziger, 1977) indicated equivalent chlorine distances equal to 2·49 Å. The rhenium to carbonyl carbon length average 1·89 (1) Å and the C—O bond distances average 1·16 (1) Å, and within each set the bond lengths are statistically equivalent.

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Simple Oxygen Bridged Ti^IV Dimer: Structure of [Ti(μ-O)(OC6H3-2,6Pr$_2^i$)2(NC5H4-4NC4H8)]2

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Abstract. Di-μ-oxo-bis[bis(2-6-diisopropylphenola-to)-4-pyrrolindylpyridinetitanium], $[Ti_2(C_{24}H_{30}O_2)_2(O)_2(C_9H_{12}N_2)_2]$, $M_r = 1133·3$, triclinic, $P\bar{1}$, $a = 10·245$ (2), $b = 12·160$ (2), $c = 14·030$ (3) Å, $\alpha = 105·35$ (1), $\beta = 96·50$ (1), $\gamma = 110·08$ (1)°, $V = 1542$ (1) Å^3, $Z = 1$, $D_x = 1·22$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·71073$ Å, $\mu = 3·06$ cm^{-1}, $F(000) = 608·0$, $T = 135$ K, $R = 0·061$ for 3092 reflections with $I > 3\sigma(I)$. There is pseudo trigonal bipyramidal geometry around each Ti atom with two aryl oxide O atoms and one bridging O atom forming the trigonal plane. Ti—O(bridge) = 1·847 (av.); Ti—O(aryl oxide) = 1·825 Å (av.); O(bridge)—Ti—O(bridge) = 81·6 (1); Ti—O(bridge)—Ti = 98·4 (1)°; Ti—Ti(non-bonding interaction) = 2·796 (1) Å.

Introduction. We recently reported the isolation and structural characterization of a mononuclear aryl