X-Ray Crystal Structures of Two Isomers of the Hydrido–Carbonyl Anion $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$.† The Problematic Existence of Triply Bridging Hydrides in Clusters containing Interstitial Main-group Elements

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The *X*-ray crystal analyses of two different salts of the hydrido–carbido carbonylrhenate anion $[Re_7HC(CO)_{21}]^{2-}$, obtained by protonation of $[Re_7C(CO)_{21}]^{3-}$, have shown the presence of two structural isomers, differing in the location of the hydride ligand. The $[NEt_4]^+$ salt (isomer **a**) crystallizes in the monoclinic system, space group $P2_1/c$ (no. 14), with a = 10.168(3), b = 43.282(8), c = 11.505(3) Å, β = 91.72(2), and Z = 4. The $[NEt_4]^+[C_7H_7]^+$ mixed salt (isomer **b**) crystallizes in the monoclinic system, space group $P2_1$ (no. 4), with a = 12.007(4), b = 16.725(5), c = 12.004(4) Å, β = 105.79(2)°, and Z = 2. The gross features of the two structures are those of the parent anion $[Re_7C(CO)_{21}]^{3-}$, where a carbon-centred monocapped octahedron of metal atoms is surrounded by 21 terminal carbonyl ligands, three for each metal. In both isomers, the hydride ligand has been indirectly located, on the basis of potential energy computations, as doubly bridging, on an edge of the basal triangle in isomer (**2a**), in accord with the idealized C_s symmetry of the anion, and on an inter-layer edge of the octahedron in the less symmetric (C_1) isomer (**2b**). Carbon-13 and ^1H n.m.r. analyses at low temperatures have also shown the presence in solution of two isomers, rapidly exchanging at room temperature. The ratio between the two isomers is temperature dependent and for this equilibrium $\Delta H^\circ = -982$ cal mol^{-1} and $\Delta S^\circ = -1.7$ cal^{-1} K^{-1} mol^{-1} have been estimated. A possible correspondence between the two solid-state and the two solution isomers is discussed. Simple geometric considerations, showing the 'non-innocent' nature of triply bridging hydrides in clusters containing interstitial main-group elements, X, are also presented. Depending on the metal size and on the geometry of the cage, anomalous H ••• X contacts can arise; in particular, for the wide family of octahedral carbido clusters, the lack of genuine examples of μ_3-H co-ordination suggests a repulsive character of this H ••• C interaction.

In the last few years, we have synthesized and structurally characterized a series of high nuclearity carbonyl cluster anions of rhenium, containing a carbon atom at the centre of an octahedral metal cage,[1–3] and we are now investigating their chemistry. At first, we studied the reactivity of the trianion $[Re_7C(CO)_{21}]^{3-}$ (**1**),[1] which was shown to react with electrophiles,[4–6] and in particular to add the copper-triad cations or H^+ to give $[Re_7(\mu_3\text{-}X)C(CO)_{21}]^{2-}$ [X = Ag, Cu(NCMe), Au(PPh$_3$), or Ag(PPh$_3$)] and $[Re_7HC(CO)_{21}]^{2-}$ (**2**), respectively.[5] Subsequently, in a variable-temperature ^{13}C n.m.r. investigation[7] of compound (**2**), not yet structurally characterized by *X*-ray analysis, the presence in solution of two isomers was recognized and in both species the hydride ligand was proposed to occupy a triply bridging co-ordination position. In the major isomer the hydride was located as triply bridging the triangular face of the octahedron *trans* to that capped by the Re(CO)$_3$ group, by analogy with the solid-state structure of $[Re_7\{\mu_3\text{-}Au(PPh_3)\}C(CO)_{21}]^{2-}$,[7] and on the basis of the C_3 symmetry suggested by the ^{13}C n.m.r. spectra in the intermediate-exchange region (the limiting spectrum could not be obtained). We have now succeeded in obtaining crystals suitable for *X*-ray analysis of two different salts of $[Re_7HC(CO)_{21}]^{2-}$ and we report here the results of the structural investigation of the two species: in both cases the hydride ligand was indirectly located as being doubly-bridging (on different cluster edges in the two salts). The possible correspondence between these two solid-state isomers and the two solution isomers is discussed, also on the basis of the thermodynamic parameters concerning the equilibrium between the latter two. Moreover, simple geometric considerations are presented showing the 'non-innocent' nature of a μ_3-H ligand in clusters containing interstitial main-group elements, and therefore raising doubts about the possibility of such a type of hydrogen co-ordination in some classes of compounds, such as, for instance, the octahedral carbide clusters.

Results and Discussion

The synthesis of $[Re_7HC(CO)_{21}]^{2-}$ can be performed quite easily upon treatment of solutions of salts of $[Re_7C(CO)_{21}]^{3-}$ (in solvents like acetone, tetrahydrofuran, acetonitrile, or dichloromethane) with stoicheiometric amounts of a strong acid, such as HBF$_4$, H$_2$SO$_4$, or HClO$_4$. The use of low

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† μ_6-Carbido-1,2-μ-hydrido-4,5,6-μ_3-tricarbonylrhenio-hexakis(tricarbonylrhenium)(15*Re–Re*) and μ_6-carbido-1,4-μ-hydrido-4,5,6-μ_3-tricarbonylrhenio-hexakis(tricarbonylrhenium)(15*Re–Re*)

Supplementary data available (No. SUP 56704, 3 pp.): calculated and experimental equilibrium constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: cal = 4.184 J.

temperatures, as previously described,[7] is not necessary. The protonation can be reversed with a stoicheiometric quantity of $[NEt_4]OH$. Moreover, complete dissociation was observed in a basic solvent like dimethyl sulphoxide [the i.r. spectrum in solution showed only the ν(CO) bands of (**1**)]. Slow diffusion of n-pentane vapour into a concentrated dichloromethane solution of the $[NEt_4]^+$ salt of (**2**) allowed the isolation of crystals of $[NEt_4]_2[Re_7(\mu\text{-}H)C(CO)_{21}]$ (**2a**) suitable for *X*-ray analysis.

