Synthesis, Reactivity, and Structures of Cationic η^6-Arene Carbonyl Complexes of Rhenium(I). Crystal and Molecular Structures of the Two Isoelectronic 1,3,5-Trimethylbenzene Tricarbonyl Complexes of Rhenium(I) and Tungsten(0) †

Fausto Calderazzo,* Rinaldo Poli, and Aldo Barbati
Istituto Chimica Generale, University of Pisa, Via Risorgimento 35, 56100 Pisa, Italy
Pier Francesco Zanazzi
Dipartimento Scienze della Terra, University of Perugia, Piazza Università, 06100 Perugia, Italy

Cationic arene derivatives of tricarbonylrhenium(I), less methyl substituted than hexamethylbenzene, of general formula $[Re(CO)_3\{C_6H_{6-n}(CH_3)_n\}]^+$ with $[AlBr_4]^-$, $[BPh_4]^-$, or $[Re_2I_8]^{2-}$ as counter anion, have been isolated. The crystal and molecular structure of the trimethylbenzene complex $[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$ has been solved by *X*-ray diffraction methods: monoclinic, space group $P2_1/a$, with unit-cell dimensions $a = 15.687(3)$, $b = 12.876(3)$, $c = 9.690(2)$ Å, $\beta = 101.95(2)°$, and $Z = 4$; $R = 0.046$ for 1 220 observed reflections. The corresponding neutral tungsten(0) complex $[W(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}]$ is monoclinic, space group $P2_1/a$, with unit-cell dimensions $a = 8.959(2)$, $b = 16.979(3)$, $c = 8.797(2)$ Å, $\beta = 118.46(2)°$, and $Z = 4$; $R = 0.036$ for 861 observed reflections. Both complexes have an eclipsed orientation of the carbonyl groups with respect to the methyl substituents on the ring. Reduction of $[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}]^+$ with $[BH_4]^-$ afforded the trimethyl-substituted cyclohexadienyl complex, $[Re(CO)_3\{1,3,5\text{-}C_6H_4(CH_3)_3\}]$.

In connection with our current studies of rhenium(I) complexes [1] it was of interest to investigate the chemistry, reactivity, and structural properties of some $[Re(CO)_3(\eta^6\text{-arene})]^+$ derivatives. First, the arene ligand is rather labile and can be displaced by stronger Lewis bases, thus suggesting that the cationic complexes could be alternative intermediates to $[ReX(CO)_5]$ or $[Re_2X_2(CO)_8]$ and $[Re_2X_2(CO)_6(thf)_2]$ (thf = tetrahydrofuran) [1] in the preparation of compounds containing the $Re(CO)_3$ fragment. Secondly, although arenerhenium(I) tricarbonyl cationic complexes have been known for many years,[2] they have not been studied extensively and structural data on them are limited.[3] Thirdly, arene complexes of general formula $[M(CO)_3(arene)]^{n+}$ (n = 0 or 1) for which arene is 1,3,5-trimethylbenzene have been neglected [4] from a structural point of view and only one *X*-ray diffractometric study has been reported, for $[Mo(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}]$.[5] On the other hand, in view of its three-fold symmetry, this arene ligand is particularly apt for obtaining further data on the problem of ring orientation with respect to the $M(CO)_3$ moiety. Finally, the comparison of a rhenium(I) cationic complex with the corresponding isoelectronic uncharged compound of tungsten was expected to provide information about the effect of charge on the structural parameters of $M(CO)_3$(arene) molecules.

Experimental

All manipulations and reactions involving the metal complexes were carried out under an atmosphere of prepurified nitrogen. Solvents were carefully dried prior to use. Bromopentacarbonylrhenium(I) was prepared according to the literature.[6] Infrared spectra were measured with a Perkin-Elmer model 283 B instrument equipped with grating; each spectrum in the carbonyl-stretching region was calibrated with both CO and water vapour.

Preparations.—$[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$. The compound $[ReBr(CO)_5]$ (0.877 g, 2.159 mmol) was treated with $AlBr_3$ (1.295 g, 4.855 mmol) in 1,3,5-trimethylbenzene (25 cm^3) at 120 °C for 5 h. Gas evolution was noted. After cooling to room temperature, a two-layer system was apparent; the upper layer consisted mainly of unreacted 1,3,5-trimethylbenzene and was siphoned off. To the remaining red-brown viscous liquid, dichloromethane (25 cm^3) was added, which caused crystallization of a pale yellow solid. This was filtered off and dried *in vacuo* (1.12 g, 71% yield calculated as $[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$). From the mother-liquor, well formed crystals, used for the subsequent *X*-ray investigation, were obtained by cooling at about −30 °C.

The toluene and the benzene cationic complexes of rhenium(I) were obtained by similar procedures. The complexes are very sensitive to moisture, and to oxygen-containing Lewis bases (resulting in displacement of the arene ligand). For example, dissolution of the 1,3,5-trimethylbenzene complex in thf resulted in immediate transformation into the complex $[ReBr(CO)_3(thf)_2]$,[1e] as evidenced by the i.r. spectrum. In view of the high sensitivity of the complexes, especially to moisture, no satisfactory elemental analyses could be obtained.

