Preparation and Structure of a Non-carbide-stabilized Octahedral Rhenium Cluster: $[NEt_4][Re_6H_7(CO)_{18}]$†

Chung Shinn Yang *^,a^ and **Cheu Pyeng Cheng** *^,b^
[a] *Department of Chemical Engineering, Eastern Junior College of Technology and Commerce, Hu-Nei Hsing, Kaohsiung Hsien, 82901 Taiwan, Republic of China*
[b] *Department of Chemistry, National Tsing Hua University, Hsin-Chu, 30043 Taiwan, Republic of China*

The novel rhenium complex $[NEt_4][Re_6H_7(CO)_{18}]$ has been isolated from the reaction between $[Re_4H_4(CO)_{12}]$ and NEt_4BF_4 in dichloromethane with or without acetone which facilitates the reaction. Its crystal structure has been determined: monoclinic, space group $P2_1/n$, $a = 13.096(3)$, $b = 19.408(4)$, $c = 14.372(4)$ Å, $\beta = 90.65(2)°$, $Z = 4$, $R = 0.0392$ and $R' = 0.0375$ from 6498 independent reflections. This shows that the anion is a non-carbide-stabilized octahedral rhenium cluster. The Re–Re distances are consistent with all hydrides occupying μ_3-face-bridging positions.

High-nuclearity (number of metal atoms >4) transition-metal carbonyl clusters, including those with an interstitial carbide atom, are well known for late transition elements including Groups VIII and IX.[1–3] However, outside these elements, such clusters are very rare. With rhenium, for example, there are only five known clusters: $[Re_6H_2(C)(CO)_{18}]^{2-}$,[4,5] $[Re_7C(CO)_{21}]^{3-}$,[4,6] $[Re_8C(CO)_{24}]^{2-}$,[4,7] $[Re_6(CO)_{18}(\mu_4\text{-PMe})_3]$,[8] and $[Re_5(CO)_{14}(\mu_4\text{-PMe})(\mu\text{-PMe})\{\mu_3\text{-PRe(CO)}_5\}]$.[8] The first three have an octahedral core containing a central carbide atom, which serves the purpose of stabilizing the high-nuclearity cluster by providing the necessary valence electrons so that the electron count follows the 86-electron rule for an octahedral cluster. If the electrons are provided by ligands instead of interstitial carbide the steric interactions among the ligands on the cluster surface may render it unstable. This ligand steric repulsion is responsible for the scarcity of high-nuclearity carbonyl clusters for transition elements to the left of Group VIII. In confirmation of the significance of the ligand steric repulsion, the other two high-nuclearity rhenium clusters have several multielectron-donating phosphorus ligands in sterically less-demanding positions.

From the reaction between $[Re_4H_4(CO)_{12}]$[9–13] and NEt_4BF_4 in the presence of acetone we have already isolated $[NEt_4][Re_3H_2(CO)_9(BF_4)]$ which contains a BF_4^- co-ordinated to the trirhenium cluster in a μ_3-σ-FBF_3^- fashion.[14] Here we report that a non-carbide-stabilized octahedral rhenium cluster can also be obtained from this reaction.

Results and Discussion

A yellow solid product **1** was isolated in 45% yield from the reaction between $[Re_4H_4(CO)_{12}]$ and NEt_4BF_4 in dichloromethane solution with or without the presence of acetone. Its ^1H NMR spectrum indicates the presence of the NEt_4^+ cation and hydrides. The spectrum was measured with several different relaxation delays of up to 30 s to make sure that the relative numbers of protons (8:12:7) in NEt_4^+ and hydrides are accurate and free from any artifact caused by relaxation effects.

