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Structure of a Highly Unsaturated Anionic Tetrahydridononacarbonyltrirhenate Cluster

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The reaction between $H_4Re_4(CO)_{12}$ and *N*,*N*-dimethylformamide (DMF) in chloroform yields $[H_4Re_3(CO)_9]^-[Re(CO)_3(DMF)_3]^+$, **1**, quantitatively. The X-ray structure of **1** reveals that the three Re atoms in the 44-e anionic cluster $[H_4Re_3(CO)_9]^-$ form an isosceles triangle. Two hydrides bridge the two long Re−Re single-bonded edges, and another two hydrides bridge the Re−Re double-bonded edge. There is a coordinative unsaturation site on the rhenium atom not involved in the Re−Re double bond. However, the anionic cluster associates face-to-face antiprismatically with another identical unit to form a dimer in which there are donor−acceptor interactions between the hydrides bridging the Re−Re double bonds and the coordinative unsaturation sites on the other clusters. The anionic cluster reacts rapidly with donor ligand L (CO, Py, PPh_3, CH_3CN) to form $[H_4Re_3(CO)_9L]^-$. In CD_2Cl_2 solution at 183 K, $[H_4Re_3(CO)_9]^-$ has a hydride NMR pattern of 3:1 and a carbonyl group ^{13}C NMR pattern of 6:3. These NMR spectra as well as their VT NMR results and IR spectra in the solid state and solution are consistent with a solution structure of $[Re_3(\mu_3\text{-}H)(\mu_2\text{-}H)_3(CO)_9]^-$ in which two double bonds are delocalized over the rhenium triangle.

Introduction

$H_4Re_4(CO)_{12}$ is an electronically unsaturated 56-e cluster;[1] it has two delocalized double bonds and exhibits interesting chemistry. Recently, we reported that it reacts cleanly with methanol in a surprising rate law that is first order in $H_4Re_4(CO)_{12}$ and fourth order in methanol.[1d] On the basis of this kinetics, we proposed the product to be $H_4Re_4(CO)_{12}(MeOH)_4$. However, on the basis of spectroscopic data, this product is assigned by D'Alfonso et al. to be $[H_4Re_3(CO)_9]^-[Re(CO)_3(MeOH)_3]^+$.[1c] This discrepancy is due to the fact that the initial product $[H_4Re_3(CO)_9(MeOH)]^-[Re(CO)_3(MeOH)_3]^+$ is unstable and should lose rapidly one methanol since an equilibrium between $[H_4Re_3(CO)_9(MeOH)]^-$ and $[H_4Re_3(CO)_9]^-$ was observed at low temperature. This anionic trirhenium cluster $[H_4Re_3(CO)_9]^-$ has a formal electron count of 44 e which is 4 e short of the value predicted by the polyhedral skeletal electron pair theory.[2] Several examples of 44-e or lower trinuclear clusters are known;[2b] virtually all of them contain late transition metal elements which have the tendency to be stable in the 16-e or even 14-e instead of the usual 18-e configuration in mononuclear organometallic compounds.[2] No trinuclear clusters formed by transition metals from groups VI and VII with 44 e or less is known. Therefore the electronic unsaturation in $[H_4Re_3(CO)_9]^-$ must be quite unusual. When a cluster is electronically unsaturated, localized M−M double bond(s), as in $H_2Os_3(CO)_{10}$[3] and $[H_4Re_3(CO)_{10}]^-$,[4] or delocalized double bonds, as in $H_4Re_4(CO)_{12}$[1] and $Pt_2Os_4(CO)_{11}(COD)$[5] can be found. These electronically unsaturated clusters are more reactive than the saturated ones.[3,6] A ligand may also participate in reducing the effect of unsaturation, as in $Mn_2(CO)_9$[7] in which one of carbonyl groups becomes semibridging. We report here the structure of this 44-e trirhenium cluster.