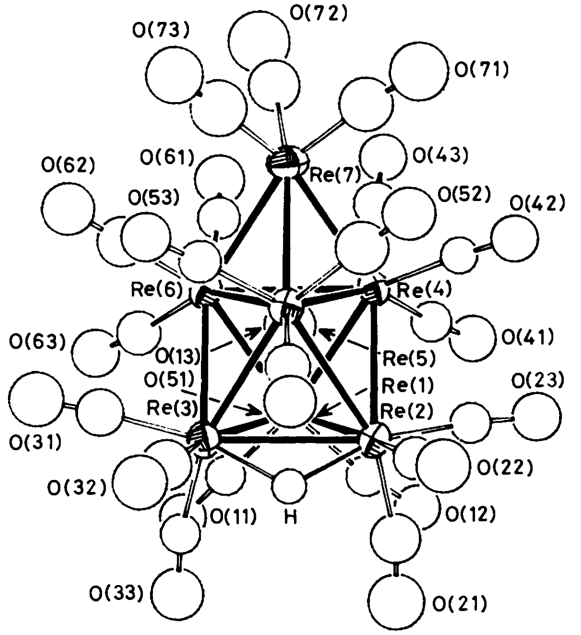

Figure 1. A view of the anion $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$ in its $[NEt_4]^+$ salt [compound (**2a**)], showing the computed H location

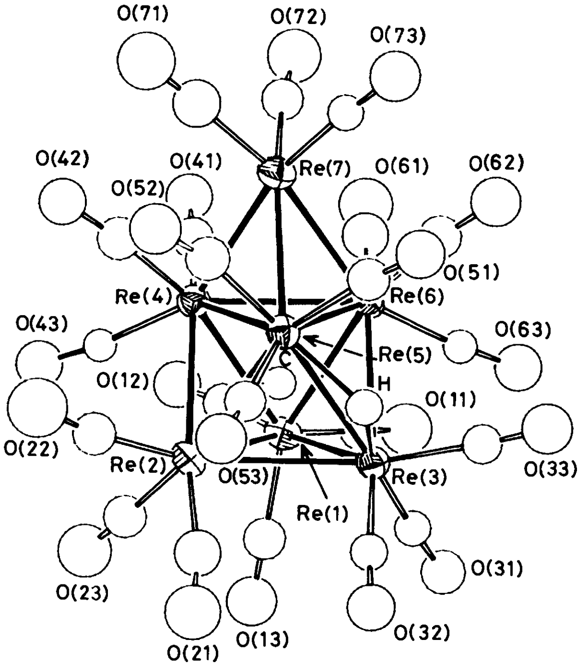

Figure 2. A view of the anion $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$ in its $[NEt_4]^+$-$[C_7H_7]^+$ mixed salt [compound (**2b**)], showing the computed H location

Some crystals of a different salt of compound (**2**) were serendipitously obtained in attempting to crystallize the products of the reaction of $[Re_7C(CO)_{21}]^{3-}$ with $[C_7H_7][BF_4]$:[6] in fact, due to the presence of water in the solvent (acetone) and, therefore, to the occurrence of the equilibrium, $C_7H_7^+ + H_2O \rightleftharpoons C_7H_7OH + H^+$, the paramagnetic anion $[Re_7C(CO)_{21}]^{2-}$ formed in the oxidation with the tropylium cation was always contaminated, in this solvent, by variable amounts of compound (**2**). The crystallization of this reaction mixture (performed using the same technique described above, in a refrigerator) gave a small amount of crystals of the mixed salt $[NEt_4][C_7H_7][Re_7(\mu\text{-}H)C(CO)_{21}]$ (**2b**), as revealed by *X*-ray analysis and confirmed by i.r., e.s.r., and ^1H n.m.r. spectra.

X-Ray Structures of the Two Isomers.—The two structurally characterized anions are reported in Figure 1 (isomer **a**) and Figure 2 (isomer **b**). The gross features of the two structures are those of the parent anion $[Re_7C(CO)_{21}]^{3-}$,[1] containing a carbon-centred monocapped octahedron of metal atoms surrounded by 21 terminal carbonyl ligands, three for each metal. The metal backbone is characterized by metal–metal interactions, which are similar in the three compounds, belonging to four different classes: (*i*) bonds within the basal triangle, (*ii*) bonds connecting

Table 1. Metal–metal bond distances (Å) in the two isomers of $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$ [compounds (**2a**) and (**2b**)] and in the parent trianion $[Re_7C(CO)_{21}]^{3-}$ (**1**) (e.s.d.s all of 0.001 Å). See the text for the classification of the Re–Re distances. Asterisks indicate the Re–H–Re interactions

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

Table 2. Metal–carbide bond distances (Å) in the two isomers of $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$

Compound	(**2a**)	(**2b**)
Re(1)–C	2.11(2)	2.11(2)
Re(2)–C	2.13(2)	2.10(2)
Re(3)–C	2.14(2)	2.17(2)
Re(4)–C	2.13(2)	2.09(2)
Re(5)–C	2.10(2)	2.19(2)
Re(6)–C	2.13(2)	2.11(2)

Table 3. Bond distances (Å) and angles (°) within the $Re(CO)_3$ moieties in the two isomers of $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$

Compound (**2a**)