The structure of compound **1** with atomic numbering is shown in Fig. 1. Fractional coordinates are given in Table 1, selected bond distances and bond angles in Table 2. The six rhenium atoms form an octahedron and each is co-ordinated by three nearly mutually perpendicular carbonyl groups. The Re–Re bond distances fall into three distinct groups: (1) 3.051–3.083 Å in the triangular plane of Re(1)–Re(2)–Re(6); (2) 3.199–3.235 Å in the triangular planes of Re(1)–Re(3)–Re(5) and Re(3)–Re(4)–Re(5); and (3) 3.245–3.263 Å for the remaining four bond distances [Re(2)–Re(4), Re(2)–Re(5), Re(3)–Re(6) and Re(4)–Re(6)]. The large Re–Re distances in the third group all occur in the triangular faces sharing an edge with the Re(1)–Re(2)–Re(6) triangle. The bond-distance variations can be understood by considering the contraction of the Re(1)–Re(2)–Re(6) triangle from a regular octahedron keeping Re(1) at its original position. If the Re(1)–Re(3)–Re(5) and Re(4)–Re(3)–Re(5) triangles remain unchanged, then Re(2)–Re(4) and Re(6)–Re(4) must be lengthened because of geometrical constraints. If the contraction of the triangle is accompanied by a slight adjustment of bond angles such as enlargement of the Re(3)–Re(1)–Re(6) and Re(2)–Re(1)–Re(5) angles (to *ca.* 62°), then Re(3)–Re(6) and Re(2)–Re(5) must also be lengthened. Notice that Re(1)–Re(6)–Re(3) and Re(1)–Re(2)–Re(5) are also *ca.* 62°; correspondingly, the three

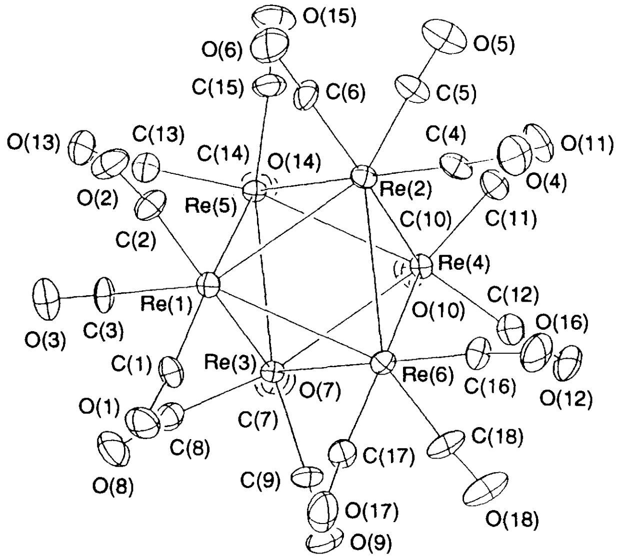

Fig. 1 An ORTEP[15] drawing of the anion of $[NEt_4][Re_6H_7(CO)_{18}]$; the cation is omitted for clarity

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Atomic coordinates (× 10^4) for $[NEt_4][Re_6H_7(CO)_{18}]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	7 601(1)	1 226(1)	8 175(1)	C(2)	6 640(14)	943(11)	9 066(13)
Re(2)	6 598(1)	2 637(1)	8 068(1)	C(3)	7 532(16)	294(10)	7 660(12)
Re(3)	8 766(1)	1 525(1)	6 281(1)	C(4)	6 687(13)	3 383(10)	8 924(12)
Re(4)	7 696(1)	2 984(1)	6 130(1)	C(5)	5 581(15)	3 141(12)	7 511(13)
Re(5)	6 446(1)	1 606(1)	6 285(1)	C(6)	5 636(15)	2 295(10)	8 904(16)
Re(6)	8 789(1)	2 563(1)	8 054(1)	C(7)	8 862(19)	1 454(13)	4 938(14)
O(1)	9 040(11)	689(8)	9 605(10)	C(8)	9 143(16)	562(12)	6 411(15)
O(2)	6 166(10)	739(8)	9 623(10)	C(9)	10 134(14)	1 705(12)	6 377(14)
O(3)	7 475(14)	−236(8)	7 419(11)	C(10)	7 712(19)	2 906(12)	4 785(14)
O(4)	6 693(13)	3 835(9)	9 436(11)	C(11)	6 789(17)	3 740(12)	6 031(15)
O(5)	4 968(15)	3 477(12)	7 196(13)	C(12)	8 651(16)	3 689(12)	6 064(14)
O(6)	5 093(13)	2 089(10)	9 414(16)	C(13)	5 963(17)	677(12)	6 357(15)
O(7)	8 946(14)	1 399(11)	4 182(10)	C(14)	6 304(14)	1 571(10)	4 949(14)
O(8)	9 451(15)	28(10)	6 429(15)	C(15)	5 146(15)	1 886(13)	6 377(19)
O(9)	10 941(11)	1 781(10)	6 367(13)	C(16)	8 814(14)	3 335(9)	8 881(11)
O(10)	7 687(13)	2 874(10)	4 002(9)	C(17)	9 725(15)	2 159(10)	8 847(15)
O(11)	6 327(16)	4 198(9)	5 859(15)	C(18)	9 882(15)	2 975(13)	7 471(13)
O(12)	9 183(13)	4 157(9)	5 998(16)	C(19)	7 729(23)	755(8)	2 437(14)
O(13)	5 597(14)	142(9)	6 405(16)	C(20)	7 716(19)	1 283(11)	1 638(15)
O(14)	6 230(12)	1 533(10)	4 163(9)	C(21)	6 381(11)	102(14)	1 997(20)
O(15)	4 317(12)	2 014(11)	6 366(14)	C(22)	5 891(22)	−581(17)	1 724(26)
O(16)	8 876(12)	3 777(8)	9 399(12)	C(23)	7 576(26)	−393(16)	3 037(14)
O(17)	10 282(14)	1 964(9)	9 362(14)	C(24)	7 045(25)	−195(17)	3 932(15)
O(18)	10 501(12)	3 252(12)	7 141(12)	C(25)	7 921(16)	−251(22)	1 423(16)
N	7 414(9)	49(7)	2 219(9)	C(26)	9 027(15)	−259(17)	1 475(22)
C(1)	8 540(14)	906(9)	9 052(12)				