Treatment of the 1,3,5-trimethylbenzene complex with NBu_4Br (about 1.5 mol per mol of complex) at room temperature for about 30 min in dichloromethane solvent led to displacement of the arene ligand and formation of $[Re_2Br_3(CO)_6]^-$, characterized [7] by the carbonyl-stretching vibrations at 2 021 and 1 918 cm^{-1}. Even the measurement of the i.r. spectrum in KBr cells gave rise to the formation of the binuclear bromide-bridged anion.

$[Re(CO)_3(arene)][BPh_4]$. The tetraphenylborate salts were obtained by an exchange reaction with $[NBu_4][BPh_4]$ and the tetrabromoaluminate described above. The preparation of the toluene derivative is reported in detail, the procedure being the same for the benzene complex of Table 1.

The toluene complex $[Re(CO)_3(C_6H_5CH_3)][AlBr_4]$ (0.507 g, 0.715 mmol) was dissolved in dichloromethane (50 cm^3) and treated with a solution of $[NBu_4][BPh_4]$ (0.549 g, 0.977 mmol) in 50 cm^3 of the same solvent. The colourless solid which

---

† *Supplementary data available* (No. SUP 23885, 16 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical and i.r. spectroscopic data for some rhenium(I) tricarbonyl derivatives

Compound	I.r. carbonyl bands (cm^{-1})			Medium	Analysis [a] (%)	
					C	H
$[Re(CO)_3(C_6H_6)][AlBr_4]$ [b]	2 083s		2 017s	CH_2Cl_2	—	—
$[Re(CO)_3(C_6H_5CH_3)][AlBr_4]$ [b]	2 072s		2 004s	CH_2Cl_2	—	—
$[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$ [b]	2 071s		2 003s	CH_2Cl_2	—	—
$[Re(CO)_3(C_6H_6)][BPh_4]\cdot0.5CH_2Cl_2$	2 072s		2 001vs	Nujol	56.9 (56.7)	3.8 (3.8)
$[Re(CO)_3(C_6H_5CH_3)][BPh_4]\cdot0.5CH_2Cl_2$	2 072s		1 992vs	Nujol	56.9 (57.2)	3.9 (4.0)
$[Re(CO)_3(C_6H_5CH_3)]_2[Re_2I_8]$	2 063s	1 997s	1 990s	Nujol	11.2 (11.4)	0.8 (0.8)
$[Re(CO)_3\{1,3,5\text{-}C_6H_4(CH_3)_3\}]$ [c]	2 021s	1 943s	1 932s	n-Hexane	36.7 (36.8)	3.4 (3.3)

[a] Calculated values in parentheses. [b] CaF_2 cells. [c] Trimethylcyclohexadienyl derivative.

precipitated was filtered off and dried *in vacuo* (65% yield). The tetraphenylborate salt was found to be relatively stable in air. In *sym*-tetrachloroethane, it absorbed carbon monoxide at atmospheric pressure at 24.0 °C. The observed CO : Re molar ratio was 1.8 and the typical[8] CO stretching vibrations of $[ReCl(CO)_5]$ were observed in solution (2 153w, 2 045s, and 1 990m cm^{-1}).

$[Re(CO)_3(C_6H_5CH_3)]_2[Re_2I_8]$. The tetrabromoaluminate salt (0.446 g, 0.629 mmol) was added to a dichloromethane (100 cm^3) solution of $[NBu_4]_2[Re_2I_8]$[9] (0.592 g, 0.316 mmol). The brown solid obtained was filtered off and dried *in vacuo* (47% yield). The compound could be handled in air without appreciable decomposition.

Reaction of $[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$ *with* $[BH_4]^-$.—The tetrabromoaluminate salt (0.735 g, 1.00 mmol) suspended in dichloromethane (10 cm^3) was treated with $[N(PPh_3)_2][BH_4]$[10] (0.665 g, 1.20 mmol) at room temperature for a few minutes. The reaction was monitored by i.r. spectroscopy in the carbonyl-stretching region. After evaporation of the solvent under reduced pressure, the solid residue was treated with n-hexane (30 cm^3) and from this solution the colourless cyclohexadienyl derivative crystallized out at ' dry-ice ' temperature; it was filtered off and dried *in vacuo* (40% yield). The i.r. bands in the carbonyl-stretching region are in Table 1. The ^1H n.m.r. spectrum of the product in C_6D_6 showed the presence of the two isomers A and B, corresponding to hydride attack at a methyl-substituted and at an unsubstituted ring position, respectively. Isomer A (positive downfield shifts in p.p.m. from $SiMe_4$ as internal standard): 5.08 (s, 1 H); 2.43 (s, 2 H); 1.75 (s, 6 H); and 1.18 (d, 3 H). Isomer B: 4.45 (s, 2 H); 2.65 (d, 1 H); 2.08 (s, 3 H); and 1.47 (s, 6 H). Another less resolved resonance was at 3.86 (complex pattern, isomers A + B). Isomer A was obtained pure by recrystallization from n-hexane: 5.08 (s, 1 H); 3.63 (quartet, 1 H); 2.43 (s, 2 H); 1.75 (s, 6 H); and 1.18 (d, 3 H).

