

Synthesis and Crystal Structures of the Carbido Cluster Anions $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ and $[\text{Re}_6(\mu\text{-H})\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{-\dagger}$

Tiziana Beringhelli,^a Giuseppe D'Alfonso,^{*a} Henriette Molinari^b and Angelo Sironi^{*c}

^a Dipartimento di Chimica Inorganica e Metallorganica, Via Venezian 21, 20133 Milano, Italy

^b Dipartimento di Chimica Organica e Industriale, Via Golgi 19, 20133 Milano, Italy

^c Istituto di Chimica Strutturistica Inorganica, Via Venezian 21, 20133 Milano, Italy

The reaction of the carbido cluster anion $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ with I_2 in MeCN, under CO, allows the removal of the $\text{Re}(\text{CO})_3^+$ capping moiety, affording the octahedral cluster dianion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ almost quantitatively. The anion, characterized by single-crystal X-ray analysis as its $[\text{PPh}_4]^+$ salt, has an idealized C_3 symmetry and consists of a carbon-centred metal octahedron surrounded by 18 terminal (three for each metal atoms) and one doubly bridging carbonyl ligand. The same species is obtained by dissolving the monoanion $[\text{Re}_7\text{C}(\text{CO})_{22}]^-$ in MeCN. Variable-temperature ^{13}C NMR spectra indicate that the bridging carbonyl, in solution, is completely delocalized on the cluster edges and interchanges with the terminal carbonyls. The ion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ can be reversibly protonated, affording $[\text{Re}_6(\mu\text{-H})\text{C}(\mu\text{-CO})(\text{CO})_{18}]^-$, characterized by single-crystal X-ray analysis as its $[\text{NEt}_4]^+$ salt (CH_2Cl_2 clathrate). The carbonyl connectivity pattern resembles that of the parent anion, although the presence of the H ligand in a doubly bridging location (detected by the atom-pair potential method) lowers the symmetry to C_1 . The ion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ is also able to react with Group 11 cations, as Ag^+ , Cu^+ or $\text{Au}(\text{PPh}_3)^+$, giving adducts which can be considered intermediate between molecular complexes and ion pairs, on the basis of the $\nu(\text{CO})$ frequencies and of the ^{13}C NMR spectrum of the silver derivative.

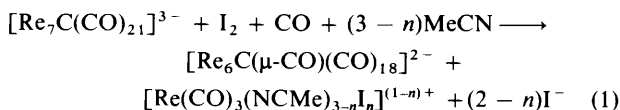
Most studies on the reactivity of rhenium carbide clusters have focused^{1,2} on the addition of electrophilic species X^+ to the trianion $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$,³ resulting, for $\text{X} = \text{ML}_n$, in the formation of Re_7M bimetallic clusters of octahedral *trans*-bicapped structure ($\text{M} = \text{Rh}, \text{Ir}, \text{Pd}, \text{Pt}, \text{Ag}, \text{Cu}, \text{Au}$ or Hg). We report here on reactions which allow a decrease in cluster nuclearity, by removing the $\text{Re}(\text{CO})_3^+$ moiety capping the octahedral cage. Both oxidizing agents and nucleophiles have to be used, in order to stabilize the two fragments. The octahedral carbide complex so formed, of formula $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$, contains the largest number of carbonyls ever found on an octahedral cluster and is still capable of giving addition reactions, with electrophiles such as H^+ or cations of Group 11. The formation of $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ has been briefly reported.⁴

Results and Discussion

Treatment of $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$, in acetonitrile, at room temperature, and under a carbon monoxide atmosphere, with a stoichiometric amount of I_2 afforded instantaneously and almost quantitatively, as judged by IR monitoring, the novel dianion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ **2** containing an octahedral cluster of rhenium atoms, as shown by the X-ray single-crystal analysis discussed below. The $\text{Re}(\text{CO})_3^+$ capping moiety was recovered stabilized by molecules of the solvent acetonitrile and by iodide anions, formed according to equation (1) ($n = 0-2$). Indeed the IR spectra of the reaction mixtures invariably showed bands attributable to the cationic complex $[\text{Re}(\text{CO})_3(\text{NCMe})_3]^+$ (2055s and 1955s cm^{-1})⁵ and to the neutral

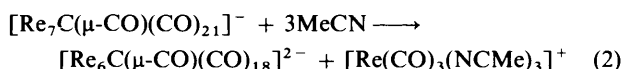
derivative $[\text{Re}(\text{CO})_3(\text{NCMe})_2\text{I}]$ (2037s, 1937s and 1915s cm^{-1}). The latter product, which is the dominant one, has been identified by comparison with a sample obtained by refluxing $[\text{Re}(\text{CO})_5\text{I}]$ in MeCN, as reported for the analogous chloro and bromo derivatives.⁶ The IR spectra of the reaction mixtures exhibited also a weak band at *ca.* 2020 cm^{-1} , indicative of the possible presence of the anionic complex $[\text{Re}(\text{CO})_3(\text{NCMe})\text{I}_2]^-$: treatment of $[\text{Re}(\text{CO})_3(\text{NCMe})_2\text{I}]$ with 1 equivalent of NET_4I , in CH_2Cl_2 , gives a species exhibiting $\nu(\text{CO})$ bands at 2019s, 1911s and 1889s cm^{-1} (MeCN). We have observed that in acetonitrile solution $[\text{Re}(\text{CO})_3(\text{NCMe})_3]\text{BF}_4$ does not react with a slight excess of NET_4I ; therefore, the instantaneous formation of $[\text{Re}(\text{CO})_3(\text{NCMe})_2\text{I}]$ {and possibly of $[\text{Re}(\text{CO})_3(\text{NCMe})\text{I}_2]^-$ } originates from a pathway different from the substitution of nitrile ligands in $[\text{Re}(\text{CO})_3(\text{NCMe})_3]^+$. The reactions of I_2 with carbonyl cluster anions result either in simple oxidation⁷ or in I^+ addition, often with breaking of metal-metal bonds.⁸ The iodine-containing fragments could therefore originate from intermediate products of electrophile addition on the capping vertex.

The rationale for reaction (1) can be provided by the following considerations. The Mingos capping principle⁹ requires a decrease of 12 valence electrons (v.e.s) for cluster decapping. Nucleophiles are often used to stabilize the removed fragment: for instance, CO for the transformations $[\text{Ru}_6\text{C}(\text{CO})_{17}] \rightarrow [\text{Ru}_5\text{C}(\text{CO})_{15}]^{10a}$ and $[\text{Ru}_5\text{C}(\text{CO})_{14}(\text{AuPR}_3)_2] \rightarrow [\text{Ru}_4\text{C}(\text{CO})_{12}(\text{AuPR}_3)_2]$,^{10b} Br^- for $[\text{Fe}_5\text{C}(\text{CO})_{15}] \rightarrow [\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$,¹¹ halides for $[\text{Rh}_{10}(\text{CO})_{21}]^{2-} \rightarrow [\text{Rh}_9(\text{CO})_{19}]^{3-}$,¹² $\text{Ru}(\text{CO})_2$, $\text{Fe}(\text{CO})_3^{2+}$ and $\text{Rh}(\text{CO})_2^+$ being the 12 v.e. fragments lost. Compound **1** does not react with nucleophiles, due to its high negative charge.

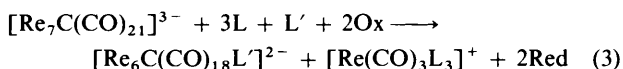


[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

We have now found, however, that the monoanion $[\text{Re}_7\text{C}(\mu\text{-CO})(\text{CO})_{21}]^-$ (obtained by oxidation of **1** with C_7H_7^+ , in CH_2Cl_2 , under CO)¹³ 'disproportionates' in acetonitrile, according to equation (2), giving quantitatively compound **2**.