Table 2 Selected bond distances (Å) and angles (°) for $[NEt_4][Re_6H_7(CO)_{18}]$

Re(1)–Re(2)	3.076(1)	Re(3)–Re(6)	3.249(1)	Re(3)–Re(4)	3.205(1)	Re(2)–Re(5)	3.256(1)
Re(1)–Re(6)	3.083(1)	Re(1)–Re(3)	3.235(1)	Re(4)–Re(5)	3.199(1)	Re(3)–Re(5)	3.230(1)
Re(2)–Re(6)	3.051(1)	Re(2)–Re(4)	3.263(1)	Re(1)–Re(5)	3.225(1)	Re(4)–Re(6)	3.245(1)

Re(2)–Re(1)–Re(3)	91.7(1)	Re(2)–Re(1)–Re(5)	62.2(1)	Re(3)–Re(1)–Re(5)	60.0(1)
Re(2)–Re(1)–Re(6)	59.4(1)	Re(3)–Re(1)–Re(6)	61.8(1)	Re(5)–Re(1)–Re(6)	91.3(1)
Re(1)–Re(2)–Re(4)	90.6(1)	Re(1)–Re(2)–Re(5)	61.2(1)	Re(4)–Re(2)–Re(5)	58.8(1)
Re(1)–Re(2)–Re(6)	60.4(1)	Re(4)–Re(2)–Re(6)	61.8(1)	Re(5)–Re(2)–Re(6)	91.3(1)
Re(1)–Re(3)–Re(4)	88.8(1)	Re(1)–Re(3)–Re(5)	59.9(1)	Re(4)–Re(3)–Re(5)	59.6(1)
Re(1)–Re(3)–Re(6)	56.8(1)	Re(4)–Re(3)–Re(6)	60.4(1)	Re(5)–Re(3)–Re(6)	88.3(1)
Re(2)–Re(4)–Re(3)	88.9(1)	Re(2)–Re(4)–Re(5)	60.5(1)	Re(3)–Re(4)–Re(5)	60.6(1)
Re(2)–Re(4)–Re(6)	55.9(1)	Re(3)–Re(4)–Re(6)	60.5(1)	Re(5)–Re(4)–Re(6)	88.8(1)
Re(1)–Re(5)–Re(2)	56.7(1)	Re(1)–Re(5)–Re(3)	60.2(1)	Re(2)–Re(5)–Re(3)	88.6(1)
Re(1)–Re(5)–Re(4)	89.1(1)	Re(2)–Re(5)–Re(4)	60.7(1)	Re(3)–Re(5)–Re(4)	59.8(1)
Re(1)–Re(6)–Re(2)	60.2(1)	Re(1)–Re(6)–Re(3)	61.4(1)	Re(2)–Re(6)–Re(3)	91.9(1)
Re(1)–Re(6)–Re(4)	90.8(1)	Re(2)–Re(6)–Re(4)	62.3(1)	Re(3)–Re(6)–Re(4)	86.7(1)
Re(2)–Re(1)–C(1)	129.0(5)	Re(3)–Re(1)–C(1)	105.6(5)	Re(5)–Re(1)–C(1)	164.0(5)
Re(6)–Re(1)–C(1)	87.0(5)	Re(2)–Re(1)–C(2)	88.2(6)	Re(3)–Re(1)–C(2)	163.9(6)
Re(5)–Re(1)–C(2)	106.3(6)	Re(6)–Re(1)–C(2)	130.5(6)	C(1)–Re(1)–C(2)	86.8(8)
Re(2)–Re(1)–C(3)	141.6(6)	Re(3)–Re(1)–C(3)	82.6(5)	Re(5)–Re(1)–C(3)	82.6(5)
Re(6)–Re(1)–C(3)	141.4(5)	C(1)–Re(1)–C(3)	88.8(8)	C(2)–Re(1)–C(3)	87.5(8)
Re(1)–C(1)–O(1)	174(2)	Re(1)–C(2)–O(2)	172(2)	Re(1)–C(3)–O(3)	176(2)