The reaction of $[N(PPh_3)_2][BH_4]$ with $[Re(CO)_3(C_6H_5CH_3)][AlBr_4]$ led to the formation of the corresponding cyclohexadienyl compound with carbonyl-stretching vibrations at 2 024s, 1 946s, and 1 934s cm^{-1} in n-hexane as solvent.

The trimethylcyclohexadienyl derivative $[Re(CO)_3\{1,3,5\text{-}C_6H_4(CH_3)_3\}]$ reacted immediately with $[CPh_3][BF_4]$ in dichloromethane giving the cationic arene derivative, as evidenced by its i.r. spectrum in the carbonyl-stretching region.

Crystal and Molecular Structure Determinations.—(*a*) $[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$. The *X*-ray measurements were carried out on a computer-controlled Philips PW1100 single-crystal diffractometer, with graphite monochromatized Mo-K_α radiation. A crystal with dimensions 0.42 × 0.12 × 0.08 mm was sealed in a glass capillary to prevent its decomposition. The determination of the cell parameters was by a least-squares method applied to the setting angles of 25 reflections.

Crystal data. $C_{12}H_{12}AlBr_4O_3Re$, $M = 737.04$, monoclinic, space group $P2_1/a$ (from systematic extinctions), $a = 15.687(3)$, $b = 12.876(3)$, $c = 9.690(2)$ Å, $\beta = 101.95(2)°$, $U = 1\,914.8$ Å^3, $Z = 4$, $D_c = 2.555$ g cm^{-3}, $F(000) = 1\,344$, $\lambda = 0.710\,69$ Å, $\mu = 146.6$ cm^{-1}.

The intensity data were collected in the range $2 \leqslant \theta \leqslant 20°$ by the ω—2θ scan technique; scan speed 0.05° s^{-1}, scan width 1.4°. Three reflections were monitored every 180 min, their intensity oscillating within 2%. The intensities of 1 850 independent reflections were corrected for Lorentz and polarization factors. An absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections, using the method of North *et al.*;[11] the transmission factors were in the range 0.98—0.65. 630 Reflections having $I \leqslant 3\sigma(I)$ were omitted from further computations. The structure was solved by the Patterson method and refined by full-matrix least squares with the program SHELX 76.[12] The phenyl group was constrained to a perfect hexagon (C–C 1.395 Å) and refined as a rigid group. An attempt was made to relieve this constraint; however, the *R* factor slightly increased and, in addition, the C–C ring distances and the angles at the ring carbon atoms did not show any systematic variation. The hydrogen atoms (with the exception of those of the methyl groups) were included at calculated positions (C–H 1.08 Å) and with an overall isotropic thermal parameter $U = 0.02$ Å^2. Anisotropic thermal parameters were refined for Re and Br. The refinement converged at $R = 0.046$ and $R' = 0.049$ for 100 parameters and 1 220 observed reflections $\{R' = [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}/(\Sigma w F_o^2)^{\frac{1}{2}}$, $w = [\sigma^2(F_o) + 0.0029F_o^2]^{-1}\}$.

(*b*) $[W(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}]$. The compound was prepared according to the literature method[13] from $[W(CO)_3(CH_3CN)_3]$[14] and the aromatic hydrocarbon at 120 °C and recrystallized from n-heptane. The *X*-ray measurements were carried out as described above with a crystal of dimensions 0.46 × 0.15 × 0.12 mm.

Crystal data. $C_{12}H_{12}O_3W$, $M = 388.08$, monoclinic, space group $P2_1/a$, $a = 8.959(2)$, $b = 16.979(3)$, $c = 8.797(2)$ Å, $\beta = 118.46(2)°$, $Z = 4$, $D_c = 2.189$ g cm^{-3}, $F(000) = 744$, $\lambda = 0.710\,69$ Å, $\mu = 99.9$ cm^{-1}.

1 040 Independent reflections were measured in the range $2 \leqslant \theta \leqslant 20°$ by the ω—2θ scan technique; scan speed 0.06° s^{-1}, scan width 1.6°. The data were collected as above; transmission factors ranged between 0.97 and 0.59. 179 Reflections with $I \leqslant 3\sigma(I)$ were considered unobserved. The structure was solved and refined as above. The refinement converged to $R = 0.036$ and $R' = 0.039$ for 60 parameters and 861 observed reflections. Weights were assigned according to $w = [\sigma^2(F_o) + 0.0003F_o^2]^{-1}$. The tungsten atom was refined anisotropically.