This reaction is analogous to that previously observed¹⁴ for the monoanion $[\text{Re}_7\text{H}_2\text{C}(\text{CO})_{21}]^-$, which affords, by reaction with MeCN, the octahedral dianion $[\text{Re}_6\text{H}_2\text{C}(\text{CO})_{18}]^{2-}$ and $[\text{Re}(\text{CO})_3(\text{NCMe})_3]^+$. The Re_7 monoanions behave therefore as adducts between an octahedral dianion and the 12 v.e. capping moiety $\text{Re}(\text{CO})_3^+$, which can be removed by nucleophiles such as MeCN. For complexes carrying a high negative charge, such as **1**, cluster decapping requires the use both of oxidizing agents (such as I_2 or C_7H_7^+) and suitable nucleophiles (such as CO and MeCN), according to reaction (3). The proton is able to act both as L' and Ox.



A related oxidative cluster fragmentation was used¹¹ to convert the dianion $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ into $[\text{Fe}_5\text{C}(\text{CO})_{15}]$, C_7H_7^+ being the oxidizing agent and MeOH the nucleophile stabilizing the removed iron ion.

It is noteworthy that the complex $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$,¹⁵ which formally contains a $\text{Re}(\text{CO})_3^+$ group capping compound **1**, does not split in MeCN, even at reflux. This peculiar stability is demonstrated also by its lack of reaction with I_2 (under CO, in MeCN) and with $\text{CF}_3\text{SO}_3\text{H}$ (in MeCN).

The presence in $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ of a carbonyl in the unusual (for rhenium complexes) bridging location was spectroscopically revealed by a weak, broad band in the IR spectrum at about 1820 cm^{-1} . On the contrary, the ^{13}C NMR spectrum (obtained from a ^{13}CO -enriched sample) showed, even at 173 K, only two resonances, at δ 421.8 (attributable to the carbide atom) and at 197.8, due to all the 19 CO ligands. This means that low-energy interconversion pathways exist, leading to the complete delocalization of the bridging carbonyl on the cluster edges and to its interchange with the terminal carbonyls.

Upon treatment with a slight excess of $\text{CF}_3\text{SO}_3\text{H}$, at room temperature, in CH_2Cl_2 or tetrahydrofuran, compound **2** could be protonated, affording quantitatively the monoanion $[\text{Re}_6\text{HC}(\mu\text{-CO})(\text{CO})_{18}]^-$, characterized by X-ray analysis (see below). Also in this case, the presence of the bridging carbonyl was spectroscopically detected only by IR spectroscopy (1835 cm^{-1}). The ^{13}C NMR spectrum showed only one carbonylic resonance, at δ 194, besides the carbide (δ 413.5, 173 K, $[\text{H}_8]$ tetrahydrofuran). It has been previously observed, e.g. in $[\text{Re}_6\text{H}_2\text{C}(\text{CO})_{18}]^{2-}$ and in $[\text{Re}_7\text{H}_2\text{C}(\text{CO})_{21}]^-$,^{14,16} that the presence of a hydride ligand raises the barrier to the carbonyl scrambling localized on each metal atom. In the present case, on the contrary, the hydride seems ineffective in freezing the delocalized bridging-terminal carbonyl interchange observed in these systems. This could be due to an intramolecular concerted movement of the bridging carbonyl and of the bridging hydride on the cluster surface, or, more likely, to a fast dissociation of the H ligand, acidic in tetrahydrofuran solution (see below). In line with this dynamic behaviour, no isomers of **3** were observed, in contrast to the Re_7 ^{14,17} and Re_5 ¹⁸ hydridocarbido complexes.

Compound **3** in solution behaves as a weak acid, partially dissociating in solvents like tetrahydrofuran or acetone. The amount of dissociation is quite erratic, and is probably related to the opposite effect of traces of water (in the solvents or in the sample) and of $\text{CF}_3\text{SO}_3\text{H}$ (in the sample). Crystals for the X-ray analysis had to be grown, even in CH_2Cl_2 , in the presence of some $\text{CF}_3\text{SO}_3\text{H}$ to avoid preferential crystallization of

compound **2** (less soluble). The deprotonation could be driven to completion by using a slight excess of NBu_4OH , in tetrahydrofuran.

In acetonitrile compound **3** decomposes, giving $[\text{Re}(\text{CO})_3(\text{NCMe})_3]^+$ and a species not yet identified, but certainly of nuclearity lower than six (likely pentanuclear). The formation of $[\text{Re}_5\text{HC}(\text{CO})_{16}]^{2-}$ is expected, on the basis of the previous considerations, through a reaction analogous to (2) but the IR data do not agree with those reported for this anion.¹⁸ Further investigation of this important point is in progress.

Compound **2** is also able to add cations of Group 11, such as Ag^+ or Cu^+ . By treatment of a solution of **2**, in tetrahydrofuran or acetone, with 1 equivalent of AgBF_4 or $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$, the $\nu(\text{CO})$ bands in the IR spectrum shifted immediately to higher frequencies, in agreement with the formation of a 1:1 adduct $[\text{Re}_6\text{MC}(\text{CO})_{19}]^-$ ($\text{M} = \text{Ag}$ **4a** or Cu **4b**). The ^1H NMR spectra of both species showed only the resonances of the cation $\text{N}(\text{PPh}_3)_2^+$, thus ruling out the presence of MeCN co-ordinated to Cu. The ^{13}C NMR spectrum of **4a** showed only one carbonylic resonance (δ 194.2), broadened at 173 K, indicating either a dissociative behaviour of Ag^+ or its fast movement on the surface of the cluster.

By dissolution in MeCN, compound **4b** was converted quantitatively back into **2**, in a reaction that resembles the cleavage of the $\text{Re}(\text{CO})_3^+$ capping moiety in $[\text{Re}_7\text{C}(\text{CO})_{22}]^-$.

Differently from compound **1**, $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ did not react with $[\text{AuCl}(\text{PPh}_3)]$. However, by treatment with a solution of the $\text{Au}(\text{PPh}_3)^+$ cation, obtained by addition of a deficiency of AgBF_4 to a solution of $[\text{AuCl}(\text{PPh}_3)]$, the adduct **4c** was obtained, analogous to **4a** and **4b**, on the basis of the close similarity of the IR spectra.

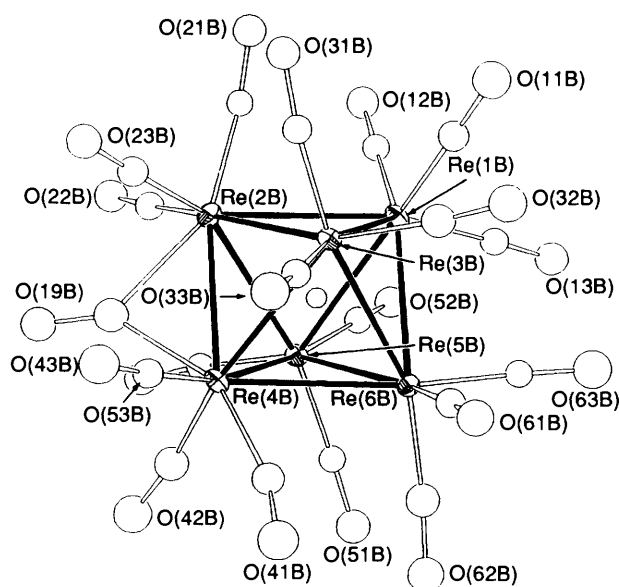
It is likely that in compounds **4** the Group 11 metal atoms are co-ordinated as a bridge on a face of the rhenium octahedral cluster, by analogy with the corresponding derivatives of **1**.^{1,2} No crystal suitable for X-ray analysis could be grown to confirm this hypothesis, in spite of several attempts using different counter ions.