Re(1)–C(11)	1.82(3)	C(11)–O(11)	1.18(3)	Re(1)–C(11)–O(11)	178(2)
Re(1)–C(12)	1.88(3)	C(12)–O(12)	1.19(3)	Re(1)–C(12)–O(12)	172(2)
Re(1)–C(13)	1.86(3)	C(13)–O(13)	1.18(3)	Re(1)–C(13)–O(13)	176(2)
Re(2)–C(21)	1.88(3)	C(21)–O(21)	1.18(3)	Re(2)–C(21)–O(21)	169(3)
Re(2)–C(22)	1.89(3)	C(22)–O(22)	1.17(3)	Re(2)–C(22)–O(22)	176(2)
Re(2)–C(23)	1.82(3)	C(23)–O(23)	1.21(3)	Re(2)–C(23)–O(23)	173(2)
Re(3)–C(31)	1.92(3)	C(31)–O(31)	1.15(3)	Re(3)–C(31)–O(31)	173(3)
Re(3)–C(32)	1.84(3)	C(32)–O(32)	1.20(3)	Re(3)–C(32)–O(32)	179(2)
Re(3)–C(33)	1.87(3)	C(33)–O(33)	1.18(3)	Re(3)–C(33)–O(33)	170(2)
Re(4)–C(41)	1.86(2)	C(41)–O(41)	1.20(3)	Re(4)–C(41)–O(41)	174(2)
Re(4)–C(42)	1.89(3)	C(42)–O(42)	1.15(3)	Re(4)–C(42)–O(42)	175(2)
Re(4)–C(43)	1.89(3)	C(43)–O(43)	1.19(3)	Re(4)–C(43)–O(43)	170(2)
Re(5)–C(51)	1.90(3)	C(51)–O(51)	1.19(3)	Re(5)–C(51)–O(51)	176(2)
Re(5)–C(52)	1.93(4)	C(52)–O(52)	1.15(3)	Re(5)–C(52)–O(52)	179(3)
Re(5)–C(53)	1.89(3)	C(53)–O(53)	1.15(3)	Re(5)–C(53)–O(53)	177(2)
Re(6)–C(61)	1.93(3)	C(61)–O(61)	1.14(3)	Re(6)–C(61)–O(61)	172(2)
Re(6)–C(62)	1.93(3)	C(62)–O(62)	1.17(3)	Re(6)–C(62)–O(62)	170(3)
Re(6)–C(63)	1.92(3)	C(63)–O(63)	1.15(3)	Re(6)–C(63)–O(63)	174(2)
Re(7)–C(71)	1.80(4)	C(71)–O(71)	1.18(4)	Re(7)–C(71)–O(71)	173(3)
Re(7)–C(72)	1.86(3)	C(72)–O(72)	1.18(3)	Re(7)–C(72)–O(72)	173(3)
Re(7)–C(73)	1.83(3)	C(73)–O(73)	1.20(3)	Re(7)–C(73)–O(73)	175(3)

Compound (**2b**)

Re(1)–C(11)	1.83(3)	C(11)–O(11)	1.19(3)	Re(1)–C(11)–O(11)	177(2)
Re(1)–C(12)	1.85(2)	C(12)–O(12)	1.20(3)	Re(1)–C(12)–O(12)	172(2)
Re(1)–C(13)	1.91(2)	C(13)–O(13)	1.15(3)	Re(1)–C(13)–O(13)	178(2)
Re(2)–C(21)	1.87(3)	C(21)–O(21)	1.14(3)	Re(2)–C(21)–O(21)	171(2)
Re(2)–C(22)	1.85(3)	C(22)–O(22)	1.19(3)	Re(2)–C(22)–O(22)	171(3)
Re(2)–C(23)	1.90(3)	C(23)–O(23)	1.18(3)	Re(2)–C(23)–O(23)	179(2)
Re(3)–C(31)	1.83(2)	C(31)–O(31)	1.22(3)	Re(3)–C(31)–O(31)	175(2)
Re(3)–C(32)	1.88(2)	C(32)–O(32)	1.18(2)	Re(3)–C(32)–O(32)	176(2)
Re(3)–C(33)	1.91(2)	C(33)–O(33)	1.15(3)	Re(3)–C(33)–O(33)	176(2)
Re(4)–C(41)	1.89(2)	C(41)–O(41)	1.18(3)	Re(4)–C(41)–O(41)	176(2)
Re(4)–C(42)	1.86(3)	C(42)–O(42)	1.23(3)	Re(4)–C(42)–O(42)	173(2)
Re(4)–C(43)	1.90(2)	C(43)–O(43)	1.19(2)	Re(4)–C(43)–O(43)	172(2)
Re(5)–C(51)	1.92(2)	C(51)–O(51)	1.15(3)	Re(5)–C(51)–O(51)	173(2)
Re(5)–C(52)	1.92(3)	C(52)–O(52)	1.20(3)	Re(5)–C(52)–O(52)	164(2)
Re(5)–C(53)	1.92(2)	C(53)–O(53)	1.17(3)	Re(5)–C(53)–O(53)	175(2)
Re(6)–C(61)	1.89(3)	C(61)–O(61)	1.19(3)	Re(6)–C(61)–O(61)	170(2)
Re(6)–C(62)	1.88(2)	C(62)–O(62)	1.21(3)	Re(6)–C(62)–O(62)	170(2)
Re(6)–C(63)	1.89(2)	C(63)–O(63)	1.21(3)	Re(6)–C(63)–O(63)	172(2)
Re(7)–C(71)	1.94(3)	C(71)–O(71)	1.15(3)	Re(7)–C(71)–O(71)	174(3)
Re(7)–C(72)	1.85(2)	C(72)–O(72)	1.20(3)	Re(7)–C(72)–O(72)	173(2)
Re(7)–C(73)	1.84(2)	C(73)–O(73)	1.19(2)	Re(7)–C(73)–O(73)	176(2)

the basal to the central triangle, which are alternatively three longer and three shorter, (*iii*) bonds within the central triangle, and (*iv*) bonds involving the capping Re atom (see Table 1).

In Table 2 the metal–carbide interactions are reported, while Table 3 contains the main metal–carbonyl bonding parameters. The stereochemistry of the ligands has an idealized C_3 symmetry in $[Re_7C(CO)_{21}]^{3-}$, C_s in (**2a**), and C_1 in (**2b**). This suggests that the co-ordination of the hydride ligand is different in (**2a**) with respect to (**2b**) and that in both cases highly symmetric μ_3-co-ordination of the hydride on the basal triangle can be ruled out.