Table 2. Fractional atomic co-ordinates for $[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$; estimated standard deviations refer to the last digit

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Re	0.214 0(1)	0.304 3(1)	0.234 1(1)	C(8)	0.275 6(6)	0.445 9(10)	0.141 1(13)
C(1)	0.145 7(15)	0.223 7(19)	0.331 2(24)	C(9)	0.186 2(6)	0.448 4(10)	0.085 6(13)
O(1)	0.101 1(11)	0.178 4(12)	0.389 6(18)	C(10)	0.096 0(16)	0.454 2(19)	0.420 2(27)
C(2)	0.181 3(14)	0.218 3(16)	0.075 0(24)	C(11)	0.407 9(17)	0.448 1(22)	0.348 6(29)
O(2)	0.162 6(10)	0.164 3(13)	−0.022 5(18)	C(12)	0.149 6(16)	0.446 9(19)	−0.074 6(26)
C(3)	0.307 9(13)	0.211 8(16)	0.298 6(22)	Al	0.396 9(4)	0.289 3(5)	0.796 1(7)
O(3)	0.366 4(11)	0.158 2(14)	0.339 4(18)	Br(1)	0.388 8(3)	0.463 1(2)	0.805 7(4)
C(4)	0.127 5(6)	0.451 4(10)	0.175 8(13)	Br(2)	0.497 9(2)	0.242 6(2)	0.672 2(3)
C(5)	0.158 3(6)	0.451 9(10)	0.321 6(13)	Br(3)	0.264 9(2)	0.227 5(2)	0.691 2(3)
C(6)	0.247 7(6)	0.449 4 (10)	0.377 1(13)	Br(4)	0.433 4(2)	0.225 8(2)	0.019 3(3)
C(7)	0.306 4(6)	0.446 4(10)	0.286 9(13)				

Table 3. Fractional atomic co-ordinates for $[W(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}]$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
W	0.155 9(1)	0.408 5(1)	0.351 7(1)	C(5)	0.312 1(13)	0.414 8(5)	0.197 3(14)
C(1)	0.149 5(21)	0.521 4(11)	0.353 6(22)	C(6)	0.417 6(13)	0.384 0(5)	0.361 1(14)
O(1)	0.146 7(16)	0.590 8(7)	0.351 4(17)	C(7)	0.369 0(13)	0.316 5(5)	0.417 0(14)
C(2)	−0.082 9(25)	0.406 1(10)	0.290 8(25)	C(8)	0.214 9(13)	0.279 9(5)	0.308 9(14)
O(2)	−0.229 6(19)	0.401 9(8)	0.242 9(20)	C(9)	0.109 4(13)	0.310 7(5)	0.145 1(14)
C(3)	0.210 6(26)	0.407 4(11)	0.598 4(28)	C(10)	0.363 5(27)	0.487 2(12)	0.137 9(29)
O(3)	0.242 5(20)	0.402 6(8)	0.737 5(23)	C(11)	0.491 2(29)	0.281 7(14)	0.607 8(29)
C(4)	0.158 0(13)	0.378 1(5)	0.089 3(14)	C(12)	−0.056 6(25)	0.268 2(12)	0.028 2(26)

The atomic scattering factors were taken from ref. 12 for Br, O, C, and H, and from ref. 15 for Re, W, and Al; corrections for anomalous dispersion were included. The atomic co-ordinates for the two compounds are listed in Tables 2 and 3, respectively.

Results and Discussion

The η^6-arene complexes of rhenium(I) of the type $[Re(CO)_3(arene)]^+$ appear to be less stable (or more reactive) than the corresponding manganese(I) derivatives,[16] $[Mn(CO)_3(arene)]^+$. The latter were obtained by the reaction of $[MnCl(CO)_5]$ with the arene and $AlCl_3$, followed by hydrolysis. Only the hexamethylbenzene complex of rhenium(I), $[Re(CO)_3\{C_6(CH_3)_6\}]^+$, was synthesized[2] from $[ReCl(CO)_5]$–arene–$AlCl_3$. Mention has been made[2] of other less methyl-substituted arene cations, but no experimental details were given. If a hydrolytic treatment was carried out, from our experience we suspect that the less methyl-substituted products would have been obtained only with difficulty, in view of their low stability (see below) towards water. Preliminary crystal and molecular structural data for the toluene and the hexamethylbenzene rhenium cations have been reported[3] {prepared by reaction of $[ReBr(CO)_5]$ or $[Re_2Br_2(CO)_8]$ with the aromatic hydrocarbon}, as the $[Re_2Br_3(CO)_6]^-$ derivatives [equation (1)].

$$3[ReBr(CO)_5] + \text{arene} \longrightarrow [Re(CO)_3(\text{arene})][Re_2Br_3(CO)_6] + 6CO \quad (1)$$

We found that the use of $[ReBr(CO)_5]$–arene–$AlBr_3$ (aluminium bromide clearly functioning as a halogen abstractor) leads to the formation of cationic arene complexes of rhenium(I), as shown by i.r. data in the carbonyl-stretching region and by *X*-ray structure determination of the 1,3,5-trimethylbenzene derivative, see equation (2). It is worth noting that, to the best of our knowledge, this is the first case of manganese(I) and rhenium(I) carbonyl-arene complexes for which the tetrahalogenoaluminate salt, as the primary product of the reaction, has been identified.

$$[ReBr(CO)_5] + \text{arene} + AlBr_3 \xrightarrow{\text{Arene}} [Re(CO)_3(\text{arene})][AlBr_4] + 2CO \quad (2)$$