The $\nu(\text{CO})$ bands of the adducts **4** appear at lower frequencies than those of **3**, indicating a higher localization of the negative charge on the rhenium cluster in the Re_6M^- adducts than in Re_6H^- . The same was observed for the corresponding derivatives of compound **1**.¹ Due to the protonic polarization of the H ligand in **3**, this means that the derivatives **4** can be considered intermediate between molecular complexes and ion pairs.

*Crystal Structures of $[\text{PPh}_4]_2[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]$ **2** and $[\text{NEt}_4][\text{Re}_6\text{HC}(\mu\text{-CO})(\text{CO})_{18}]\cdot\text{CH}_2\text{Cl}_2$ **3**.*—A view of the anion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ is shown in Fig. 1. It consists of a carbon-centred metal octahedron surrounded by 18 terminal (three for each metal atom) and one doubly bridging carbonyl ligand. The overall symmetry is C_1 but reasonably close to C_s , the idealized mirror plane passing through Re(3), Re(5) and the bridging CO ligand. There are two independent anions (A and B) in the asymmetric unit, slightly differing in the rotameric orientation of some $\text{Re}(\text{CO})_3$ moiety. This conformational difference together with the different (local) packing environments (the large spread of metal-metal bond distances is often attributed to intra- or inter-molecular steric effects)¹⁹ is possibly responsible for the more regular metal octahedron of molecule A (Re-Re 2.965–3.062, average 3.006 Å) with respect to B (Re-Re 2.930–3.117, average 3.012 Å). The ion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ could be considered the 'most sterically crowded' octahedral binary carbonyl metal cluster on the basis of the carbonyl-to-metal ratio alone (19:6). However, this single parameter is not a good indicator of steric crowding and should be weighted in order to account for differences in the metal-metal bond lengths and in the metal cluster shape.* The ion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$, indeed, easily adds H^+ affording the even more crowded $[\text{Re}_6(\mu\text{-H})\text{C}(\mu\text{-CO})(\text{CO})_{18}]^-$, where the ligand sphere is augmented by a doubly bridging hydrogen ligand as shown in Fig. 2. The

Table 1 Relevant bond distances (Å) within compounds **2** (molecules A and B) and **3**

	2A	2B	3		2A	2B	3
Re(1)–Re(2)	3.010(1)	3.019(1)	2.979(1)	Re(5)–C(53)	1.86(2)	1.89(2)	1.88(2)
Re(1)–Re(3)	2.983(1)	3.042(1)	2.955(1)	Re(6)–C(61)	1.76(3)	1.86(2)	1.89(2)
Re(1)–Re(5)	3.012(1)	2.950(1)	2.981(1)	Re(6)–C(62)	1.83(2)	1.89(2)	1.96(2)
Re(1)–Re(6)	3.062(1)	3.117(1)	3.168(1)	Re(6)–C(63)	1.97(3)	1.82(2)	1.92(2)
Re(2)–Re(3)	3.014(1)	2.979(1)	3.092(1)	Re(2)–C(19)	2.22(3)	2.26(2)	2.28(2)
Re(2)–Re(4)	2.965(1)	2.930(1)	2.896(1)	Re(4)–C(19)	2.29(3)	2.11(2)	2.11(2)
Re(2)–Re(5)	3.014(1)	3.058(1)	3.061(1)	C(11)–O(11)	1.18(3)	1.20(2)	1.17(3)
Re(3)–Re(4)	3.001(1)	3.065(1)	3.024(1)	C(12)–O(12)	1.24(3)	1.21(2)	1.15(2)
Re(3)–Re(6)	3.014(1)	2.965(1)	2.971(1)	C(13)–O(13)	1.32(4)	1.17(2)	1.13(2)
Re(4)–Re(5)	3.006(1)	2.974(1)	3.039(1)	C(21)–O(21)	1.21(3)	1.18(2)	1.18(2)
Re(4)–Re(6)	3.020(1)	3.004(1)	3.057(1)	C(22)–O(22)	1.22(2)	1.21(2)	1.13(2)
Re(5)–Re(6)	2.970(1)	3.047(1)	2.954(1)	C(23)–O(23)	1.26(4)	1.16(2)	1.15(2)
Re(1)–C(11)	1.84(3)	1.84(2)	1.86(3)	C(31)–O(31)	1.18(2)	1.22(2)	1.24(3)
Re(1)–C(12)	1.79(4)	1.83(2)	1.91(2)	C(32)–O(32)	1.16(2)	1.17(2)	1.15(2)
Re(1)–C(13)	1.82(4)	1.87(2)	1.90(2)	C(33)–O(33)	1.24(2)	1.21(2)	1.18(2)
Re(2)–C(21)	1.87(3)	1.90(2)	1.88(2)	C(41)–O(41)	1.25(3)	1.17(2)	1.14(2)
Re(2)–C(22)	1.81(2)	1.88(2)	1.92(2)	C(42)–O(42)	1.27(3)	1.22(2)	1.16(3)
Re(2)–C(23)	1.79(4)	1.89(2)	1.93(2)	C(43)–O(43)	1.21(3)	1.18(2)	1.15(2)
Re(3)–C(31)	1.84(2)	1.83(2)	1.80(4)	C(51)–O(51)	1.21(3)	1.20(2)	1.15(2)
Re(3)–C(32)	1.86(2)	1.87(2)	1.88(2)	C(52)–O(52)	1.21(2)	1.17(2)	1.18(2)
Re(3)–C(33)	1.82(2)	1.83(2)	1.90(2)	C(53)–O(53)	1.20(2)	1.16(2)	1.13(2)
Re(4)–C(41)	1.79(3)	1.93(2)	1.92(2)	C(61)–O(61)	1.20(3)	1.17(2)	1.12(2)
Re(4)–C(42)	1.85(3)	1.85(2)	1.93(3)	C(62)–O(62)	1.22(2)	1.21(2)	1.13(2)
Re(4)–C(43)	1.83(3)	1.88(2)	1.96(2)	C(63)–O(63)	1.09(3)	1.22(2)	1.14(2)
Re(5)–C(51)	1.80(3)	1.84(2)	1.91(2)	C(19)–O(19)	1.23(3)	1.18(2)	1.15(2)
Re(5)–C(52)	1.84(3)	1.92(2)	1.87(3)				

**Fig. 1** A view of the anion $[\text{Re}_6\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$ (molecule B)

average Re–Re bond distance for this cluster (3.015 Å) is intermediate, and marginally different, to those found in **2** (3.009 Å) and in $[\text{Re}_6(\mu\text{-H})_2\text{C}(\text{CO})_{18}]^{2-}$ (3.022 Å).^{16,17} Hence, in the present case, cage expansion seems to be a minor answer to ligand crowding, in contrast to what happens in $[\text{Fe}_3\text{M}(\text{CO})_{14}]^{2-}$ (M = Cr, Mo or W) where the average Fe–Fe bond distance is 0.1 Å longer than that expected from other (less-crowded) clusters.²² On the other hand, the local crowding around the doubly bridging carbonyl ligand, in compounds **2** and **3**, is partially transferred to the other metal centres through

* Generalizing Tolman's cone-angle concept,²⁰ Mingos²¹ has proposed those of 'cluster' and 'M(CO)_n' cone angles. This is an empirical way to account for variance in the shape and dimensions of the metal cluster and it was deduced, for an octahedron of edge 2.90 Å, that the maximum number of carbonyl ligands is 18.

long-range semibringing interactions [Re(1B)⋯C(21B) 3.09 Å, Re(2B)–C(21B)–O(21B) 171°; Re(6B)⋯C(41B) 2.86 Å, Re(4B)–C(41B)–O(41B) 163° in **2** (molecule B); Re(1)⋯C(23) 2.85 Å, Re(2)–C(23)–O(23) 166°; Re(6)⋯C(43) 2.95 Å, Re(4)–C(43)–O(43) 172° in **3**].