The location of the hydride ligands in transition-metal clusters is often left to stereochemical considerations such as those concerning metal–metal bond lengthening and/or the presence of holes in the ligand arrangement. Van der Waals potential energy computations are of great utility in this context, provided the parameters for all the pertinent interactions are available. We have used the Orpen program[8] to inspect the possible locations of the hydride ligands in the two isomers of the title compound. The interstitial carbide atom was omitted from the computation, avoiding any *a priori* assumption on the character of the C(carbido)•••H interaction, because the usual non-bonding potential was strongly repulsive for such an interaction when the hydride was placed in μ_3 locations. Selected results of the computations are reported in Table 4.

The hole found in the basal face of $[Re_7C(CO)_{21}]^{3-}$, which does not possess a hydride ligand, simply shows that the 21 carbonyl groups fail to occupy the space around a Re_7 cluster in a homogeneous way. Therefore, the holes found in the same position in (**2a**) and (**2b**) do not necessarily imply the presence of hydride ligands.

In (**2a**), in accord with the idealized C_s symmetry of the whole anion, the hydride can be placed on one 'basal' edge (Figure 1). In (**2b**), the lack of symmetry and the presence of a co-ordination hole on an 'interlayer' edge can be explained only by locating the hydride atom on that edge (Figure 2). It is interesting to note that whilst in compound (**2b**) it is possible to envisage a (very small) lengthening of the H-bridged Re(3)–Re(5) bond with respect to the mean value for its class, in

Table 4. Potential energy values (arbitrary units), computed by the Orpen program,[8] for different hydride locations on the two isomers of $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$ [compounds (**2a**) and (**2b**)] and on the parent trianion (**1**). The carbido atom has been omitted from the computations: for the μ_3 locations, in fact, a 2 Å C–H interaction raises the energy by *ca.* 10 units

Hydride location	(**1**)	(**2a**)	(**2b**)
μ_3 On the basal face	1.5	5.3	4.5
μ On a basal edge	~13*	2.7	~13*
μ On an interlayer edge	>25	>25	7.0

* 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.

compound (**2a**) the H-bridged Re(2)–Re(3) interaction is the shortest within its class (see Table 1). Thus the criterion widely adopted,[9] at least in small cluster species, for the indirect location of the hydrides, *i.e.* the lengthening of the M–M interaction, must be regarded critically.

The recently characterized[6] $[Re_7C(CO)_{22}]^-$ anion contains a carbonyl ligand bridging a basal edge: the close similarity of the overall ligand stereochemistry of this species with that of (**2a**) further supports the hydride location assigned here.

N.M.R. Studies.—The behaviour, in solution, of $[Re_7HC(CO)_{21}]^{2-}$ has been studied by n.m.r. and our data are essentially similar to those reported by Shapley and co-workers.[7] Two isomers are present in solution, which undergo rapid exchange at room temperature resulting in almost collapsed resonances for the hydride and carbide atoms; separate signals for the two isomers appear at temperatures below 0 °C (Figure 3). Some information on the location of the hydride in the two species can be provided by the carbonyl resonances. In the intermediate-exchange region (0 to −60 °C), the major isomer shows an apparent C_3 symmetry (three signals, in the ratio 3:9:9 with respect to the carbide resonance). On lowering the temperature further, the two resonances of higher intensity broaden, merge, and give rise to a number of signals not well identified. In fact it was impossible to freeze the fluxionality completely, even at −120 °C (in C_4D_8O–$CHFCl_2$, 1:1) at 75.4 MHz. It was therefore impossible to determine, with certainty, whether the process responsible for this low-temperature collapse is the local scrambling of the carbonyls about each metal atom or if some kind of facile hydride scrambling is also involved. The number and relative intensities of the carbonyl resonances of the minor isomer are difficult to ascertain, due to its low concentration at low temperature and to the presence of the strong resonances of the major isomer, probably partially overlapping.

Analysis of the ^1H n.m.r. spectra at different temperatures showed that the relative ratio of the two isomers in solution is temperature dependent, ranging from *ca.* 3 at −20 °C to *ca.* 5 at −80 °C. The ratio of the integrated intensities of the hydridic resonances therefore provided the equilibrium constants at different temperatures for the reaction minor isomer $\rightleftharpoons$ major isomer. The thermodynamic parameters for this equilibrium, calculated from a least-squares fit of ln K against $1/T$ (see Figure 4), are: ΔH° -982 ± 23 cal mol^{-1} {comparable with the value of -842 ± 13 cal mol^{-1} obtained in the same way by Kaesz and co-workers[10] for the two isomers of $[Ru_4H_3(CO)_{12}]^-$} and ΔS° -1.7 ± 0.1 cal K^{-1} mol^{-1}. These values indicate that the major isomer has a higher symmetry and a higher stability with respect to the minor one.

Correspondence between the two solid state and the two solution isomers can be considered. In fact the negative value of