On the other hand, the tetrabromoaluminate salts obtained by reaction (2) are very sensitive to moisture and no reproducible and reliable analytical data could be obtained for them. In addition, the arene ligand is rapidly displaced by oxygen-containing Lewis bases such as tetrahydrofuran and complete decomposition of the less methyl-substituted complexes occurs in the presence of water. Hydrolysis of $[AlBr_4]^-$ and the presence of the resulting acidic medium is probably at least partly responsible for the observed instability of the tetrabromoaluminate salts towards water. Reaction with Br^- leads to displacement of the arene ligand with formation of the dimeric anion $[Re_2Br_3(CO)_6]^-$.[3,7] The corresponding anionic complexes of Group 6B metals, $[M_2X_3(CO)_6]^{3-}$ (M = Mo or W), are likewise obtained by arene displacement from $[M(CO)_3(arene)]$,[17] and the niobium species $[Nb_2Cl_3(CO)_8]^-$ has recently been shown[18] by *X*-ray diffraction methods to be a chloride-bridged complex of seven-co-ordinated niobium. The arene ligand is loosely bonded to rhenium(I), as shown also by the displacement of toluene from the corresponding cation by carbon monoxide and formation of $[ReCl(CO)_5]$ in $C_2H_2Cl_4$, clearly by a process of chloride abstraction from the solvent. We believe that the observed lower stability of the rhenium(I) complexes with respect to their manganese(I) analogues could be due to the more easily accessible seven-co-ordination for rhenium, necessary for attack on the cation by a Lewis base in an associative mechanism. The weakly soluble tetraphenylborate salts, obtained by exchange from the tetrabromoaluminates [equation (3)] on the contrary, were sufficiently stable.

$$[Re(CO)_3(\text{arene})][AlBr_4] + [NBu_4][BPh_4] \xrightarrow{CH_2Cl_2} [Re(CO)_3(\text{arene})][BPh_4] + [NBu_4][AlBr_4] \quad (3)$$

Also the toluene octaiododirhenate(III) salt was prepared by the exchange reaction (4). Both the tetraphenylborate and

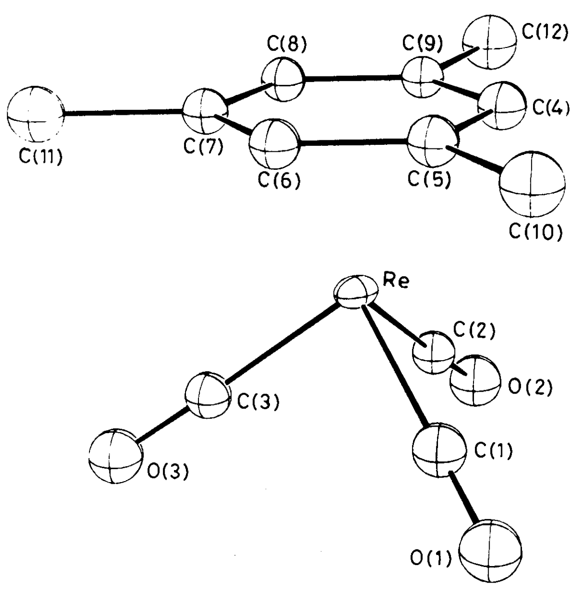


Figure 1. View of $[Re(CO)_3\{1,3,5-C_6H_3(CH_3)_3\}]^+$, with the atomic numbering scheme. The same labelling was used for the tungsten complex $[W(CO)_3\{1,3,5-C_6H_3(CH_3)_3\}]$

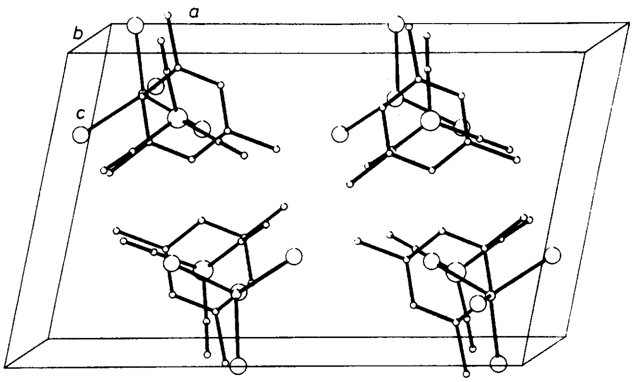
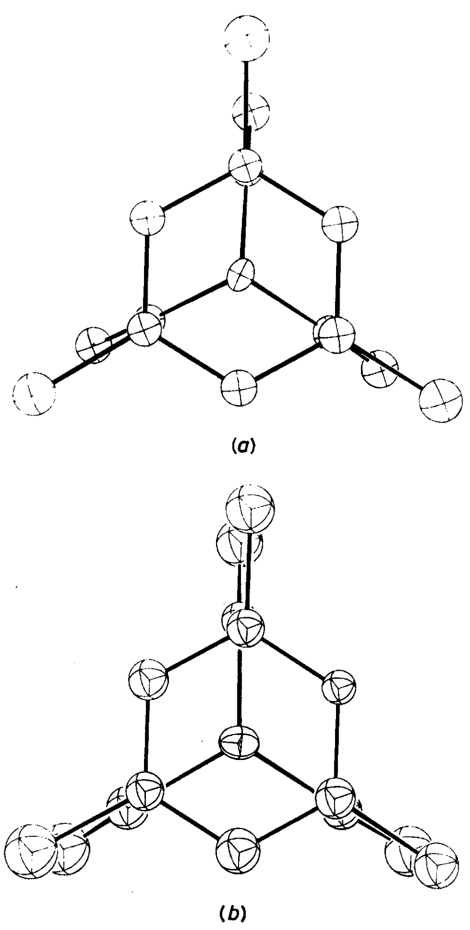