The indirect location of hydride ligands is often based on stereochemical considerations such as metal–metal bond lengthening and/or the presence of holes in the ligand arrangement. The latter is certainly a superior criterion but it should be pointed out that a misfit between the cluster shape and the ligand polyhedron can sometimes produce a co-ordination hole even in the absence of any hydridic ligand.^{3,14,17} In the present case we have used an atom-pair potential approach to inspect the possible locations of the hydride ligand. As previously discussed,¹⁷ we deliberately omitted the interstitial carbide atom from the computations, to avoid any *a priori* assumption on the character of the C_{carbido}⋯H interaction, the usual non-bonding potential being strongly repulsive for such an interaction when the hydride is in a μ₃ location. The HYDEX program,²³ clearly locates the hydride ligand as μ bridging the Re(3)–Re(6) edge which is among the shorter octahedral edges [2.971(1) Å]. On the contrary, the 'bond-lengthening' criterion would have assigned the μ-H to the Re(1)–Re(6) edge which is (by far) the longest [3.168(1) Å]. The potential-energy values in the two cases are very different (5.4 and 21.6, arbitrary units) and there is no chance to have the μ-H on the Re(1)–Re(6) edge. Also the faces sharing the Re(3)–Re(6) edge are 'possible' low-energy co-ordination sites for a μ₃-H (6.2 and 7.4 units for 4/3/6 and 1/3/6 faces, respectively) but, in line with the arguments outlined in ref. 17, have been discarded. Molecular graphics can also help in the location of hydridic ligands or, as in the present case, can consolidate the atom-pair potential results,²⁴ and the 'hydrogen co-ordination' hole in the ligand envelope is evident in the van der Waals surface of the $[\text{Re}_6(\mu\text{-H})\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{-}$ anion (Fig. 3).

Experimental

The reactions were performed under N₂, in Schlenk tubes. Solvents were deoxygenated and dried by standard methods.

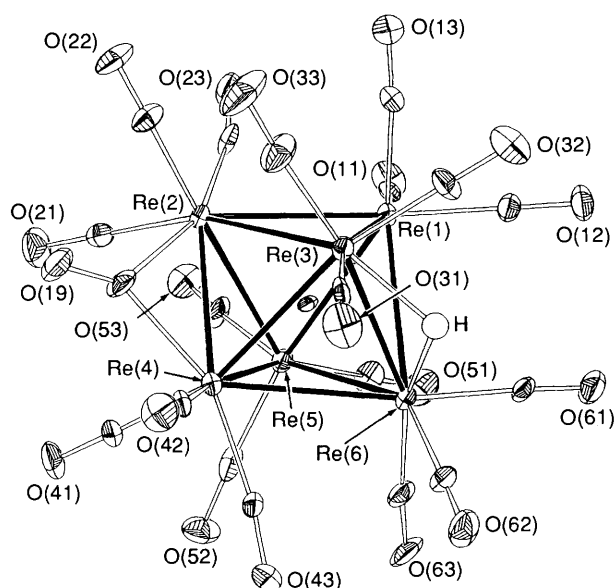


Fig. 2 A view of the anion $[\text{Re}_6(\mu\text{-H})\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$, showing the computed hydride location

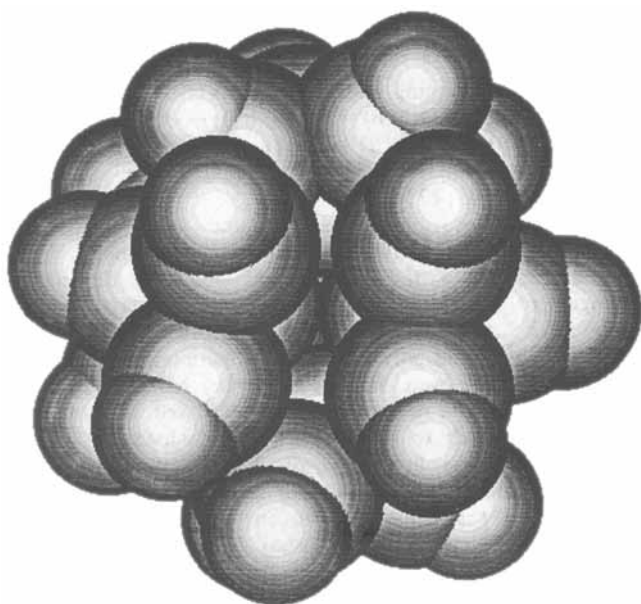


Fig. 3 A view of the van der Waals surface of the anion $[\text{Re}_6(\mu\text{-H})\text{C}(\mu\text{-CO})(\text{CO})_{18}]^{2-}$, showing the 'hydrogen co-ordination' hole in the ligand envelope. The picture has been obtained with the program SMILE.²⁵ Oxygen and carbon atoms have been drawn as intersecting spheres of the appropriate van der Waals radii, while for the Re atoms the covalent radius has been used, therefore allowing a clear view of the surface ligand contacts²⁴

Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer (0.1 mm CaF_2 cells) equipped with a Data System 10, NMR spectra on Varian XL200 or XL300 spectrometers. Elemental analyses were performed on a Perkin-Elmer CHN 2400 instrument.

The ion $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ was prepared by literature methods;²⁶ $[\text{Re}(\text{CO})_3(\text{NCMe})_2\text{I}]$ was prepared almost quantitatively by refluxing $[\text{Re}(\text{CO})_5\text{I}]$ in MeCN, using the method reported in ref. 6 for the corresponding chloro and bromo derivatives.

Synthesis of $[\text{NEt}_4]_2[\text{Re}_6\text{C}(\text{CO})_{19}]$.—The salt $\text{Cs}_3[\text{Re}_7\text{C}$

$(\text{CO})_{21}]$ (100 mg, 0.043 mmol) was dissolved in MeCN (5 cm^3) saturated with CO and treated at room temperature, under CO, with a freshly prepared solution of I_2 in MeCN (0.022 mol dm^{-3} , 2 cm^3 , 0.044 mmol). The colour of the solution turned immediately from red to brown and IR monitoring showed the complete disappearance of the bands of the starting compound. The solvent was removed and the residue, dissolved in MeOH, was treated with a saturated methanolic solution of NEt_4Br and then with water, causing the formation of a red-brown precipitate. Extraction with tetrahydrofuran (to eliminate traces of unreacted starting material) gave a solution from which pure $[\text{NEt}_4]_2[\text{Re}_6\text{C}(\text{CO})_{19}]$ was obtained by evaporation (52 mg, 0.027 mmol, isolated yields 62.8%) (Found: C, 22.60; H, 2.10; N, 1.40. $\text{C}_{36}\text{H}_{40}\text{N}_2\text{O}_{19}\text{Re}_6$ requires C, 22.50; H, 2.10; N, 1.50%); $\nu_{\text{max}}(\text{CO})$ (tetrahydrofuran): 1991s, 1976s, 1908m, 1897m and 1820w (br) cm^{-1} .