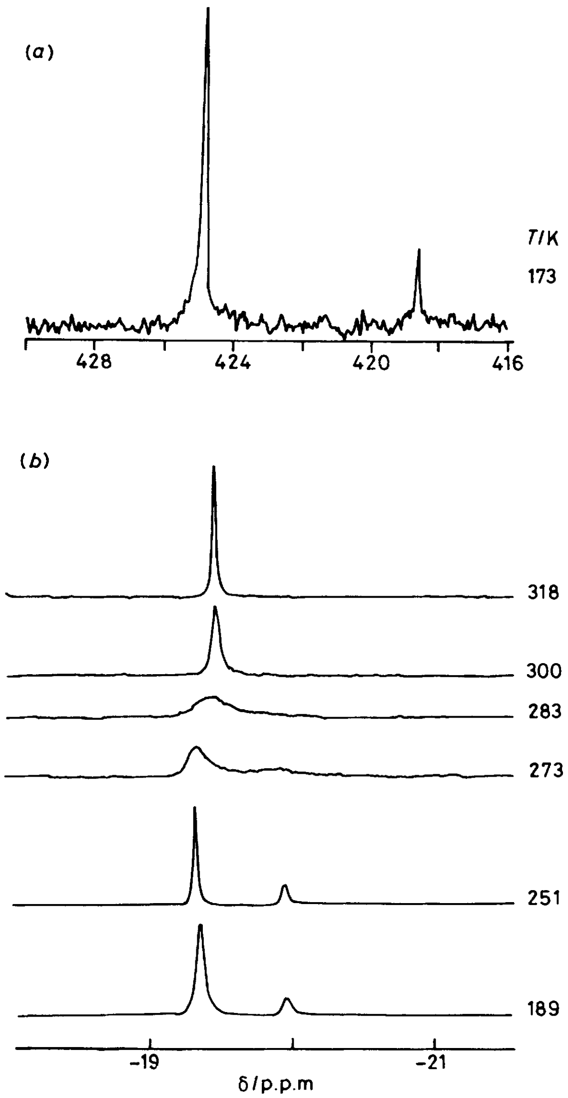

Figure 3. (*a*) The low-field region of the ^{13}C n.m.r. spectrum of $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}$ (75.4 MHz, 173 K), showing the carbide signals; (*b*) the hydridic regions of the ^1H n.m.r. spectra (80.13 MHz) at different temperatures

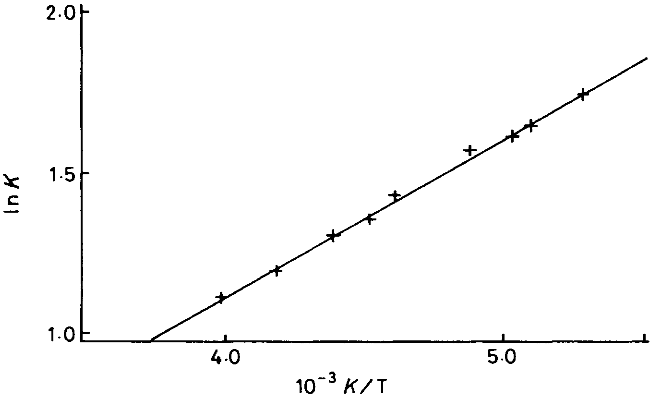

Figure 4. Temperature variation of the constants for the isomer equilibrium, estimated in acetone solution by ^1H n.m.r. analysis. The solid line was calculated by a least-squares fit of the experimental (+) values

Table 5. Positional parameters and their estimated standard deviations for $[NEt_4]_2[Re_7(\mu\text{-}H)C(CO)_{21}]$ **(2a)**

Atom	*x*	*y*	*z*
Re(1)	0.351 3(1)	0.140 49(3)	0.122 28(9)
Re(2)	0.107 9(1)	0.122 96(3)	−0.021 44(9)
Re(3)	0.107 2(1)	0.182 78(3)	0.112 61(9)
Re(4)	0.182 3(1)	0.088 29(3)	0.198 56(9)
Re(5)	−0.047 3(1)	0.129 06(3)	0.199 93(9)
Re(6)	0.193 6(1)	0.148 14(3)	0.330 46(8)
Re(7)	0.032 0(1)	0.095 34(3)	0.411 14(9)
C(11)	0.445(2)	0.176 1(7)	0.105(2)
O(11)	0.502(2)	0.199 5(5)	0.091(2)
C(12)	0.434(3)	0.125 6(7)	−0.011(2)
O(12)	0.487(2)	0.113 0(5)	−0.088(2)
C(13)	0.487(3)	0.126 7(7)	0.220(2)
O(13)	0.569(2)	0.116 8(6)	0.285(2)
C(21)	0.190(3)	0.134 8(8)	−0.159(3)
O(21)	0.238(2)	0.147 2(6)	−0.238(2)
C(22)	−0.054(3)	0.116 9(7)	−0.104(2)
O(22)	−0.154(2)	0.111 4(6)	−0.152(2)
C(23)	0.154(2)	0.084 3(7)	−0.066(2)
O(23)	0.175(2)	0.059 1(5)	−0.107(2)
C(31)	0.125(3)	0.212 9(8)	0.235(3)
O(31)	0.125(2)	0.232 5(6)	0.302(2)
C(32)	−0.046(3)	0.204 1(8)	0.081(3)
O(32)	−0.145(2)	0.218 5(5)	0.061(2)
C(33)	0.204(2)	0.2092 2(7)	0.020(2)
O(33)	0.267(2)	0.222 3(5)	−0.050(2)
C(41)	0.330(3)	0.070 9(7)	0.133(2)
O(41)	0.421(2)	0.057 2(5)	0.092(2)
C(42)	0.075(2)	0.054 1(6)	0.157(2)
O(42)	0.016(2)	0.032 9(5)	0.126(2)
C(43)	0.256(3)	0.066 8(7)	0.328(2)
O(43)	0.315(2)	0.052 0(5)	0.399(2)
C(51)	−0.179(3)	0.144 4(7)	0.094(2)
O(51)	−0.266(2)	0.152 9(5)	0.031(2)
C(52)	−0.160(3)	0.093 1(8)	0.199(3)
O(52)	−0.227(2)	0.071 6(5)	0.196(2)
C(53)	−0.145(3)	0.151 6(7)	0.309(2)
O(53)	−0.204(2)	0.166 3(5)	0.372(2)
C(61)	0.299(3)	0.125 1(7)	0.443(2)
O(61)	0.370(2)	0.114 5(5)	0.511(2)
C(62)	0.090(3)	0.169 2(8)	0.444(3)
O(62)	0.044(2)	0.182 1(5)	0.522(2)
C(63)	0.331(3)	0.178 3(8)	0.352(2)
O(63)	0.409(2)	0.196 8(5)	0.374(2)
C(71)	−0.042(3)	0.057 5(9)	0.414(3)
O(71)	−0.098(2)	0.033 7(6)	0.406(2)
C(72)	0.118(3)	0.081 0(8)	0.546(3)
O(72)	0.178(3)	0.075 1(7)	0.632(2)
C(73)	−0.083(3)	0.111 0(9)	0.515(3)
O(73)	−0.166(2)	0.121 3(6)	0.576(2)
C	0.150(2)	0.135 6(6)	0.155(2)
N(1)	0.646(2)	0.034 4(6)	−0.255(2)
C(111)	0.651(3)	0.044 9(8)	−0.126(2)
C(112)	0.616(3)	0.065 2(9)	−0.322(3)
C(113)	0.229(3)	−0.018 3(8)	0.286(3)
C(114)	0.461(3)	−0.009 7(7)	0.281(2)
C(115)	0.683(4)	0.019 0(9)	−0.041(3)
C(116)	0.596(4)	0.059(1)	−0.453(3)
C(117)	−0.102(3)	0.036 9(9)	−0.270(3)
C(118)	0.397(4)	0.021 4(9)	−0.258(3)
N(2)	−0.371(2)	0.208 4(5)	0.728(2)
C(221)	0.581(3)	0.177 5(9)	−0.232(3)
C(222)	0.644(3)	0.271 0(8)	0.337(3)
C(223)	0.545(3)	0.277 3(8)	0.137(3)
C(224)	−0.229(3)	0.206 1(8)	0.676(3)
C(225)	0.559(3)	0.155 1(8)	−0.339(3)
C(226)	−0.307(3)	0.238 5(9)	0.316(3)
C(227)	0.401(3)	0.272 8(8)	0.167(3)
C(228)	−0.123(3)	0.192 9(8)	0.765(3)

