Synthesis, Solid-state (*X*-Ray) and Solution (Nuclear Magnetic Resonance) Studies of the Hydridocarbido Carbonyl Cluster Anion $[Re_7H_2C(CO)_{21}]^-$ †

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The protonation of $[Re_7H(C)(CO)_{21}]^{2-}$ with CF_3SO_3H in dichloromethane solution produces $[Re_7H_2C(CO)_{21}]^-$ which behaves as a strong acid, being completely dissociated in basic solvents. In acetonitrile the compound loses the capping $Re(CO)_3$ unit, giving the octahedral dianion $[Re_6H_2C(CO)_{18}]^{2-}$. The $[NEt_4]^+$ salt crystallizes in the monoclinic system, space group $P2_1/c$ (no. 14), with $a = 9.394(3)$, $b = 15.669(3)$, $c = 27.983(6)$ Å, $\beta = 90.87(3)°$, and $Z = 4$. The structure of the anion is closely related to that of the parent compounds $[Re_7H(C)(CO)_{21}]^{2-}$ and $[Re_7C(CO)_{21}]^{3-}$, where a carbon-centred monocapped octahedron of rhenium atoms is surrounded by 21 terminal carbonyl ligands, three for each metal. The two hydride ligands have been indirectly located on the basis of potential-energy computations as double bridging, one on an edge of the basal triangle and the other one on an inter-layer edge. The ^1H n.m.r. spectra at low temperature show the presence in solution of three isomers (ratio *ca.* 1:1.5:10) rapidly exchanging at room temperature. The possible locations of the hydrides in these species are also discussed in the light of the variable-temperature ^{13}C n.m.r. spectra.

We have recently reported[1] the *X*-ray crystal-structure analysis of two isomers of the hydridocarbido carbonyl cluster anion $[Re_7H(C)(CO)_{21}]^{2-}$, obtained by protonation of the trianion $[Re_7C(CO)_{21}]^{3-}$.[2] In both cases potential-energy computations led to the location of the H ligand as double bridging, in the solid-state structure, in contrast with the triple-bridging co-ordination previously suggested[3] on the basis of the apparent C_3 symmetry shown by the solution n.m.r. spectra of the CO ligands. We also evidenced the 'non-innocent' nature of the μ_3-H co-ordination in clusters containing interstitial main-group atoms. In particular, for octahedral carbide clusters, we showed the possibility of a repulsive interaction between the interstitial carbon atom and a triple-bridging hydride. We have now succeeded in bonding a second H ligand to the $[Re(CO)_3]_7C$ moiety. Also in this case, the *X*-ray analysis and potential-energy computations have located the two H ligands as double bridging and the n.m.r. spectra have shown the presence of more than one isomer in solution. In this case it was possible, in contrast to studies on $[Re_7H(C)(CO)_{21}]^{2-}$, to obtain a ^{13}C n.m.r. spectrum quite near to the stopped-exchange region, showing, for the major isomer, a C_1 symmetry, in accord with the solid-state structure.

Results and Discussion

The carbido-cluster anion $[Re_7C(CO)_{21}]^{3-}$, (1), as previously reported,[1,3] can be readily protonated by strong acids such as H_2SO_4, $HClO_4$, or HBF_4, to give the hydridic derivative $[Re_7H(C)(CO)_{21}]^{2-}$, (2). No further protonation of compound (2) was observed by addition of an excess of the strong aqueous acids mentioned above or of CF_3SO_3H in acetone or tetrahydrofuran solution. However, treatment of a dichloromethane solution of compound (2) with a slight excess of CF_3SO_3H caused an immediate shift of the ν(CO) bands to higher frequencies, in accord with the occurrence of a second protonation (no H_2 evolution was observed). The $[NEt_4]^+$ salt of the dihydride $[Re_7H_2C(CO)_{21}]^-$, (3), was then isolated by crystallization of the reaction mixture with n-pentane and the formulation was confirmed by elemental analyses, n.m.r. spectra, and an *X*-ray crystal-structure determination (see below).

Compound (3) in solution behaves as a strong acid, being completely dissociated in donor solvents, such as acetone, methanol, or tetrahydrofuran. This explains the failure to observe the second protonation step in these solvents, even with CF_3SO_3H. After removal of the solvent under vacuum, the residue again gave the ν(CO) bands of compound (3), upon dissolution in CH_2Cl_2. Perhaps the best proof of the acidic strength of compound (3) is the impossibility to protonate further compound (2), even in CH_2Cl_2, with a strong acid like $HBF_4 \cdot OEt_2$.[3] In line with this behaviour, any attempt to obtain a neutral trihydridic derivative, by use of a large excess of CF_3SO_3H in CH_2Cl_2, failed.