Salts with different cations $[\text{PPh}_4^+$ or $\text{N}(\text{PPh}_3)_2^+$] were obtained analogously, and with comparable yields, starting from $[\text{NEt}_4]_3[\text{Re}_7\text{C}(\text{CO})_{21}]$. The compound is quite stable: tetrahydrofuran solutions of $[\text{NEt}_4]_2[\text{Re}_6\text{C}(\text{CO})_{19}]$ did not show significant changes of the $\nu(\text{CO})$ bands, after a period of 3 d, either under N_2 , CO or in the air.

Synthesis of $[\text{NEt}_4][\text{Re}_6\text{HC}(\text{CO})_{19}]$.—The salt $[\text{NEt}_4]_2[\text{Re}_6\text{C}(\text{CO})_{19}]$ (90 mg, 0.047 mmol) was dissolved in tetrahydrofuran (5 cm^3) and treated at room temperature with $\text{CF}_3\text{SO}_3\text{H}$ (4.4 μl , 0.050 mmol). Infrared monitoring showed the instantaneous disappearance of the reagent. The volume of the solution was reduced under vacuum to about 1 cm^3 and the addition of a saturated aqueous solution of NEt_4Br , acidified with $\text{CF}_3\text{SO}_3\text{H}$, resulted in the formation of a brown precipitate of $[\text{NEt}_4][\text{Re}_6\text{HC}(\text{CO})_{19}]$, which was further purified by dissolution in CH_2Cl_2 , containing a drop of $\text{CF}_3\text{SO}_3\text{H}$, and precipitation with heptane (68 mg, 0.038 mmol, isolated yields 81%) (Found: C, 19.00; H, 1.35; N, 0.70. $\text{C}_{28}\text{H}_{21}\text{NO}_{19}\text{Re}_6$ requires C, 18.70; H, 1.20; N, 0.80%); $\nu_{\text{max}}(\text{CO})$ (CH_2Cl_2): 2080vw, 2028 (sh), 2013vs, 1994 (sh), 1935m, and 1835w (br) cm^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2, \text{hydridic region}) -18.0$. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane vapour into a CH_2Cl_2 solution, under N_2 , in the presence of some $\text{CF}_3\text{SO}_3\text{H}$. The crystal used for the data collection was sealed in a capillary tube immediately after its isolation from the mother-liquor.

Reactions of $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$ with Cations of Group 11.—Salts of $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$ with different cations $[\text{NEt}_4^+$ or $\text{N}(\text{PPh}_3)_2^+$] dissolved in tetrahydrofuran or acetone were treated at room temperature with 1 equivalent of AgBF_4 (**4a**), $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (**4b**) or the solution obtained by treating $[\text{AuCl}(\text{PPh}_3)]$ with 0.8 equivalent of AgBF_4 , in tetrahydrofuran (**4c**). In all cases IR monitoring showed the instantaneous disappearance of the reagent: $\nu(\text{CO})$ in thf; **4a**, 2060w, 2010 (sh), 2002s, 1990vs, 1925mw and 1835w (br); **4b**, 2060w, 2010 (sh), 2002s, 1995vs, 1928m and 1835w (br); **4c**, 2060w, 2015 (sh), 2005s, 1995vs, 1930mw and 1835w (br) cm^{-1} .

Crystallography.—**Crystal data.** Compound **2**, $\text{C}_{65}\text{H}_{40}\text{O}_{19}\text{P}_2\text{Re}_6$, $M = 2340.2$, triclinic, space group $P1$ (no. 2), $a = 20.278(4)$, $b = 25.125(4)$, $c = 14.219(2)$ Å, $\alpha = 91.06(1)$, $\beta = 109.58(1)$, $\gamma = 77.74(1)^\circ$, $U = 6659(3)$ Å³, $F(000) = 4320$, $Z = 4$, $D_c = 2.334$ g cm^{-3} , Mo-K α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 111.3$ cm^{-1} .

Compound **3**, $\text{C}_{29}\text{H}_{23}\text{Cl}_2\text{O}_{19}\text{NRe}_6$, $M = 1877.6$, triclinic, space group $P1$ (no. 2), $a = 10.442(3)$, $b = 13.771(2)$, $c = 15.471(2)$ Å, $\alpha = 98.92(1)$, $\beta = 107.94(1)$, $\gamma = 92.31(1)^\circ$, $U = 2082(1)$ Å³, $F(000) = 1680$, $Z = 2$, $D_c = 2.995$ g cm^{-3} , Mo-K α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 178.2$ cm^{-1} .

Intensity measurements. Well shaped crystals of compounds **2** and **3**, the latter in a sealed tube under N_2 and CH_2Cl_2 vapours, were mounted on an Enraf-Nonius CAD-4 diffractometer. The setting angles of 25 intense reflections having θ values in the