angles [Re(1)–Re(5)–Re(2), Re(1)–Re(3)–Re(6) and Re(2)–Re(4)–Re(6)] opposing the three edges of the contracted Re(1)–Re(2)–Re(6) triangle are *ca.* 56° which are the smallest among the inter-rhenium angles. The Re–Re bonds in the second and third groups are much longer than those in $[Re_6H_2(C)(CO)_{18}]^{2-}$ (2.939–3.096 Å),[5] $[Re_7C(CO)_{21}]^{3-}$ (2.927–3.084 Å),[6] $[Re_8C(CO)_{24}]^{2-}$ (2.962–3.001 Å)[7] and $[Re_4C(CO)_{15}I]^-$ (2.887–3.012 Å),[16] clearly indicating that the interstitial carbides stabilize these rhenium clusters.

Although no hydride was located directly in the structure determination it is obvious that there are seven hydrides in compound **1** as indicated by the ^1H NMR data. Furthermore, with seven hydrides the valence electron count of 86 for a stable *closo* octahedral cluster is fulfilled. Unfortunately, it is not possible to infer the bonding mode of the hydrides from their chemical shift [δ(H) −16.78]. Scarcity of rhenium clusters with face-bridging hydride is one problem, since there is only one well characterized example: $[Re_4H_4(CO)_{12}]$ [δ(H) −4.98]. Furthermore, the chemical shift may not be a good indicator of the bonding mode of hydride in rhenium compounds. For example, the chemical shifts of edge-bridging hydrides exhibit a wide range, e.g. $[Re_3H_3(CO)_9(OR)]^-$ (δ −11.3 for R = Et,[17] −11.5 for R = Me),[18] $[Re_3H_3(CO)_{10}(C_5H_5N)_2]$ (δ −9.24, −13.24)[19] and $[Re_3H_3(CO)_{11}(PPh_3)]$ (δ −15.90, −17.11 and −17.20).[20] However, from the fact that the Re–Re bonds in the Re(1)–Re(2)–Re(6) triangle are short while the remaining Re–Re bonds are considerably longer, all hydrides appear to be face bridging and to occupy all triangular faces of the rhenium octahedron except the Re(1)–Re(2)–Re(6) triangle. Unlike the well documented observation that a metal–metal bond is lengthened when it is edge-bridged by a hydride, examples of metal–metal bond lengthening in the presence of face-bridging hydride are scarce. However in $[Ru_6H_2(CO)_{18}]$[21] and $[Os_6H(CO)_{18}]^-$[22] the lengthening of the metal–metal bonds by a face-bridging hydride is clearly demonstrated. In the face-bridging positions the steric repulsion of hydrides by the carbonyl groups is minimized. Both the ^1H NMR signal of the hydrides and the ^{13}C NMR signal of the carbonyls remain very sharp at −90 °C, indicating that the fluxional motion of the hydrides in solution is rapid even at this low temperature.