The behaviour of compound (3) in acetonitrile is noteworthy. Infrared and n.m.r. analyses of solutions of compound (3) in this solvent revealed the formation of the previously characterized[4] hydridocarbido carbonyl cluster $[Re_6H_2C(CO)_{18}]^{2-}$, due to cleavage of the capping $Re(CO)_3$ moiety, as $[Re(CO)_3(NCMe)_3]^+$,[5] according to reaction (1). In this case therefore

$$[Re_7H_2C(CO)_{21}]^- + 3MeCN \longrightarrow [Re_6H_2C(CO)_{18}]^{2-} + [Re(CO)_3(NCMe)_3]^+ \quad (1)$$

the nucleophilicity of the solvent [MeCN is a good ligand for rhenium(I) carbonyl compounds] is more effective than its basicity. A similar 'disproportionation' reaction has already

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† μ_6-Carbido-1,1,1,2,2,2,3,3,3,4,4,4,5,5,5,6,6,6-octadecacarbonyl-1,4;4,5-dihydrido-1,2,3-tricarbonylrhenio-*octahedro*-hexarhenate (1−).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

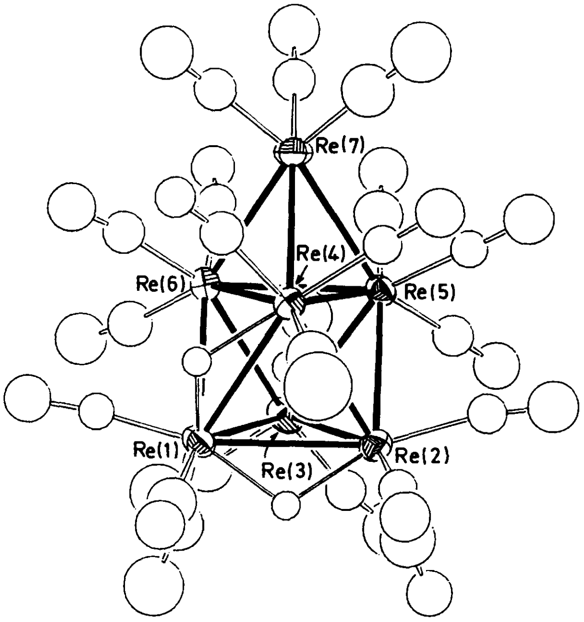


Figure 1. A view of the anion $[Re_7(\mu\text{-}H)_2C(CO)_{21}]^-$ (**3**) in its $[NEt_4]^+$ salt showing the computed H locations

Table 1. Metal–metal bond distances (Å) in $[Re_7C(CO)_{21}]^{3-}$ (**1**), the parent anions $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$, isomers (**2a**) and (**2b**), and $[Re_7(\mu\text{-}H)_2C(CO)_{21}]^-$ (**3**) [estimated standard deviations (e.s.d.s) in (**1**), (**2a**), and (**2b**) are all 0.001 Å, and 0.002 Å in (**3**)]. See text for classication of Re–Re distances

Compound	(**1**)	(**2a**)	(**2b**)	(**3**)
Class (*i*)				
Re(1)–Re(2)	3.084	3.032	3.036	3.007*
Re(1)–Re(3)	3.069	3.083	3.007	3.080
Re(2)–Re(3)	3.086	3.014*	3.099	3.100
Mean	3.080	3.043	3.047	3.062
Class (*ii*)				
Re(1)–Re(4)	3.015	2.986	3.059	3.031*
Re(1)–Re(6)	2.981	2.941	3.016	3.018
Re(2)–Re(4)	2.981	3.019	2.945	3.046
Re(2)–Re(5)	3.012	3.048	3.011	2.968
Re(3)–Re(5)	2.969	2.996	3.010*	3.007
Re(3)–Re(6)	3.022	3.028	2.989	2.944
Mean	3.017/2.977	3.021/2.985	3.020/2.990	3.024/2.981
Class (*iii*)				
Re(4)–Re(5)	2.952	2.927	3.021	2.960
Re(4)–Re(6)	2.957	3.003	2.950	2.928
Re(5)–Re(6)	2.955	2.952	2.973	3.017
Mean	2.955	2.961	2.981	2.968
Class (*iv*)				
Re(4)–Re(7)	2.917	2.939	2.915	2.988
Re(5)–Re(7)	2.927	2.927	2.962	2.977
Re(6)–Re(7)	2.943	2.979	2.983	2.913
Mean	2.929	2.948	2.953	2.959

* Re–H–Re interactions.

been observed in a rhodium cluster[6] [equation (2)].

$$[Rh_8C(CO)_{19}] + 4MeCN \longrightarrow [Rh_6C(CO)_{15}]^{2-} + 2[Rh(CO)_2(NCMe)_2]^+ \quad (2)$$

X-Ray Analysis.—A view of the anion $[Re_7(\mu\text{-}H)_2C(CO)_{21}]^-$ is reported in Figure 1. The gross features of the structure, that is, the presence of a carbon-centred monocapped octahedron of metal atoms, surrounded by 21 terminal carbonyl ligands, three for each metal, are in common with the parent compounds $[Re_7C(CO)_{21}]^{3-}$ (**1**) and the two isomers of $[Re_7H(C)(CO)_{21}]^{2-}$, (**2a**) and (**2b**). The metal–metal interactions, as in compounds (**1**) and (**2**), belong to four different classes: (*i*) bonds within the basal triangle, (*ii*) bonds connecting the basal to the central triangle (alternatively three longer and three shorter), (*iii*) bonds within the central triangle, and (*iv*) bonds involving the capping rhenium atom (see Table 1).