Table 2 Positional parameters for $[\text{PPh}_4]_2[\text{Re}_6\text{C}(\text{CO})_{19}]$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Re(1A)	0.825 79(5)	0.562 13(4)	0.091 97(8)	Re(1B)	0.184 77(4)	-0.161 60(3)	-0.567 31(6)
Re(2A)	0.700 58(5)	0.571 65(4)	0.164 53(8)	Re(2B)	0.193 59(4)	-0.137 29(3)	-0.769 38(6)
Re(3A)	0.684 64(4)	0.633 47(4)	-0.024 30(7)	Re(3B)	0.322 54(4)	-0.202 34(3)	-0.613 09(6)
Re(4A)	0.678 93(6)	0.692 19(4)	0.159 47(8)	Re(4B)	0.314 12(4)	-0.084 73(3)	-0.678 09(6)
Re(5A)	0.823 77(5)	0.623 41(4)	0.275 45(7)	Re(5B)	0.183 77(4)	-0.048 58(3)	-0.621 42(6)
Re(6A)	0.805 74(5)	0.686 44(4)	0.090 50(8)	Re(6B)	0.321 27(4)	-0.114 67(3)	-0.470 77(6)
C(A)	0.756(1)	0.627 8(7)	0.125(1)	C(B)	0.254(1)	-0.126 6(7)	-0.613(1)
C(11A)	0.802(2)	0.522(1)	-0.019(2)	C(11B)	0.206(1)	-0.235 5(9)	-0.535(2)
O(11A)	0.788(1)	0.495 9(9)	-0.091(2)	O(11B)	0.216(1)	-0.283 3(8)	-0.516(1)
C(12A)	0.906(2)	0.568(1)	0.071(3)	C(12B)	0.089(1)	-0.160 1(8)	-0.630(2)
O(12A)	0.963(1)	0.577 4(9)	0.065(2)	O(12B)	0.026 2(8)	-0.159 0(6)	-0.672(1)
C(13A)	0.872(2)	0.503(2)	0.180(3)	C(13B)	0.159(1)	-0.147 5(9)	-0.453(2)
O(13A)	0.884(1)	0.461(1)	0.242(2)	O(13B)	0.141 2(9)	-0.135 8(7)	-0.384(1)
C(21A)	0.605(1)	0.564(1)	0.113(2)	C(21B)	0.138(1)	-0.191 4(8)	-0.789(1)
O(21A)	0.544(1)	0.559(1)	0.081(2)	O(21B)	0.107 7(8)	-0.227 3(6)	-0.811(1)
C(22A)	0.730(1)	0.535(1)	0.285(2)	C(22B)	0.107(1)	-0.092 1(9)	-0.851(2)
O(22A)	0.751(1)	0.507 8(8)	0.364(2)	O(22B)	0.051 3(9)	-0.065 7(7)	-0.907(1)
C(23A)	0.720(2)	0.504(2)	0.123(3)	C(23B)	0.235(1)	-0.175 0(9)	-0.859(2)
O(23A)	0.728(2)	0.457(1)	0.090(2)	O(23B)	0.257 1(9)	-0.257 4(7)	-0.917(1)
C(31A)	0.613(1)	0.691(1)	-0.092(2)	C(31B)	0.295(1)	-0.257 1(9)	-0.693(2)
O(31A)	0.570(1)	0.731 0(8)	-0.134(1)	O(31B)	0.275 5(8)	-0.295 4(6)	-0.739 (1)
C(32A)	0.623(1)	0.587(1)	-0.081(2)	C(32B)	0.363(1)	-0.251(1)	-0.500(2)
O(32A)	0.588(1)	0.555 6(8)	-0.115(1)	O(32B)	0.383(1)	-0.258 8(7)	-0.432(1)
C(33A)	0.717(1)	0.627(1)	-0.130(2)	C(33B)	0.412(1)	-0.218 2(8)	-0.622(2)
O(33A)	0.742(1)	0.621 9(8)	-0.198(1)	O(33B)	0.470 1(9)	-0.231 2(7)	-0.634(1)
C(41A)	0.662(2)	0.757(1)	0.094(2)	C(41B)	0.397(1)	-0.069(1)	-0.575(2)
O(41A)	0.640(1)	0.801(1)	0.045(2)	O(41B)	0.452(1)	-0.058 1(8)	-0.533(1)
C(42A)	0.580(2)	0.713(1)	0.122(2)	C(42B)	0.291(1)	-0.010(1)	-0.698(2)
O(42A)	0.512(1)	0.727(1)	0.097(2)	O(42B)	0.276(1)	0.039 0(8)	-0.722(1)
C(43A)	0.701(1)	0.727(1)	0.276(2)	C(43B)	0.380(1)	-0.113 4(9)	-0.742(2)
O(43A)	0.710(1)	0.746 5(8)	0.357(2)	O(43B)	0.416(1)	-0.131 1(8)	-0.790(1)
C(51A)	0.903(1)	0.572(1)	0.337(2)	C(51B)	0.208(1)	0.005 8(8)	-0.537(2)
O(51A)	0.958(1)	0.539 7(9)	0.382(2)	O(51B)	0.222 1(9)	0.042 7(7)	-0.484(1)
C(52A)	0.796(1)	0.621(1)	0.386(2)	C(52B)	0.102(1)	-0.042 5(9)	-0.578(2)
O(52A)	0.775 6(9)	0.625 5(7)	0.457(1)	O(52B)	0.051 4(8)	-0.035 3(6)	-0.555(1)
C(53A)	0.873(1)	0.678 4(9)	0.324(2)	C(53B)	0.128(1)	0.002 2(8)	-0.730(2)
O(53A)	0.906 9(9)	0.711 8(7)	0.361(1)	O(53B)	0.099 0(8)	0.035 5(6)	-0.794(1)
C(61A)	0.898(2)	0.686(1)	0.126(2)	C(61B)	0.414(1)	-0.156 1(9)	-0.409(2)
O(61A)	0.961(1)	0.682 1(9)	0.147(2)	O(61B)	0.473 2(9)	-0.179 8(7)	-0.372(1)
C(62A)	0.778(1)	0.723(1)	-0.032(2)	C(62B)	0.347(1)	-0.052(1)	-0.406(2)
O(62A)	0.760(1)	0.743 9(8)	-0.115(1)	O(62B)	0.372 9(9)	-0.014 1(7)	-0.369(1)
C(63A)	0.802(2)	0.761(1)	0.140(2)	C(63B)	0.304(1)	-0.131 0(8)	-0.358(2)
O(63A)	0.804(1)	0.800(1)	0.172(2)	O(63B)	0.294(1)	-0.140 4(8)	-0.280(1)
C(19A)	0.641(2)	0.633(1)	0.239(2)	C(19B)	0.243(1)	-0.078(1)	-0.827(2)
O(19A)	0.610(1)	0.635(1)	0.301(2)	O(19B)	0.227 4(9)	-0.052 8(7)	-0.903(1)
P(1)	0.334 4(3)	0.526 2(2)	0.415 7(4)	C(245)	0.113(1)	0.385 6(9)	0.288(2)
P(2)	0.154 8(3)	0.219 1(2)	0.332 9(4)	C(246)	0.142(1)	0.328 9(9)	0.288(2)
P(3)	0.329 0(3)	0.018 2(2)	0.912 6(4)	C(311)	0.353(1)	0.039 5(8)	0.036(1)
P(4)	0.179 7(3)	0.720 0(2)	0.828 7(4)	C(312)	0.330(1)	0.096(1)	0.053(2)
C(111)	0.366(1)	0.455 0(8)	0.406(1)	C(313)	0.353(1)	0.113(1)	0.146(2)
C(112)	0.411(1)	0.437 5(9)	0.352(2)	C(314)	0.402(1)	0.079 2(9)	1.226(2)
C(113)	0.442(1)	0.381(1)	0.351(2)	C(315)	0.427(1)	0.023(1)	0.211(2)
C(114)	0.422(1)	0.344 5(9)	0.401(2)	C(316)	0.401(1)	0.003 0(9)	0.117(2)
C(115)	0.378(1)	0.361 1(9)	0.457(2)	C(321)	0.373 1(9)	0.948 3(7)	0.910(1)
C(116)	0.351(1)	0.415 8(8)	0.458(2)	C(322)	0.427(1)	-0.065 8(8)	0.870(2)
C(121)	0.361(1)	0.540 8(8)	0.544(1)	C(323)	0.462(1)	-0.120 9(9)	0.872(2)
C(122)	0.421(1)	0.504 6(8)	0.610(2)	C(324)	0.443(1)	-0.160 4(9)	0.915(2)
C(123)	0.445(1)	0.514 4(9)	0.712(2)	C(325)	0.387(1)	-0.147 0(9)	0.956(2)
C(124)	0.412(1)	0.559 0(9)	0.748(2)	C(326)	0.353(1)	0.909 3(9)	0.954(2)
C(125)	0.351(1)	0.596(1)	0.677(1)	C(331)	0.356(1)	0.062 6(8)	0.842(1)
C(126)	0.325(1)	0.586 8(9)	0.579(2)	C(332)	0.423(1)	0.076 0(8)	0.886(2)
C(131)	0.372(1)	0.564 4(7)	0.347(1)	C(333)	0.446(1)	0.110 8(9)	0.838(2)
C(132)	0.417(1)	0.598 0(8)	0.399(1)	C(334)	0.402(1)	0.135 0(9)	0.745(2)
C(133)	0.446(1)	0.627 9(9)	0.339(2)	C(335)	0.335(1)	0.123(1)	0.701(2)
C(134)	0.425(1)	0.624 4(9)	0.242(2)	C(336)	0.310(1)	0.088 2(9)	0.750(2)
C(135)	0.379(1)	0.592(1)	0.194(2)	C(341)	0.234(1)	0.021 9(8)	0.860(2)
C(136)	0.349(1)	0.563 7(9)	0.245(2)	C(342)	0.190(1)	0.040 0(9)	0.918(2)
C(141)	0.238(1)	0.548 6(8)	0.364(1)	C(343)	0.115(1)	0.042(1)	0.870(2)
C(142)	0.207(1)	0.604 3(9)	0.334(2)	C(344)	0.086(1)	0.028(1)	0.774(2)
C(143)	0.135(1)	0.622 8(9)	0.305(2)	C(345)	0.130(1)	0.010(1)	0.716(2)
C(144)	0.092(1)	0.588(1)	0.298(2)	C(346)	0.206(1)	0.002 5(9)	0.760(2)
C(145)	0.123(2)	0.530(2)	0.342(3)	C(411)	0.151(1)	0.790 6(8)	0.854(1)
C(146)	0.199(2)	0.510(1)	0.366(3)	C(412)	0.088(1)	0.804 3(8)	0.880(2)
C(211)	0.118(1)	0.178 7(8)	0.396(1)	C(413)	0.062(1)	0.857 5(9)	0.900(2)