$\Delta S^{\ominus}$ agrees with a conversion from **(2b)** to **(2a)**, *i.e.* from C_1 and C_s symmetry, while the negative value of $\Delta H^{\ominus}$ is in accord with the higher stability of **(2a)** suggested by the calculated potential energy values.

Although lack of the ^{13}C low-temperature limiting spectra prevents any positive conclusion, the pattern of carbonyl resonances in the ratio 3:9:9, observed below 0 °C, for the major isomer could result from a scrambling of the hydride ligand on the three basal edges, so generating the apparent C_3 symmetry. As to the minor isomer, we can only state that it gives a higher number of resonances than the other isomer, and this is in accord with the lower symmetry of **(2b)** with respect to **(2a)**. Additional support for this hypothesis comes from the considerations reported below, because they raise doubts about the possibility of μ_3-H co-ordination in octahedral clusters containing interstitial carbides.

The 'Non-innocent' Nature of Triply Bridging Hydrides.—The possibility of hydride ligands giving triply bridging co-ordination on triangular faces of carbonyl cluster compounds is well established and supported by neutron diffraction studies.[9] To the best of our knowledge, however, it has not been noted that such co-ordination can become problematic in cluster complexes containing interstitial main-group elements, X. In fact, depending on the metal size and on the geometry of the cage, anomalous H · · · X distances could arise. Simple geometric considerations* allow calculation, for instance, of C–H distances of *ca.* 2.05 Å in the case of an octahedral hydride–carbide cluster of Re or Rh, while in the case of a trigonal prismatic cluster of Rh a distance of 2.42 Å is obtained, which is close to the C · · · H van der Waals distance (*ca.* 2.50 Å).[11] Interatomic distances much longer than the normal bonded contacts but shorter than the sum of the van der Waals radii are possible when, for instance, a three-centre two-electron interaction is allowed, as in the case of the M · · · H–C (M = metal) agostic interactions.[12] On the other hand, an interstitial atom could carry a positive charge (as suggested by the ^{13}C n.m.r. chemical shift values) and so interact with other atoms over shorter distances than those described by the van der Waals radii. In any case, an analysis of the literature data seems to question the possibility of the existence of triply bridging hydrides when the C · · · H distance is significantly lower than the sum of the van der Waals radii, thus suggesting a repulsive character for this C · · · H interaction. Significantly a hydride ligand was located in a triply bridging position in the trigonal prismatic cluster anion, $[Rh_6HC(CO)_{15}]^-$,[13] but found to be edge bridging in the octahedral $[Rh_6HC(CO)_{13}]^-$ species.[14] Moreover a number of hydrido–carbido carbonyl clusters of Ru and Os have been structurally characterized and invariably the hydride atoms have been directly or indirectly located as edge bridging.[15] Particularly noteworthy, for its similarity with the present case $\{[Re_7\{\mu_3\text{-}Au(PPh_3)\}C(CO)_{21}]^{2-}$ *vs.* $[Re_7(\mu\text{-}H)C(CO)_{21}]^{2-}\}$, is the structure of $[Ru_6(\mu\text{-}H)C(CO)_{15}$-

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* With d_{MM}, d_{MH}, and d_{MX} representing the metal–metal, metal–hydrogen, and metal–heteroatom distances, respectively, the X–H distance is obtained, assuming an equilateral triangular face, using the formula $[(d_{MH}^2 - \frac{1}{3}d_{MM}^2)^{\frac{1}{2}} + (d_{MX}^2 - \frac{1}{3}d_{MM}^2)^{\frac{1}{2}}]$. In the examples reported in the text, for the carbide of Re or Rh, the following values have been assumed: Re–Re 3.04, Re–H 1.95, Re–C 2.12 Å; Rh–Rh 2.91, Rh–H 1.90, Rh–C 2.05 Å for the octahedron; Rh–Rh 2.78, Rh–H 1.90, and Rh–C 2.13 Å for the prism.