Table 2. Bond distances (Å) and angles (°) within the $Re(CO)_3$ moieties in compound (**3**)

Re(1)–C(11)	1.94(5)	C(11)–O(11)	1.12(5)
Re(1)–C(12)	1.80(5)	C(12)–O(12)	1.27(5)
Re(1)–C(13)	1.84(4)	C(13)–O(13)	1.21(4)
Re(2)–C(21)	1.98(4)	C(21)–O(21)	1.13(4)
Re(2)–C(22)	1.88(4)	C(22)–O(22)	1.11(4)
Re(2)–C(23)	1.89(6)	C(23)–O(23)	1.13(5)
Re(3)–C(31)	1.88(4)	C(31)–O(31)	1.18(5)
Re(3)–C(32)	1.90(5)	C(32)–O(32)	1.14(5)
Re(3)–C(33)	1.91(4)	C(33)–O(33)	1.14(4)
Re(4)–C(41)	1.91(4)	C(41)–O(41)	1.15(4)
Re(4)–C(42)	1.92(4)	C(42)–O(42)	1.19(4)
Re(4)–C(43)	1.85(5)	C(43)–O(43)	1.20(5)
Re(5)–C(51)	1.83(4)	C(51)–O(51)	1.21(4)
Re(5)–C(52)	1.89(4)	C(52)–O(52)	1.19(4)
Re(5)–C(53)	1.80(5)	C(53)–O(53)	1.22(5)
Re(6)–C(61)	1.91(4)	C(61)–O(61)	1.15(4)
Re(6)–C(62)	2.01(4)	C(62)–O(62)	1.14(4)
Re(6)–C(63)	1.90(5)	C(63)–O(63)	1.13(5)
Re(7)–C(71)	1.82(5)	C(71)–O(71)	1.22(5)
Re(7)–C(72)	1.87(5)	C(72)–O(72)	1.16(4)
Re(7)–C(73)	1.78(5)	C(73)–O(73)	1.23(5)

Re(1)–C(11)–O(11)	166(4)	Re(4)–C(43)–O(43)	172(5)
Re(1)–C(12)–O(12)	170(4)	Re(5)–C(51)–O(51)	177(3)
Re(1)–C(13)–O(13)	172(3)	Re(5)–C(52)–O(52)	178(4)
Re(2)–C(21)–O(21)	169(4)	Re(5)–C(53)–O(53)	171(4)
Re(2)–C(22)–O(22)	174(3)	Re(6)–C(61)–O(61)	173(4)
Re(2)–C(23)–O(23)	177(5)	Re(6)–C(62)–O(62)	165(3)
Re(3)–C(31)–O(31)	170(4)	Re(6)–C(63)–O(63)	171(4)
Re(3)–C(32)–O(32)	175(5)	Re(7)–C(71)–O(71)	176(5)
Re(3)–C(33)–O(33)	171(3)	Re(7)–C(72)–O(72)	177(4)
Re(4)–C(41)–O(41)	173(4)	Re(7)–C(73)–O(73)	179(4)
Re(4)–C(42)–O(42)	172(3)		

The metal–carbide bond distances are in the range 2.11(4)—2.17(4) Å (mean 2.13 Å). Table 2 contains the main metal–carbonyl bonding parameters. The carbonyls' stereochemistry has no apparent symmetry but a closer view reveals that it is intermediate between those of the two isomers of compound (**2**), the main departure from the C_s symmetry of (**2a**) being localized on the $Re(CO)_3$ moiety of Re(4) which is bent and rotated so as to unhinder the Re(1)–Re(4) edge. Thus the basal $Re_3(CO)_9$ moiety resembles that of (**2a**) while the upper $Re_4(CO)_{12}$ one resembles that of (**2b**). This suggests that the co-ordination sites of the two H ligands are those in (**2a**) and (**2b**).

The indirect location of the hydride ligands in transition-metal clusters is often based on stereochemical considerations (metal–metal bond lengthening and/or holes in the ligand arrangement). We have used the Orpen program[7] to inspect the possible locations of the hydride ligands. As previously discussed,[1] we have deliberately omitted the interstitial carbide atom from the computation, 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 μ_3 location. Selected results of the computations are reported in Table 3.