Table 2 (continued)

Atom	x	y	z	Atom	x	y	z
C(212)	0.134(1)	0.182 0(8)	0.497(2)	C(414)	0.099(1)	0.897 7(9)	0.890(2)
C(213)	0.107(1)	0.151 9(9)	0.554(2)	C(415)	0.158(1)	0.883 7(8)	0.858(2)
C(214)	0.057(1)	0.122(1)	0.494(2)	C(416)	0.185(1)	0.829 2(8)	0.843(1)
C(215)	0.041(1)	0.116 5(9)	0.396(2)	C(421)	0.136 1(9)	0.708 0(7)	0.698(1)
C(216)	0.071 4(9)	0.147 2(7)	0.343(1)	C(422)	0.087(1)	0.746 9(8)	0.631(1)
C(221)	0.249(1)	0.196 6(8)	0.385(2)	C(423)	0.059(1)	0.733 6(8)	0.532(2)
C(222)	0.277(1)	0.144(1)	0.418(2)	C(424)	0.077(1)	0.680 2(9)	0.503(2)
C(223)	0.354(1)	0.124 0(9)	0.460(2)	C(425)	0.129(1)	0.642 3(9)	0.572(2)
C(224)	0.396(1)	0.157(1)	0.467(2)	C(426)	0.159(1)	0.652 1(8)	0.674(1)
C(225)	0.372(2)	0.212(2)	0.447(3)	C(431)	0.274(1)	0.704 8(8)	0.856(1)
C(226)	0.296(2)	0.232(1)	0.392(2)	C(432)	0.300(1)	0.727 6(8)	0.787(2)
C(231)	0.126(1)	0.206 7(7)	0.201(1)	C(433)	0.378(1)	0.716 6(9)	0.813(2)
C(232)	0.161(1)	0.158(1)	0.175(2)	C(434)	0.425(1)	0.682(1)	0.895(2)
C(233)	0.138(2)	0.147(1)	0.070(2)	C(435)	0.394(1)	0.656(1)	0.950(2)
C(234)	0.083(1)	0.183(1)	0.002(2)	C(436)	0.319(1)	0.668(1)	0.933(2)
C(235)	0.047(1)	0.231 1(9)	0.033(2)	C(441)	0.150 6(9)	0.678 3(7)	0.907(1)
C(236)	0.069(1)	0.243 3(8)	0.131(1)	C(442)	0.100(1)	0.650 7(8)	0.861(1)
C(241)	0.123(1)	0.290 5(8)	0.344(1)	C(443)	0.074(1)	0.622 4(9)	0.924(2)
C(242)	0.076(1)	0.309 2(7)	0.396(1)	C(444)	0.102(1)	0.626 2(9)	1.032(2)
C(243)	0.051(1)	0.364 8(9)	0.400(2)	C(445)	0.155(1)	0.655 2(9)	1.074(2)
C(244)	0.067(1)	0.402 2(9)	0.342(2)	C(446)	0.181(1)	0.684 0(9)	1.012(2)

Table 3 Positional parameters for $[\text{NEt}_4][\text{Re}_6\text{HC}(\text{CO})_{10}]\cdot\text{CH}_2\text{Cl}_2$, with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Re(1)	0.055 87(8)	0.172 28(6)	0.135 64(6)	C(51)	-0.069(2)	0.371(2)	0.043(1)
Re(2)	0.324 17(7)	0.280 56(6)	0.243 99(6)	O(51)	-0.164(2)	0.359(1)	-0.021(1)
Re(3)	0.136 68(7)	0.192 90(6)	0.338 71(6)	C(52)	0.080(2)	0.528(2)	0.169(2)
Re(4)	0.208 24(8)	0.411 97(6)	0.358 58(6)	O(52)	0.070(2)	0.614(1)	0.181(1)
Re(5)	0.085 83(7)	0.390 99(6)	0.150 43(6)	C(53)	0.190(2)	0.405(2)	0.073(1)
Re(6)	-0.078 75(7)	0.316 52(6)	0.255 30(6)	O(53)	0.249(2)	0.410(1)	0.023(1)
C	0.118(2)	0.294(1)	0.242(1)	C(61)	-0.243(2)	0.243(2)	0.181(1)
C(11)	0.041(2)	0.171(1)	0.012(2)	O(61)	-0.343(1)	0.202(1)	0.138(1)
O(11)	0.033(2)	0.175(1)	-0.064 3(9)	C(62)	-0.159(2)	0.346(2)	0.355(1)
C(12)	-0.110(2)	0.089(2)	0.090(2)	O(62)	-0.205(1)	0.366(1)	0.411(1)
O(12)	-0.207(1)	0.037(1)	0.072(1)	C(63)	-0.158(2)	0.427(2)	0.205(1)
C(13)	0.138(2)	0.052(1)	0.137(2)	O(63)	-0.218(1)	0.489(1)	0.176(1)
O(13)	0.197(2)	-0.016(1)	0.140(1)	C(19)	0.406(2)	0.367(2)	0.391(2)
C(21)	0.438(2)	0.376(2)	0.221(2)	O(19)	0.513(1)	0.380(1)	0.444(1)
O(21)	0.512(2)	0.437(1)	0.211(1)	N	0.432(2)	0.208(1)	0.817(1)
C(22)	0.476(2)	0.208(2)	0.291(1)	C(T1)	0.377(6)	0.099(4)	0.824(4)
O(22)	0.568(1)	0.167(1)	0.318(1)	C(T2)	0.301(5)	0.250(4)	0.750(4)
C(23)	0.322(2)	0.209(2)	0.126(1)	C(T3)	0.478(4)	0.276(3)	0.918(3)
O(23)	0.347(1)	0.171(1)	0.063(1)	C(T4)	0.560(6)	0.216(5)	0.779(4)
C(31)	0.134(2)	0.211(1)	0.456(2)	C(T1')	0.473(5)	0.849(4)	0.113(3)
O(31)	0.128(2)	0.223(1)	0.536(1)	C(T2')	0.493(5)	0.324(4)	0.836(4)
C(32)	0.044(2)	0.066(2)	0.304(2)	C(T3')	0.283(6)	0.203(4)	0.837(4)
O(32)	-0.013(2)	-0.012(1)	0.286(1)	C(T4')	0.402(7)	0.162(5)	0.720(5)
C(33)	0.300(2)	0.133(2)	0.383(2)	C(T5)	0.492(3)	0.046(2)	0.879(2)
O(33)	0.395(2)	0.092(2)	0.417(2)	C(T6)	0.184(3)	0.257(2)	0.778(2)
C(41)	0.299(2)	0.533(2)	0.352(2)	C(T7)	0.506(3)	0.377(2)	0.926(2)
O(41)	0.356(2)	0.604(1)	0.347(1)	C(T8)	0.529(4)	0.150(3)	0.691(3)
C(42)	0.261(2)	0.418(1)	0.491(2)	C(Cl)	0.262(5)	0.891(3)	0.473(3)
O(42)	0.300(2)	0.420(1)	0.570(1)	Cl(1)	0.175(1)	0.952 9(9)	0.534 6(9)
C(43)	0.071(2)	0.497(2)	0.380(2)	Cl(2)	0.162(2)	0.811(2)	0.369(1)
O(43)	0.003(2)	0.554(1)	0.399(1)	Cl(2')	0.208(3)	0.796(2)	0.441(3)