Figure 2. The packing of $[Re(CO)_3\{1,3,5-C_6H_3(CH_3)_3\}]^+$ and $[AlBr_4]^-$ ions in the unit cell

$$2[Re(CO)_3(C_6H_5CH_3)][AlBr_4] + [NBu_4]_2[Re_2I_8] \xrightarrow{CH_2Cl_2} [Re(CO)_3(C_6H_5CH_3)]_2[Re_2I_8] + 2[NBu_4][AlBr_4] \quad (4)$$

the octaiododirhenate(III) salts exhibit the properties of the isolated ions, as shown by the i.r. spectroscopic data. In particular, the octaiododirhenate(III) could be expected to undergo displacement of the arene by the iodo-ligands of $[Re_2I_8]^{2-}$ with formation of the already reported mixed-valence complex $[Re_4I_8(CO)_6]$.[19] Although displacement of the arene was noted at elevated temperature, no straightforward formation of the tetranuclear product could be observed.

The *X*-ray diffractometric study of $[Re(CO)_3\{1,3,5-C_6H_3(CH_3)_3\}]^+$ has clarified the molecular structure of the cation in comparison with that of the corresponding neutral species of tungsten(0). A view of the rhenium cation is shown in Figure 1 together with the numbering scheme used. Figure 2 shows the packing of the rhenium(I) complex and the relationship of the cation to the $[AlBr_4]^-$ anion. In the rhenium(I) cation the three-fold axis of symmetry of the $Re(CO)_3$ moiety almost coincides with the centre of the arene, see Figure 3. The rhenium atom is approximately equidistant from the ring carbon atoms, the Re–C distance being 2.33 Å. The perpendicular distance of the rhenium atom from the ring plane is 1.855(2) Å. Both these distances compare quite well with the corresponding distances in the $[V(CO)_4\{1,2,4,5-C_6H_2(CH_3)_4\}]^+$ cation[20] (average V–C distance 2.33 Å, perpendicular distance from the metal atom to the ring 1.87 Å). Considering that we are dealing in both cases with positively charged arene complexes and that the ionic radius should be substantially the same for vanadium(I) and rhenium(I) (the increase in radius due to the change from a 3*d* to a 4*d* or 5*d* element is probably compensated by the larger effective nuclear charge for rhenium), the data do not reveal any significant change in bond strength on going from vanadium to rhenium, at least as far as the metal–arene bond is concerned.


(*a*)

(*b*)

Figure 3. Views of (*a*) $[Re(CO)_3\{1,3,5-C_6H_3(CH_3)_3\}]^+$ and (*b*) $[W(CO)_3\{1,3,5-C_6H_3(CH_3)_3\}]$ along the normal to the aromatic ring

A preliminary structural report[3] mentioned that the Re–C(ring) bond distance averages 2.33 Å for both $[Re(CO)_3(C_6H_5CH_3)]^+$ and $[Re(CO)_3\{C_6(CH_3)_6\}]^+$, with $[Re_2Br_3(CO)_6]^-$ as counter anion. The tricarbonyl moiety of our rhenium compound possesses approximate C_{3v} symmetry and has C–Re–C angles of around 90°. The mean bond distances in the tricarbonylrhenium moiety of the cation are 1.89 and 1.15 Å for Re–C and C–O, respectively.

Concerning the C–C distances to the methyl groups, one [C(7)–C(11), see Table 4] appears to be somewhat longer, although the large estimated standard deviation does not allow any further speculation. The methyl groups are almost coplanar with the six-membered ring, the deviation of the methyl carbons from the least-squares plane determined by the benzene ring being: C(10), −0.010; C(11), +0.031; and C(12), +0.006 Å. Three cases are known of 1,3,5-trimethyl-

Table 4. Relevant bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $[W(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}]$ and $[Re(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}][AlBr_4]$