Table 3. Potential-energy values (arbitrary units) computed by the Orpen program [7] for different hydride locations on compounds (**1**), (**2a**), (**2b**), and (**3**). The carbido atom has been omitted from the computations for the μ_3 locations: a 2-Å C–H interaction raises the energy by *ca.* 10 units. For compound (**3**) the potential energy for the μ sites takes account of the mutual H • • • H interactions

Hydride location	(**1**)	(**2a**)	(**2b**)	(**3**)[a]
μ_3 On the basal face	1.5	5.3	4.5	8.2
μ On the less-hindered basal edge	13[b]	2.7	13[b]	5.4
μ On the less-hindered interlayer edge	>25	>25	7.0	4.1

[a] The less-hindered basal Re(1)–Re(2) and interlayer Re(1)–Re(4) edges share a common triangular face. A μ_3-H on that face would feel a potential energy of 7.0 units. [b] The program failed to find a proper μ location because of the strong repulsion with the CO ligands and the reported energy value corresponds to a pseudo-μ location, *i.e.* to a μ_3 co-ordination on the basal face where one of the Re–H interactions is considered repulsive.

The holes found in the basal faces of compounds (**2a**), (**2b**), and (**3**) do not imply necessarily the presence of hydride ligands, because an even larger hole is found in the same position in $[Re_7C(CO)_{21}]^{3-}$, which does *not* possess hydride ligands. Their presence simply reflects the difficulty for 21 carbonyls to occupy the space around a Re_7 cluster in a homogeneous way. It is therefore reasonable to locate the two μ-H hydrides on the unhindered basal [Re(1)–Re(2)] and interlayer [Re(1)–Re(4)] edges where we have found the two lowest minima (see Table 3). The hole on the Re(1)–Re(2)–Re(4) face is simply the result of the contemporary presence of two bridging hydrides on two edges of this face.

It is interesting that while the interlayer μ-H bridged edge is slightly lengthened (with respect to the mean value of its class), the basal one is the shortest basal edge. Similar features were found also in compounds (**2b**) and (**2a**). That is, in compound (**2b**) the μ-H interlayer edge was lengthened, while in (**2a**) the μ-H basal edge was the shortest. Thus the 'bond lengthening–μ-H presence' criterion, generally adopted for the indirect location of the hydrides, must be used cautiously.

N.M.R. Analysis.—All the experiments have been performed in CD_2Cl_2 solution to avoid dissociation of the strong acid (**3**). To improve the solubility in this solvent, the $[N(PPh_3)_2]^+$ salt was used. At 193 K, the ^1H n.m.r. spectrum exhibits four signals in the hydridic region: two at δ −17.05 and −18.75 and two of much higher intensity at δ −20.27 and −21.60 (Figure 2). This spectrum suggests the presence in solution of two different isomers, both with non-equivalent hydrides. However, the relative ratios of the integrated intensities of the resonances are *ca.* 1:1:10:13 respectively. The significant difference in the integrals of the two high-field signals was maintained either by varying the relaxation delay from 0 to 10 s, by changing the nature of the counter ion [NEt_4^+, NBu_4^+, or $N(PPh_3)_2^+$], or by further lowering the temperature. This can be accounted for by assuming that three isomers are present. Two different hypotheses can be envisaged. The first implies the presence of a minor species, (**A**), with non-equivalent hydrides, and two major species (**B**) and (**C**), both having equivalent hydrides [ratio (**A**):(**B**):(**C**) = 1:5:6.5]. The second one requires two species having non-equivalent hydrides [with the minor one, (**A**), giving the two low-field resonances, and the other one, (**B**), having hydrides resonating at δ −20.27 and −21.60] while the hydrides of the third isomer (**C**) would give a unique resonance at −21.60 p.p.m., accidentally overlapping the high-field signal of the major isomer (**B**) [ratio (**A**):(**B**):(**C**) = 1:10:1.5]. The resonance of the carbido atom in the parent dianion $[Re_7H(C)(CO)_{21}]^{2-}$ was sensitive to the location of the hydride