range 10.0–14.0° were used in each case to determine by least-squares fit the unit-cell parameters together with an orientation matrix relating the crystal axes to the diffractometer axes. Data collections were performed by the ω scan method, within the limits $3 < \theta < 24$ (2) and $3 < \theta < 25$ (3). A total of 21 080 [9407 with $I > 3\sigma(I)$] (2) and 7303 [3486 with $I > 3\sigma(I)$] (3) diffracted intensities were collected at room temperature with variable scan speed (from 2 to 20° min⁻¹) and variable scan range of $(a + 0.35\tan \theta)$, with $a = 0.7$ (2) and 1.2° (3), the maximum scanning times for reflection being 60 (2) and 70 s (3). The crystal stability under diffraction conditions was checked by monitoring three standard reflections every 60 min. Final drift corrections were 1.00–1.10 (2) and 1.00–1.30 (3). The

diffracted intensities were corrected for Lorentz polarization and background effects. An empirical absorption correction, based on Ψ scans (Ψ 0–360° every 10°) of three suitable reflections with χ values close to 90° was applied,²⁷ the relative transmission factors having values in the ranges 1.00–0.90 (2) and 1.00–0.83 (3).

Structure solutions and refinements. All the calculations were performed on a PDP 11/73 computer using the SDP-Plus Structure Determination Package.²⁸ Scattering factors for neutral atoms and anomalous dispersion corrections were taken from refs. 29 and 30, respectively. Both structures were solved by deconvolution of the Patterson map (Re atoms only), successive Fourier-difference maps showing the locations of all the non-

hydrogen atoms. The refinements were carried out by full-matrix least squares, minimizing the function $\sum w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{1/2}/2F_oL_p$ and $\sigma^2(I)$ is the standard deviation for each reflection as derived from counting statistics, k ($=0.035$) is a coefficient for improving the goodness of fit and L_p is the Lorentz-polarization factor. Anisotropic thermal parameters were assigned to all the Re atoms and, in **3**, also to chlorine and to all the carbonyl atoms. The $[\text{NEt}_4]^+$ cation and the clathrate CH_2Cl_2 molecule, in **3**, are disordered; hence, the four *N*-bound carbon atoms and one Cl atom were doubled and refined as half atoms. The final values of the conventional agreement indices *R* and *R'* were 0.046 and 0.051 (**2**) and 0.038 and 0.040 (**3**). Maximum residuals in the final Fourier difference synthesis were, in both cases, of ca. $2 \text{ e } \text{\AA}^{-3}$ close to the metal atoms. The final positional parameters are given in Tables 2 (**2**) and 3 (**3**).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support and the Italian Consiglio Nazionale delle Ricerche (CNR) for providing instrumental facilities. The referees are acknowledged for their helpful criticisms.

References

- 1 T. Beringhelli, G. D'Alfonso, M. Freni, G. Ciani and A. Sironi, *J. Organomet. Chem.*, 1985, **295**, C7.
- 2 T. J. Henly, J. R. Shapley, A. L. Rheingold and S. J. Gelby, *Organometallics*, 1988, **7**, 441; T. J. Henly, S. R. Scott and J. R. Shapley, *Inorg. Chem.*, 1988, **27**, 2551; T. J. Henly and J. R. Shapley, *Organometallics*, 1989, **8**, 2729.
- 3 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1982, 339.
- 4 T. Beringhelli, G. Ciani, G. D'Alfonso, A. Sironi and M. Freni, *J. Chem. Soc., Chem. Commun.*, 1985, 978.
- 5 R. H. Reimann and E. Sigleton, *J. Organomet. Chem.*, 1973, **59**, C24; R. E. Christopher and L. M. Venanzi, *Inorg. Chim. Acta*, 1973, **7**, 489.
- 6 M. F. Faroni and K. F. Kraus, *Inorg. Chem.*, 1970, **9**, 1700.
- 7 G. R. John, B. F. G. Johnson, J. Lewis and A. L. Mann, *J. Organomet. Chem.*, 1979, **171**, C9; V. G. Albano, D. Braga, A. Fumagalli and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1985, 1137.
- 8 R. J. Goudsmit, P. F. Jackson, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, M. D. Vargas, D. Braga, M. McPartlin and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1985, 1795; S. R. Drake, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. D. Vargas, T. Adatia, D. Braga, K. Henrick, M. McPartlin and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1989, 1455; S. Martinengo, P. Chini, G. Giordano, A. Ceriotti, V. G. Albano and G. Ciani, *J. Organomet. Chem.*, 1975, **88**, 375; G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and S. Sironi, *J. Organomet. Chem.*, 1981, **220**, C11; G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *Inorg. Chem.*, 1983, **22**, 3115.
- 9 D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311.
- 10 (a) D. H. Farrar, P. F. Jackson, B. F. G. Johnson, J. Lewis, J. N. Nicholls and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1981, 415; (b) A. G. Cowie, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1984, 1710.
- 11 J. S. Bradley, E. W. Hill, G. B. Ansell and M. A. Modrick, *Organometallics*, 1982, **1**, 1634.
- 12 S. Martinengo, G. Ciani and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1986, 1282.
- 13 T. Beringhelli, G. D'Alfonso, M. De Angelis, G. Ciani and A. Sironi, *J. Organomet. Chem.*, 1987, **322**, C21.
- 14 T. Beringhelli, G. D'Alfonso, G. Ciani, A. Sironi and H. Molinari, *J. Chem. Soc., Dalton Trans.*, 1990, 1901.
- 15 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1982, 705.
- 16 G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi and M. Freni, *J. Organomet. Chem.*, 1983, **244**, C27.
- 17 T. Beringhelli, G. D'Alfonso, G. Ciani, A. Sironi and H. Molinari, *J. Chem. Soc., Dalton Trans.*, 1988, 1281.
- 18 T. J. Henly, S. R. Wilson and J. R. Shapley, *Organometallics*, 1987, **6**, 2618.
- 19 V. G. Albano and D. Braga, in *Accurate Molecular Structures*, eds. A. Domenicano and I. Hargittai, Oxford University Press, 1991.
- 20 C. Tolman, *Chem. Rev.*, 1977, **77**, 313.
- 21 D. P. M. Mingos, *Inorg. Chem.*, 1982, **21**, 466.
- 22 C. P. Horwitz, E. M. Holt and D. F. Shriver, *Inorg. Chem.*, 1984, **23**, 2491.
- 23 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.
- 24 K. Henrick, M. McPartlin and J. Morris, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 853.
- 25 D. Eufri and A. Sironi, *J. Mol. Graphics*, 1989, **7**, 165.
- 26 C. T. Hayward and J. R. Shapley, *Organometallics*, 1988, **7**, 448.
- 27 A. C. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- 28 B. A. Frenz and Associates, SDP Plus Version 1.0, Enraf-Nonius, Delft, 1980.
- 29 D. T. Cromer, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.3.1 (present distributor Kluwer Academic Publishers, Dordrecht).
- 30 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2.b.

Received 26th July 1991; Paper 1/03835D