The presence of face-bridging hydrides in $[Re_4H_4(CO)_{12}]$[9–13] is characterized by an eclipsed carbonyl conformation with respect to the Re–Re bonds; the CO ligands point toward the centres of the triangular faces. In contrast, in $[Re_4H_6(CO)_{12}]^{2-}$[23,24] the carbonyls are staggered and the hydrides are edge bridging. Obviously the location of the hydrides in $[Re_6H_7(CO)_{18}]^-$ cannot be deduced from the carbonyl conformations because four Re–Re bonds are opposite to the three carbonyls; no staggered or eclipsed conformation can be defined. However, the carbonyl conformations in $[Re_6H_7(CO)_{18}]^-$ have two special features which can be seen when projected along the diagonal axis as illustrated in Fig. 2. First, between the diagonal rhenium atoms, the carbonyls are eclipsed. This is unique among octahedral clusters, since the structurally known homonuclear octahedral clusters, such as $[Ru_6H(CO)_{18}]^-$,[25] $[Ru_6H_2(CO)_{18}]$,[21] $[Os_6(CO)_{18}]^{2-}$,[22] and $[Os_6H(CO)_{18}]^-$,[22] all have a staggered conformation. Secondly, a pair of carbonyls [C(3)O(3), C(10)O(10)] bisects one edge [Re(3)–Re(5)] of the square that is opposite to the short edge [Re(2)–Re(6)]. The same carbonyl conformations are observed when projected along the other two diagonal axes. This indicates that three carbonyls point toward the centre of the small triangle Re(1)–Re(2)–Re(6) that has no capping hydride, in contrast to the situation in $[Re_4H_4(CO)_{12}]$. The reason for the special configurations of the carbonyls is not clear at present.

Experimental

Dirhenium decacarbonyl was obtained from Strem Chemical Co., NEt_4BF_4 from Merck; they were used directly. All solvents (acetone, chloroform, dichloromethane and benzene) were purified according to standard procedures.[26] The compound $[Re_4H_4(CO)_{12}]$ was prepared by the reaction between $[Re_2(CO)_{10}]$ and hydrogen under refluxing decane as reported.[13]

Proton and ^{13}C NMR spectra were measured on a Varian Unity 400 MHz spectrometer, IR spectra on a Bomen Michelson Series 100 FTIR spectrometer and UV/VIS spectra on a Perkin-Elmer Lambda-5 spectrometer. Elemental analyses were obtained on a Perkin-Elmer 240C-2400 EA instrument. The mass spectrum was recorded on a JOEL SX-120A spectrometer.

Reaction between $[Re_4H_4(CO)_{12}]$ *and* NEt_4BF_4.—The compound $[Re_4H_4(CO)_{12}]$[9–13] (0.14 mmol) was allowed to react with acetone (14 mmol) in CH_2Cl_2 (25 cm^3) for 8 h at room temperature under nitrogen, then NEt_4BF_4 (0.1 mmol) was added. After 30 min the mixture was separated with silica gel TLC using $CHCl_3$–C_6H_6–Me_2CO (3:3:4) as eluent. A yellow solid, **1**, was obtained at $R_f = 0.7$ with an isolated yield of 45%. A single crystal was obtained by slow evaporation of a CH_2Cl_2–C_6H_{14} (1:1) solution of the cluster. Alternatively, **1** can be obtained from the direct reaction between $[Re_4H_4(CO)_{12}]$ and NEt_4BF_4 in the absence of acetone. The compound $[Re_4H_4(CO)_{12}]$ (0.14 mmol) was dissolved in dichloromethane (25 cm^3) and NEt_4BF_4 (0.1 mmol) added. With constant stirring and under a nitrogen atmosphere, the reaction was allowed to proceed for about 3 d until the red colour of $[Re_4H_4(CO)_{12}]$ had disappeared. Then **1** was obtained from the reaction mixture following the above separation and purification procedure. Obviously, acetone can facilitate the formation of **1**.