Table 4. Positional parameters for $[NEt_4][Re_7H_2C(CO)_{21}]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re(1)	0.352 8(2)	0.410 80(9)	0.820 95(6)
Re(2)	0.602 5(2)	0.332 1(1)	0.771 43(5)
Re(3)	0.652 0(2)	0.431 75(9)	0.865 93(6)
Re(4)	0.394 3(1)	0.219 06(9)	0.824 72(5)
Re(5)	0.690 3(1)	0.241 54(8)	0.860 23(5)
Re(6)	0.442 3(2)	0.319 80(9)	0.911 60(5)
Re(7)	0.488 3(2)	0.136 1(1)	0.916 03(6)
C	0.523(4)	0.330(2)	0.842(1)
C(11)	0.213(5)	0.422(3)	0.769(2)
O(11)	0.130(3)	0.411(2)	0.741(1)
C(12)	0.394(5)	0.522(3)	0.815(2)
O(12)	0.400(4)	0.603(2)	0.810(1)
C(13)	0.219(4)	0.439(2)	0.865(1)
O(13)	0.121(3)	0.462(2)	0.890(1)
C(21)	0.759(4)	0.255(2)	0.754(1)
O(21)	0.848(3)	0.217(2)	0.737(1)
C(22)	0.519(4)	0.304(2)	0.712(1)
O(22)	0.462(3)	0.292(2)	0.678(1)
C(23)	0.707(5)	0.420(3)	0.742(2)
O(23)	0.775(3)	0.472(2)	0.725 0(9)
C(31)	0.799(4)	0.494(2)	0.837(1)
O(31)	0.902(3)	0.520(2)	0.818(1)
C(32)	0.603(5)	0.543(3)	0.887(2)
O(32)	0.570(4)	0.606(2)	0.903(1)
C(33)	0.774(3)	0.427(2)	0.921(1)
O(33)	0.841(3)	0.414(2)	0.955(1)
C(41)	0.229(4)	0.162(3)	0.848(1)
O(41)	0.122(2)	0.135(2)	0.859 7(8)
C(42)	0.481(4)	0.111(2)	0.810(1)
O(42)	0.525(3)	0.045(2)	0.795(1)
C(43)	0.321(5)	0.203(3)	0.763(2)
O(43)	0.259(4)	0.191(3)	0.726(1)
C(51)	0.760(4)	0.142(2)	0.835(1)
O(51)	0.809(3)	0.076(2)	0.820(1)
C(52)	0.876(4)	0.281(2)	0.847(1)
O(52)	0.991(3)	0.307(2)	0.839(1)
C(53)	0.764(5)	0.215(3)	0.918(2)
O(53)	0.832(3)	0.203(2)	0.955(1)
C(61)	0.260(4)	0.285(2)	0.934(1)
O(61)	0.145(3)	0.270(2)	0.944(1)
C(62)	0.546(4)	0.287(2)	0.972(1)
O(62)	0.599(3)	0.287(2)	1.009 2(9)
C(63)	0.414(4)	0.425(3)	0.944(2)
O(63)	0.385(3)	0.482(2)	0.966(1)
C(71)	0.534(5)	0.027(3)	0.901(2)
O(71)	0.569(4)	−0.045(2)	0.889(1)
C(72)	0.320(4)	0.096(2)	0.943(1)
O(72)	0.213(3)	0.071(2)	0.958(1)
C(73)	0.567(4)	0.111(2)	0.972(1)
O(73)	0.620(3)	0.093(2)	1.012(1)
N	1.010(4)	0.304(3)	0.585(2)
C(1)	1.002(8)	0.222(5)	0.553(3)
C(2)	1.177(6)	0.276(3)	0.600(2)
C(3)	1.012(6)	0.378(4)	0.555(2)
C(4)	0.94(1)	0.272(6)	0.631(3)
C(5)	0.97(1)	0.154(7)	0.588(4)
C(6)	1.277(4)	0.288(3)	0.562(1)
C(7)	1.06(1)	0.462(8)	0.595(5)
C(8)	0.765(9)	0.334(6)	0.612(3)

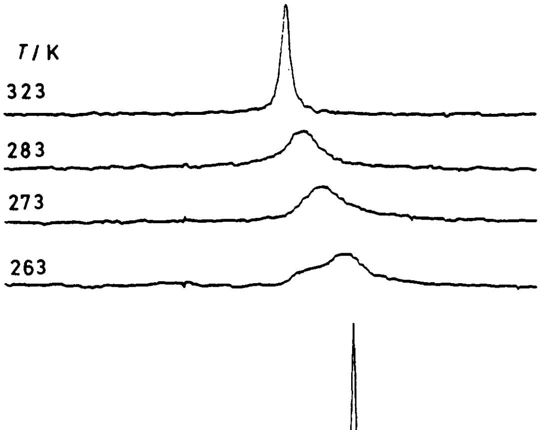


Figure 2. The hydridic region of the ^1H n.m.r. spectra of compound (**3**) at different temperatures, in CD_2Cl_2 ($CDCl_3$ for the spectrum at 323 K)

(two different signals were observed for the two isomers of this species). For compound (**3**) therefore (apart from accidental overlap) three different signals should be observed, with quite different intensity ratios in the two hypotheses, corresponding to the different relative amounts of the three isomers (**A**)—(**C**) in the two cases. Indeed, at 178 K the ^{13}C n.m.r. spectrum {recorded on a ^{13}C-enriched sample obtained from ^{13}CO-enriched $[Re_2(CO)_{10}]$} shows at low field, in the region of the resonances of the carbido atoms co-ordinated in a metal cage, only one main signal, at 405.2 p.p.m., attributable to the dominant isomer (**B**), in line with the second hypothesis. Another resonance can be detected at 415.1 p.p.m. (intensity about 1:6) while the signal of the third species could not be identified with certainty due to the low signal-to-noise ratio.