	Rhenium complex	Tungsten complex
M–C(1)	1.88(2)	1.92(2)
M–C(2)	1.88(2)	1.94(2)
M–C(3)	1.90(2)	1.98(2)
M–C(4)	2.33(2)	2.37(2)
M–C(5)	2.33(2)	2.37(2)
M–C(6)	2.32(2)	2.34(2)
M–C(7)	2.33(2)	2.32(2)
M–C(8)	2.33(2)	2.32(2)
M–C(9)	2.33(2)	2.35(2)
M–C *	1.855(2)	1.886(2)
C(1)–O(1)	1.15(2)	1.18(2)
C(2)–O(2)	1.16(2)	1.18(2)
C(3)–O(3)	1.15(2)	1.12(2)
C(5)–C(10)	1.50(3)	1.49(2)
C(7)–C(11)	1.58(3)	1.62(3)
C(9)–C(12)	1.54(3)	1.53(2)
Al–Br(1)	2.244(7)	—
Al–Br(2)	2.258(7)	—
Al–Br(3)	2.255(7)	—
Al–Br(4)	2.272(7)	—
Br(1)–Al–Br(2)	109.9(3)	—
Br(1)–Al–Br(3)	108.4(3)	—
Br(1)–Al–Br(4)	108.9(3)	—
Br(2)–Al–Br(3)	110.3(3)	—
Br(2)–Al–Br(4)	110.1(3)	—
Br(3)–Al–Br(4)	109.2(3)	—

	Rhenium complex	Tungsten complex
C(1)–M–C(2)	90(1)	89.4(7)
C(1)–M–C(3)	88(1)	89.6(8)
C(2)–M–C(3)	88(1)	88.1(8)
C(1)–M–C(4)	102(1)	103.9(7)
C(1)–M–C(5)	88(1)	89.3(7)
C(1)–M–C(6)	103(1)	102.2(7)
C(1)–M–C(7)	136(1)	134.1(7)
C(1)–M–C(8)	162(1)	162.3(7)
C(1)–M–C(9)	134(1)	135.9(7)
C(2)–M–C(4)	104(1)	104.2(7)
C(2)–M–C(5)	136(1)	135.7(7)
C(2)–M–C(6)	162(1)	163.3(7)
C(2)–M–C(7)	134(1)	136.3(7)
C(2)–M–C(8)	102(1)	104.0(7)
C(2)–M–C(9)	89(1)	90.3(7)
C(3)–M–C(4)	165(1)	161.6(7)
C(3)–M–C(5)	136(1)	136.1(7)
C(3)–M–C(6)	104(1)	103.8(7)
C(3)–M–C(7)	91(1)	88.7(7)
C(3)–M–C(8)	105(1)	102.2(7)
C(3)–M–C(9)	137(1)	134.4(7)
O(1)–C(1)–M	177(2)	178.3(15)
O(2)–C(2)–M	179(2)	175.1(17)
O(3)–C(3)–M	178(2)	176.3(18)
C(10)–C(5)–C(6)	119(2)	120.0(9)
C(10)–C(5)–C(4)	121(2)	120.0(9)
C(11)–C(7)–C(8)	120(2)	120.3(9)
C(11)–C(7)–C(6)	120(2)	119.7(9)
C(12)–C(9)–C(4)	118(2)	121.2(9)
C(12)–C(9)–C(8)	122(2)	118.8(9)

* Perpendicular distance of the metal from the ring.

benzene complexes showing deviation of the methyl groups from the ring plane.

Of major importance is the orientation of the carbonyl groups with respect to the methyl substituents of the ring. As shown in Figure 3, the methyl groups are eclipsed with respect to the carbonyl groups. This is an electronic effect, and had been anticipated earlier in the case of the $[V(CO)_4\{1,2,4,5\text{-}C_6H_2(CH_3)_4\}]^+$ cation.[18] The problem of the orientation of the carbonyl groups in tricarbonyl chromium arene complexes has been treated extensively:[4,21] with electron-releasing substituents such as methyl, the metal orbitals binding the arene preferably overlap with the region in space of maximum electronic density on the ring, *i.e.* at 60° with respect to the carbonyl groups. Also the mesitylene complex of molybdenum, $[Mo(CO)_3\{1,3,5\text{-}C_6H_3(CH_3)_3\}]$, for which *X*-ray structural data are available, has an eclipsed orientation of the carbonyl groups with respect to the methyl substituents.[5]

The $[AlBr_4]^-$ anion has a virtually perfect tetrahedral geometry. The $[AlBr_4]^-$ tetrahedra and the $[Re(CO)_3(arene)]^+$ cations have three-fold axes of symmetry almost parallel to the *b* axis and roughly aligned alternatively in columns running along this direction. Each column is surrounded by four other columns shifted by about 1.5 *b*, in such a way that each ion has six ions of different sign around it: one above and one below in the same column and four belonging to four different columns in a plane parallel to [1 0 0]. This arrangement roughly resembles that of a distorted sodium chloride structure, in which Na^+ and Cl^- are substituted by the corresponding positively and negatively charged complex ions. The interionic distances are long: no distance was found to be shorter than 0.5 Å plus the sum of the van der Waals radii. The cations and the anions in the crystal are thus loosely bonded. This may explain why reaction (2) carried out in the arene itself as 'solvent' results in a biphasic liquid system: the lower layer, which contains most of the tetrabromoaluminate salt, probably comprises a solution of the arene in the ionic derivative, corresponding to insertion of the arene between the ions and characterized by a rather small lattice energy. This phenomenon is presumably common to all syntheses of metal-arene cationic complexes, obtained by the so-called 'Friedel-Crafts reductive reaction' of anhydrous metal halides with arene in the presence of aluminium chloride.[22]

The data of Table 4 allow a comparison to be made between the rhenium(I) and the tungsten(O) complexes. The first observation is that the bond distances involving the metal tend to be shorter for the rhenium derivative. This is attributable to the contraction of the metal orbitals due to the positive charge and the data certainly cannot be taken to support any strengthening of the bond on going from tungsten(O) to rhenium(I). Apart from this, the structural parameters for the two complexes are very similar, including the eclipsed orientation of the carbonyl groups with respect to the methyl substituents, see Figure 3, and the coplanarity of the methyl groups with the six-membered ring; the deviations of the methyl carbons from the least-squares plane of the benzene ring in the tungsten complex are −0.008 [C(10)], +0.015 [C(11)], and −0.033 Å [C(12)].