Table 6. Positional parameters and their estimated standard deviations for $[NEt_4][C_7H_7][Re_7(\mu\text{-}H)C(CO)_{21}]$ (**2b**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	−0.106 06(7)	0.000	0.334 13(7)	O(51)	−0.233(1)	0.173(1)	−0.192(1)
Re(2)	0.035 79(7)	0.144 70(6)	0.304 23(7)	C(52)	−0.174(2)	0.289(2)	0.069(2)
Re(3)	−0.029 50(7)	0.0128 7(6)	0.116 23(7)	O(52)	−0.172(1)	0.361(1)	0.069(2)
Re(4)	−0.211 31(7)	0.167 38(5)	0.288 04(7)	C(53)	0.015(2)	0.225(1)	0.066(2)
Re(5)	−0.130 05(7)	0.178 45(5)	0.071 42(7)	O(53)	0.099(1)	0.257(1)	0.058(2)
Re(6)	−0.277 04(7)	0.043 17(6)	0.107 54(7)	C(61)	−0.411(2)	0.021(2)	0.156(2)
Re(7)	−0.374 34(7)	0.208 06(6)	0.067 25(8)	O(61)	−0.486(1)	−0.002(1)	0.196(2)
C	−0.119(2)	0.090(1)	0.209(2)	C(62)	−0.363(2)	0.052(2)	−0.049(2)
C(11)	−0.175(2)	−0.098(1)	0.320(2)	O(62)	−0.414(1)	0.046(1)	−0.150(1)
O(11)	−0.220(2)	−0.162(1)	0.315(2)	C(63)	−0.273(2)	−0.066(1)	0.070(2)
C(12)	−0.165(2)	0.007(2)	0.461(2)	O(63)	−0.283(1)	0.137(1)	0.048(1)
O(12)	−0.196(1)	0.021(1)	0.546(1)	C(71)	−0.410(2)	0.321(2)	0.072(2)
C(13)	0.035(2)	−0.046(2)	0.427(2)	O(71)	−0.435(2)	0.386(1)	0.082(2)
O(13)	0.120(1)	−0.072(1)	0.484(2)	C(72)	−0.516(2)	0.190(1)	0.096(2)
C(21)	0.184(2)	0.133(2)	0.285(2)	O(72)	−0.608(2)	0.171(1)	0.110(2)
O(21)	0.280(2)	0.132(1)	0.285(2)	C(73)	−0.446(2)	0.221(1)	−0.088(2)
C(22)	0.062(2)	0.252(2)	0.338(2)	O(73)	−0.491(1)	0.224(1)	−0.190(2)
O(22)	0.065(2)	0.322(1)	0.350(2)	C(1)	−0.136(2)	−0.308(2)	0.179(2)
C(23)	0.105(2)	0.125(2)	0.464(2)	C(2)	−0.041(2)	−0.352(2)	0.214(2)
O(23)	0.148(2)	0.115(1)	0.563(2)	C(3)	−0.025(2)	−0.430(2)	0.240(2)
C(31)	0.009(2)	−0.088(1)	0.175(2)	C(4)	−0.110(2)	−0.488(2)	0.230(3)
O(31)	0.036(1)	−0.156(1)	0.206(1)	C(5)	−0.224(2)	−0.481(2)	0.194(2)
C(32)	0.122(2)	0.019(1)	0.102(2)	C(6)	−0.289(2)	−0.409(2)	0.160(2)
O(32)	0.215(1)	0.021(1)	0.086(1)	C(7)	−0.248(2)	−0.332(2)	0.157(2)
C(33)	−0.080(2)	−0.038(1)	−0.031(2)	N	−0.503(2)	0.376(1)	−0.521(2)
O(33)	−0.115(1)	−0.065(1)	−0.123(2)	C(111)	−0.508(2)	0.463(2)	−0.511(3)
C(41)	−0.342(2)	0.144(2)	0.341(2)	C(112)	−0.525(2)	0.349(2)	−0.640(2)
O(41)	−0.425(1)	0.134(1)	0.374(1)	C(113)	−0.382(2)	0.346(2)	−0.457(3)
C(42)	−0.241(2)	0.276(2)	0.286(2)	C(114)	−0.585(2)	0.343(2)	−0.460(3)
O(42)	−0.254(1)	0.349(1)	0.298(1)	C(115)	−0.422(2)	0.512(2)	−0.569(3)
C(43)	−0.136(2)	0.193(1)	0.445(2)	C(116)	−0.641(3)	0.369(2)	−0.720(3)
O(43)	−0.100(1)	0.213(1)	0.543(1)	C(117)	−0.330(2)	0.368(2)	−0.329(3)
C(51)	−0.201(2)	0.175(2)	−0.092(2)	C(118)	−0.604(2)	0.253(2)	−0.470(2)

(NO)],[15e] in which the doubly bridging location of the hydride contrasts with the triply bridging co-ordination found for $Au(PPh_3)$ in the related $[Ru_6\{\mu_3\text{-}Au(PPh_3)\}C(CO)_{15}(NO)]$.[16] These results provide a new warning in the use of the isolobal analogy between H and $Au(PR_3)$ for stereochemical purposes.

A μ_3 location for the hydrides of $[Re_6H_2C(CO)_{18}]^{2-}$ was suggested by some of us[3] from an analysis of computed contacts on the cluster surface, but the disorder present in the solid state could have obscured the reality. Also in that case, as in the present one, it was impossible to obtain the ^{13}C n.m.r. limiting spectrum: the available data[3] can however be rationalized also locating the hydride ligands as doubly bridging on two edges of adjacent faces.