The variable-temperature ^1H n.m.r. spectra are reported in Figure 2. On raising the temperature first the two resonances at lower field collapse and coalesce, indicating the presence of an intramolecular scrambling process in isomer (**A**). At 243 K the different broadening of the two high-field resonances (which rules out definitely the hypothesis that implies only two isomers) indicates that an intramolecular scrambling process begins to be operative in (**B**) also. Computer simulations of the spectra, performed according to the aforementioned hypothesis, indicate that the rates of the two processes are very different [k = 1 000 for the scrambling in (**A**) and 40 s^{-1} for that in (**B**), at 243 K]. The activation free energy at the temperature of coalescence for isomer (**A**) can be estimated as 10 kcal mol^{-1} (41.84 kJ mol^{-1}). At temperatures higher than 243 K a multisite exchange process became apparent leading to mutual interconversion of the three isomers. The shift to higher frequency of the unique broad signal which is observed above 273 K is indicative of an increased amount of isomer (**A**) in the solution mixture.

Three processes, of increasing energy, are therefore revealed: (*i*) scrambling of the hydride ligands between the two sites occupied in isomer (**A**), (*ii*) scrambling of the hydride ligands between the two sites occupied in isomer (**B**), and (*iii*) multisite scrambling of the hydride ligands, equalizing the three isomers (**A**)—(**C**). A fourth process would be operative if the unique resonance of isomer (**C**) was the product of a very low activation-energy scrambling, equalizing two otherwise different hydrides. The sharpening of the signal at −21.60 p.p.m. from 193 to 223 K could be indicative of that, but definitive evidence is lacking.

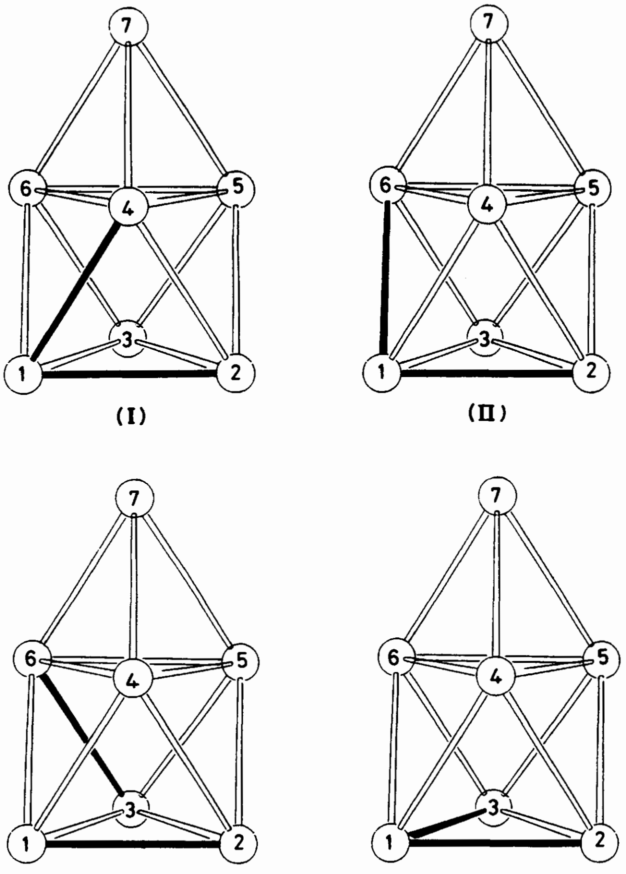
Steric and electronic requirements strongly suggest that in all three species at least one of the hydrides is bridging one edge of the basal triangle. The isomers (**A**) and (**B**) could therefore reasonably correspond to two of the three possible interlayer locations of the second hydride [shown in the Scheme, structure (**I**) being the solid-state one], while for isomer (**C**), (**IV**) is the most likely structure in the hypothesis of a non-dynamic equivalence of the hydrides.

The first three structures have C_1 symmetry and for all of them the ^{13}C n.m.r. spectrum is expected to show 21 signals in the stopped-exchange limit. However, some information on the location of the hydrides in the major isomer (**B**) could be obtained by the near-stopped-exchange region, assuming that the mobility of the three CO on each Re atom in the octahedral cage is hindered by the presence of extra ligands [H and/or capping $Re(CO)_3$].