NMR (400 MHz, CD_2Cl_2): ^1H, δ 3.24 (q, 8 H, *J* 7.2), 1.34 (tt, 12 H, *J* 7.2, $^3J_{NH}$ 2.0 Hz) and −16.78 (s, 7 H); ^{13}C, δ 7.95, 53.37 and 185. IR (CH_2Cl_2): ν(CO) 2036 and 1953 cm^{-1}. UV (CH_2Cl_2): λ 342 nm ($\varepsilon = 1.24 \times 10^4$ dm^3 mol^{-1} cm^{-1}) (Found: C, 19.05; H, 1.70; N, 0.85. $C_{26}H_{27}NO_{18}Re_6$ requires C, 17.75; H, 1.55; N, 0.80%). Mass (FAB) spectrum: *m*/*z* 1893 (13), 1891 (70), 1889 (100), 1887 (72), 1885 (36) and 1883 (12%) [theoretical for $M^+ + NEt_4$ based on rhenium isotopes: 1893 (19), 1891 (67), 1889 (100), 1887 (80), 1885 (36), 1883 (9) and 1881 (0.9%)]; cluster of peaks around 1627 (20%) due to $[Re_6H_6(CO)_{18}]^+$.

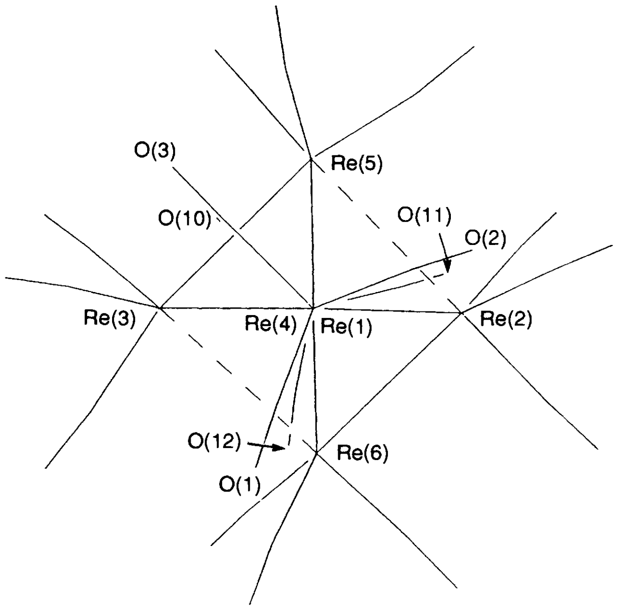

Fig. 2 Structure of $[Re_6H_7(CO)_{18}]^-$ projected along the Re(1)–Re(4) diagonal axis to indicate the eclipsed carbonyl conformations and the orientations of the carbonyl groups

Crystal Structure Analysis of Compound **1**.—*Crystal data.* $C_{26}H_{27}NO_{18}Re_6$, $M = 1758.7$, monoclinic, space group $P2_1/n$, $a = 13.096(3)$, $b = 19.408(4)$, $c = 14.372(4)$ Å, $\beta = 90.65(2)°$, $U = 3878.4(15)$ Å^3, $Z = 4$, $D_c = 3.012$ Mg m^{-3}, $F(000) = 3136$, $\mu = 18.720$ mm^{-1}.

Diffraction data were measured on a Siemens R3m/V diffractometer with a Mo-Kα radiation (λ = 0.710 73 Å) and a graphite monochromator using a θ–2θ scan ($2.5 \leqslant 2\theta \leqslant 50.0°$). A crystal of dimensions 0.60 × 0.30 × 0.09 mm was used. 6498 Independent reflections [$4363 \geqslant 3.0\sigma(I)$] were measured. An extinction correction was performed. Corrections for absorption were based on ψ scans of a few suitable reflections with χ values close to 90° (T_{max}, T_{min} = 0.567, 0.137).

The structure was solved by the heavy-atom method and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized (C–H 0.96 Å) and refined isotropically with a fixed *U* of 0.08 Å^2. However, the hydrides were not included in the refinement. Refinement was by full-matrix least squares to $R = 0.0392$ and $R' = 0.0375$ [$w^{-1} = \sigma(F) + 0.0002F^2$]. Goodness of fit: 1.07. Largest electron densities: 1.57 and 1.84 e Å^{-3}. Computations were performed on a VAX work-station using the SHELXTL PLUS program.[27]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

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