A problem related to that discussed in this paper concerns the possible existence of anomalous X $\cdots$ X contacts (of the type mentioned above) involving two interstitial atoms in a cluster. In polycarbides generally either definitely long C $\cdots$ C or bonding C–C distances are found.[17] In the dihydride $[Ni_{12}H_2(CO)_{24}]^{2-}$ the H $\cdots$ H interaction has been considered repulsive in nature.[18] On the other hand, in the case of the $[Os_{10}HC(CO)_{24}]^-$ anion,[19] the hydride ligand, assumed to occupy a tetrahedral hole on the basis of the structural similarity with the parent $[Os_{10}C(CO)_{24}]^{2-}$ anion and of the Os–H couplings,[20] should give rise to a very short H $\cdots$ C contact of 1.8 Å. This could suggest either a specific role of the metal cages in sticking together the two atoms or a positive polarization of this hydride atom (H^+ has a vanishing radius); but the observed structure could also be the result of a disordered location of the hydride ligand on all the edges on the cluster surface.

Experimental

Synthesis of $[NEt_4]_2[Re_7HC(CO)_{21}]$.—A sample (30 mg, 0.013 mmol) of $[NEt_4]_3[Re_7C(CO)_{21}]$ dissolved in an acetone–tetrahydrofuran (5 cm^3, 1:2 v/v) mixture, was treated at room temperature under nitrogen with 12 μl (*ca.* 0.014 mmol) of an aqueous solution (1.17 mol dm^{-3}) of $HClO_4$. The colour of the solution immediately turned from red to red-brown and i.r. monitoring showed complete disappearance of the reagent. The solution was concentrated under vacuum to *ca.* 1 cm^3 and treated with a saturated aqueous solution of $[NEt_4]BF_4$ (10 cm^3). After stirring for 1 h, a precipitate of $[NEt_4]_2[Re_7HC(CO)_{21}]$ was filtered off, washed with water, and dried (25 mg, 0.011 mmol, isolated yields 85%). ^1H N.m.r. spectrum of the anion [$(CD_3)_2CO$, $SiMe_4$ internal standard, −20 °C]: −19.30, −19.92 (relative intensity ratio *ca.* 3/1).

Measurement of the Isomer Equilibrium.—A sample of $[NEt_4]_2[Re_7HC(CO)_{21}]$ (150 mg) was dissolved in $(CD_3)_2CO$ and ^1H n.m.r. spectra were recorded on a Bruker 80 SY spectrometer at nine temperatures between −22 and −84 °C. The temperature, controlled by the Bruker VT 1000 equipment, was checked before and after each spectrum with a 4% methanol solution in CD_3OH. A good signal to noise ratio was achieved recording 120 scans for each spectrum and the areas of the hydridic peaks were integrated electronically, after an extremely careful regulation of the phase of the spectrum. The constants thus obtained as well as those calculated from a least-squares fit of ln *K versus* $1/T$ are reported in SUP 56704.

X-*Ray Analyses of Compounds* (**2a**) *and* (**2b**).—*Crystal data.*

Compound (**2a**), $C_{38}H_{41}N_2O_{21}Re_7$, $M = 2\,165.1$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.168(3)$, $b = 43.282(8)$, $c = 11.505(3)$ Å, $\beta = 91.72(2)°$, $Z = 4$, $D_c = 2.84$ g cm^{-3}; Mo-K_α radiation ($\lambda = 0.710\,73$ Å); μ(Mo-K_α) = 169.8 cm^{-1}.

Compound (**2b**), $C_{37}H_{28}NO_{21}Re_7$, $M = 2\,126.0$, monoclinic, space group $P2_1$ (no. 4), $a = 12.007(4)$, $b = 16.725(5)$, $c = 12.004(4)$ Å, $\beta = 105.79(2)°$, $Z = 2$, $D_c = 3.04$ g cm^{-3}; Mo-K_α radiation ($\lambda = 0.710\,73$ Å); μ(Mo-K_α) = 185.2 cm^{-1}. The following unit-cell transformation ($H = -h - l$; $K = -k$; $L = -h + l$) affords a pseudo-orthorhombic cell ($a = 14.485$, $b = 16.725$, $c = 19.150$ Å, $\beta = 89.98°$) which however, lacks the appropriate Laue symmetry.

Intensity measurements. Crystal samples of dimensions 0.30 × 0.10 × 0.05 mm [(**2a**)] and 0.20 × 0.10 × 0.10 mm [(**2b**)] were mounted on glass fibres in the air. The intensities for both compounds were collected on an Enraf-Nonius CAD4 automatic diffractometer, using graphite-monochromatized Mo-K_α radiation. The setting angles of 25 random intense reflections ($16 < 2\theta < 25°$) were used in each case to determine by least-squares fit accurate cell constants and orientation matrix. Data collections were performed by the ω-scan method, within the limits $3 < \theta < 24°$ [(**2a**)] and $3 < \theta < 25°$ [(**2b**)]. A variable scan speed (from 2 to 20° min^{-1}) and a variable scan range of ($\alpha + 0.35 \tan\theta°$), with $\alpha = 1.0$ [(**2a**)] and 0.8 [(**2b**)], were used, with a 25% extension at each end of the scan range for background determination. The total numbers of reflections measured were 7 120 [(**2a**)] and 4 228 [(**2b**)]. 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 was applied to both data sets, based on ψ-scans (ψ 0—360° every 10°) of suitable reflections with χ values close to 90°; the relative transmission factors had values in the ranges 1.00—0.34 [(**2a**)] and 1.00—0.69 [(**2b**)], respectively. Two sets of 2 899 [(**2a**)] and 2 599 [(**2b**)] 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) and the physical constants tabulated therein.

The structure solutions were based on the deconvolution of three-dimensional Patterson maps, which gave the positions of the Re atoms. Successive difference Fourier maps showed the location of all the non-hydrogen atoms. The refinements were carried out by full-matrix least squares. Anisotropic thermal parameters 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 in both cases. For compound (**2b**), which crystallizes in a non-centrosymmetric space group, in the final stages of the refinement both possible enantiomers were tested. The results presented refer to the enantiomer affording the better R and R' values. The final values of the conventional agreement indices R and R' were 0.037 and 0.040 [(**2a**)] and 0.025 and 0.029 [(**2b**)], respectively. The final positional parameters are given in Tables 5 [(**2a**)] and 6 [(**2b**)]. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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