Previous work has shown that the localized carbonyl scrambling on each metal atom of a $[Re_6(CO)_{18}C]$ cluster moiety can be frozen out (at least partially) at low temperatures when *two* additional ligands (H or capping ML_n groups) are bound to this unit {see $[Re_7C(CO)_{21}(ML_n)]^{2-}$, where $ML_n = Re(CO)_3$,[8] $Rh(CO)_2$, $Rh(CO)(PPh_3)$, Rh(cod) (cod = cyclo-octa-1,5-diene), Ir(cod), $Pd(C_3H_5)$, $Pt(C_4H_7)$, or $Pt(CH_3)_3$;[9] $[Re_7H(C)(CO)_{21}]^{2-}$;[1,3] and $[Re_6H_2C(CO)_{18}]^{2-}$[4]}, but not when only *one* such ligand is present {see $[Re_7C(CO)_{21}]^{3-}$ or $[Re_6H(C)(CO)_{18}]^{3-}$[10]}. Moreover, the presence of a bridging hydride has been reported to raise (by 20 kJ mol^{-1}) the barrier to axial–radial site exchange for the carbonyls in clusters of formula $[M_3H(CO)_9L]$ (M = Ru or Os, L = μ_3-organic ligand).[11]

At room temperature the ^{13}C n.m.r. spectrum (Figure 3) consists of three signals in the ratio 3:9:9 indicative of an apparent C_3 symmetry, as observed also for the related anions $[Re_7C(CO)_{21}]^{3-}$ and $[Re_7H(C)(CO)_{21}]^{2-}$. The number of CO signals is therefore dictated simply by the symmetry of the metallic cage, in accord with the multisite fluxionality of the H ligands indicated by the proton n.m.r. spectrum and with the localized scrambling of the CO ligands about each Re atom observed at room temperature in all the related rhenium carbido species.

On lowering the temperature the hydride movement became progressively more difficult; this caused initially a broadening of the two more intense signals, which, being at quite close frequencies, gave rise to only one broad resonance. Subsequently, at temperatures low enough to freeze any hydride fluxionality, the localized CO exchange was hindered and a



(I) (II)

(III) (IV)

Scheme.

series of resonances grew from the collapse of the broad resonance due to the 18 carbonyls of the octahedral cage. It was necessary to attain the temperature of 155 K (by adding one-third of Freon 21 to the CD_2Cl_2 solvent) to obtain a spectrum quite near to the stopped-exchange one. The signals of the minor isomers obviously could not be identified, being of much lower intensity and obscured by the resonances of (**B**), which gives 15 signals, in the ratio 3:3:1:1:2:1:1:1:1:2:1:1:1:1:1. The lower-field signal is unambiguously assigned to the carbonyls co-ordinated on the capping atom Re(7), being unchanged by a change in temperature. The second signal of intensity 3 cannot be accounted for by structure (III), while in the structures (I) and (II) it can be assigned to the carbonyls co-ordinated to Re(3), to which neither H nor the capping Re atoms are connected. In this hypothesis, therefore, the major species present in solution can have the solid-state structure (I) or the closely related structure (II): in both cases the three rhenium atoms of the basal face are well differentiated, bearing respectively two, one, and zero hydride ligands.

Experimental

The reactions were performed under N_2, using the Schlenk technique, in solvents deoxygenated and dried by standard methods. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer (0.1-mm CaF_2 cells) calibrated with polystyrene film absorptions, ^1H n.m.r. spectra on a Bruker WP 80 spectrometer operating at 80.13 MHz, and ^{13}C spectra on a Varian XL300 spectrometer operating at 75.4 MHz. The temperature was controlled by the variable-temperature units of the instruments and calibrated with methanol solutions.

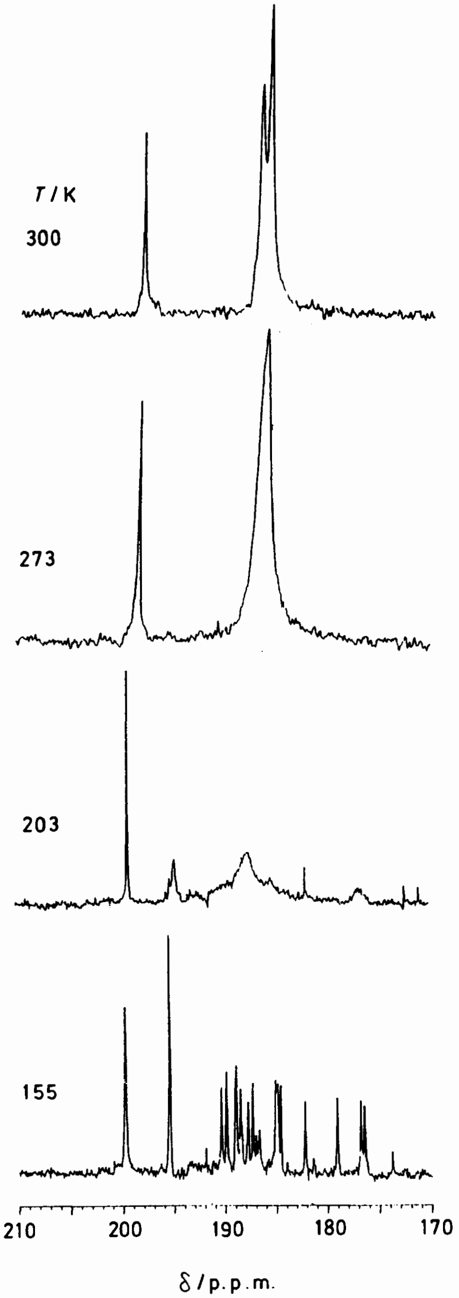


Figure 3. Carbonyl region of the $\{^1H\}$-^{13}C n.m.r. spectra of compound (3) at different temperatures in CD_2Cl_2. For the spectrum at 155 K a mixture of Freon 21 and CD_2Cl_2 was used as solvent