Treatment of the arenerhenium cations with $[BH_4]^-$ gives rise to the corresponding cyclohexadienyl derivatives [equation (5)]. This is a well known[16] reaction for the corresponding cationic manganese complexes. Examination of the ^1H

$$[Re(CO)_3\{C_6H_{6-n}(CH_3)_n\}]^+ + H^- \longrightarrow [Re(CO)_3\{C_6H_{7-n}(CH_3)_n] \quad (5)$$

n.m.r. spectrum of the products of reaction (5) established that attack by H^- occurred at both the unsubstituted and methyl-substituted ring positions of the symmetric trimethyl derivative. However, we were unable to establish the relative amounts of the isomers formed because reliable ^1H n.m.r. spectra could be obtained only on fractions which had undergone purification processes; thus, they were no longer representative of the original reaction mixture. Hydride reduction of cationic arenemanganese(I) complexes was recently reported [23] and isomer ratios obtained by ^1H n.m.r. spectrometry on the reaction products after their recrystallization. No evidence of reduction beyond the cyclohexadienyl stage [23] was obtained under our experimental conditions. (We wish to thank a referee for drawing our attention to this point.) Hydrogen removal from the trimethylcyclohexadienyl complex was promptly achieved by $[CPh_3][BF_4]$.

Acknowledgements

The authors thank the National Research Council (C.N.R., Rome) and the Ministry of Education for support of this work.

References

1 (*a*) J. L. Atwood, J. K. Newell, W. E. Hunter, I. Bernal, F. Calderazzo, I. P. Mavani, and D. Vitali, *J. Chem. Soc., Dalton Trans.*, 1978, 1189; (*b*) I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *Gazz. Chim. Ital.*, 1976, **106**, 971; (*c*) J. D. Korp, I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *J. Chem. Soc., Dalton Trans.*, 1979, 1942; (*d*) F. Calderazzo, D. Vitali, R. Poli, J. L. Atwood, R. D. Rogers, J. M. Cummings, and I. Bernal, *ibid*, 1981, 1004; (*e*) D. Vitali and F. Calderazzo, *Gazz. Chim. Ital.*, 1972, **102**, 587.

2 G. Winkhaus and H. Singer, *Z. Naturforsch., Teil B*, 1963, **18**, 418.

3 R. L. Davis and N. C. Baenziger, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 475.

4 E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, and T. A. Albright, *Chem. Rev.*, 1982, **82**, 499 and refs. therein.

5 D. E. Koshland, S. E. Pyers, and J. P. Chesick, *Acta Crystallogr., Sect. B*, 1977, **33**, 2013.

6 E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

7 B. J. Brisdon, D. A. Edwards, and J. W. White, *J. Organomet. Chem.*, 1978, **161**, 233.

8 J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1962, **1**, 933.

9 W. Preez and L. Rudzik, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 150.

10 S. W. Kirtley, M. A. Andrews, R. Bau, G. W. Grynkewick, T. J. Marks, D. L. Tipton, and B. R. Whittlesey, *J. Am. Chem. Soc.*, 1977, **99**, 7154.

11 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

12 G. M. Sheldrick, SHELX 76, A Program for Crystal Structure Determination, University of Cambridge, 1976.

13 R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.

14 D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101.

16 G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 3807.

17 J. F. White and M. F. Farona, *J. Organomet. Chem.*, 1972, **37**, 119.

18 F. Calderazzo, G. Pampaloni, and P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.*, 1982, 1304.

19 F. Calderazzo, F. Marchetti, R. Poli, D. Vitali, and P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.*, 1981, 893; *J. Chem. Soc., Dalton Trans.*, 1982, 1665.

20 F. Calderazzo, G. Pampaloni, D. Vitali, and P. F. Zanazzi, *J. Chem. Soc., Dalton Trans.*, 1982, 1993.

21 O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 1966, 822; *ibid.*, 1967, 228, 1619; M. A. Bush, T. A. Dullforce, and G. A. Sim, *Chem. Commun.*, 1969, 1491; T. A. Albright, *Acc. Chem. Res.*, 1982, **15**, 149 and refs. therein.

22 E. O. Fischer and H. P. Fritz, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 56; F. Calderazzo, *Inorg. Chem.*, 1964, **3**, 810.

23 M. Brookhart and A. Lukacs, *Organometallics*, 1983, **2**, 649.

Received 11*th July* 1983; *Paper* 3/1191