Computer simulations of the spectra were performed on a personal computer using a modified version of the program POLY[12] that calculates the bandshape for the exchange of spin $\frac{1}{2}$ nuclei between many uncoupled sites with arbitrary population. Elemental analyses were performed by the Microanalytical Laboratory of the University of Milano. The starting compounds were prepared as previously described.[1,13]

Synthesis of $[NEt_4][Re_7H_2C(CO)_{21}]$.—The salt $[NEt_4]_2$-$[Re_7H(C)(CO)_{21}]$ (30 mg, *ca.* 0.014 mmol) was dissolved in CH_2Cl_2 (3 cm^3) and treated at room temperature with CF_3SO_3H (1.5 µl, 0.017 mmol). Infrared monitoring showed the instantaneous disappearance of the reagent. The solution was concentrated under vacuum to about 1 cm^3 and transferred to a small test-tube placed in a vessel containing n-pentane and a drop of CF_3SO_3H. The diffusion of the n-pentane vapour allowed the isolation, after one night, of needle-shaped red-brown crystals of $[NEt_4][Re_7H_2C(CO)_{21}]$ (*ca.* 10 mg, 0.005 mmol; 35% yield) (Found: C, 17.95; H, 1.20; N, 0.60. $C_{30}H_{22}NO_{21}Re_7$ requires C, 17.70; H, 1.10; N, 0.70%). $\nu_{max.}(CO)(CH_2Cl_2)$: 2 085vw, 2 025vs, 2 000 (sh), and 1 950m cm^{-1}; $\delta_H(CD_2Cl_2$, 193 K) −17.05, −18.75, −20.27, and −21.60 (1:1:10.3:13.2).

Crystal data. Compound (**3**), $C_{30}H_{22}NO_{21}Re_7$, $M = 2\,035.9$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.394(3)$, $b = 15.669(3)$, $c = 27.983(6)$ Å, $\beta = 90.87(3)^\circ$, $U = 4\,118.8$ Å^3, $Z = 4$, $D_c = 3.28$ g cm^{-3}, $F(000) = 3\,608$, Mo-K_α radiation ($\lambda = 0.710\,73$ Å), μ(Mo-K_α) = 208.5 cm^{-1}.

Intensity measurements. A crystal of dimensions 0.25 × 0.10 × 0.05 mm was mounted on a glass fibre in air. The intensities were collected on an Enraf–Nonius CAD4 automatic diffractometer, using graphite-monochromatized Mo-K_α radiation. The setting angles of 25 random intense reflections ($16 < 2\theta < 25^\circ$) were used to determine by least-squares fit accurate cell constants and the orientation matrix. The data collection was performed by the ω-scan method, within the limits $3 < \theta < 24^\circ$. A variable scan speed (from 2 to 20° min^{-1}) and a variable scan range of $(0.9 + 0.35\tan\theta)^\circ$ was used, with a 25% extension at each end of the scan range for background determination. The total number of reflections measured was 6 449. No significant decay of the crystal sample upon *X*-ray exposure was observed. The intensities were corrected for Lorentz and polarization 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; the relative transmission factors had values in the range 1.00—0.88. 1 964 Independent significant reflections, with $I > 3\sigma(I)$, were used in the structure solutions and refinements.

Structure solutions and refinements. All computations were performed on a PDP 11/34 computer, using the Enraf–Nonius structure determination package (SDP)[14] and the physical constants tabulated therein. The structure solution was based on the deconvolution of the three-dimensional Patterson map, which gave the positions of the Re atoms. Successive Fourier-difference maps showed the location of all the non-hydrogen atoms. The refinements were carried out by full-matrix least squares. Anisotropic thermal factors were assigned to all the metal atoms. Weights were assigned according to the formula $w = 4F_o^2/\sigma(F_o^2)^2$, where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{\frac{1}{2}}/L_p$ (I and L_p being the integrated intensity and the Lorentz-polarization correction, respectively); p was assumed equal to 0.03. The final values of the conventional agreement indices R and R' were 0.036 and 0.038, respectively. A final Fourier-difference map showed electron-density ripples of *ca.* 1.3 e Å^{-3} close to the Re atom positions, but no other regions of significant electron density. The final positional parameters are given in Table 4.

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

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