Results and Discussion

The reaction of $H_4Re_4(CO)_{12}$ with *N*,*N*-dimethylformamide (DMF) in chloroform yields a yellow product

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(1) (a) Beringhelli, T.; D'Alfonso, G.; Zarini, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2407. (b) Wang, S. R.; Cheng, C. P. *J. Organomet. Chem.* **1995**, *490*, 111. (c) Beringhelli, T.; D'Alfonso, G. *J. Chem. Soc., Chem. Commun.* **1994**, 2613. (d) Wang, S. R.; Cheng, C. P. *J. Chem. Soc., Chem. Commun.* **1993**, 470. (e) Wang, S. R.; Wang, S.-L.; Cheng, C. P.; Yang, C. S. *J. Organomet. Chem.* **1992**, *431*, 215. (f) Saillant, R. B.; Barcelo, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1970**, *92*, 5739. (g) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, 4687. (h) Kaesz, H. D.; Knox, S. A. R.; Koepke, J. W.; Saillant, R. B. *J. Chem. Soc., Chem. Commun.* **1971**, 477. (i) Johnson, J. R.; Kaesz, H. D. *Inorg. Synth.* **1978**, *18*, 60.

(2) (a) Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 29. (b) Mingos, D. M. P.; May, A. S. In *The chemistry of Metal Cluster Complexes*; Shriver, D. S., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 2.

(3) For a review see: Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(4) (a) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1986**, 2691. (b) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* **1985**, *24*, 2666. (c) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1327. (d) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Romiti, P.; Sironi, A.; Freni, M. *Inorg. Chem.* **1984**, *23*, 2849. (e) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A.; Albinati, A. *J. Organomet. Chem.* **1977**, *136*, c49.

(5) Adams, R. D.; Wu, W. *Organometallics* **1991**, *10*, 35. (b) Adams, R. D.; Wu, W. *Inorg. Chem.* **1991**, *30*, 3605.

(6) (a) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127. (b) Mingos, D. M. P.; May, A. In *Chemistry of Metal Clusters*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter II.

(7) (a) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (b) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785. (c) Dunkin, I. R.; Harter, P.; Shields, C. *J. Am. Chem. Soc.* **1984**, *106*, 7248.

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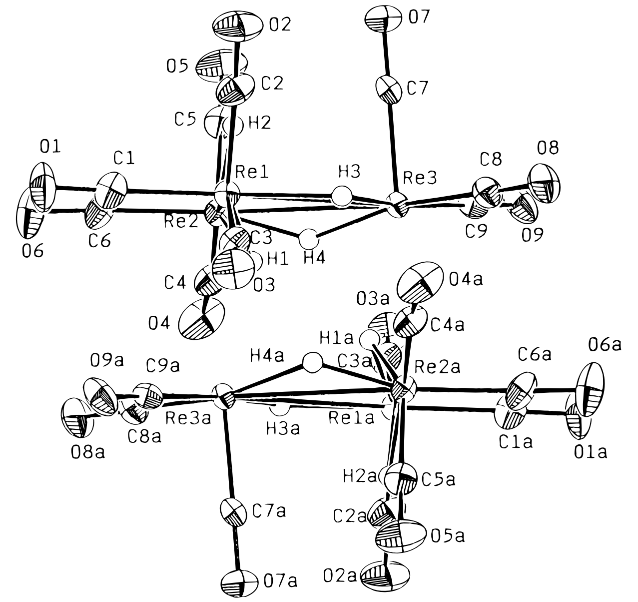

Figure 1. ORTEP drawing of the structure of two anionic clusters of **1**, $[H_4Re_3(CO)_9]^-[Re(CO)_3(DMF)_3]^+$.

Table 1. Relevant Bond Distances (Å) and Angles (deg) in the Anionic Cluster of 1, $[H_4Re_3(CO)_9]^-[Re(CO)_3(DMF)_3]^+$, with Atomic Labeling in Figure 1

Bond Distances			
Re1−Re2	2.8915(17)	Re1−Re3	3.2414(22)
Re2−Re3	3.2815(19)	Re1−C1	1.921(12)
Re1−C2	1.898(11)	Re1−C3	1.932(11)
Re2−C4	1.921(11)	Re2−C5	1.856(13)
Re2−C6	1.921(12)	Re3−C7	1.900(11)
Re3−C8	1.920(11)	Re3−C9	1.896(11)
Re1−H1	1.96(8)	Re1−H2	1.73(9)
Re1−H3	1.88(9)	Re2−H1	1.64(9)
Re2−H2	2.13(6)	Re2−H4	1.57(8)
Re3−H1	2.54(9)	Re3−H2	3.02(9)

Bond Angles			
Re2−Re1−Re3	63.00(4)	Re1−Re2−Re3	63.82(5)
Re2−Re3−Re1	53.18(4)	Re2−Re1−C1	91.5(3)
Re2−Re1−C2	121.1(4)	Re2−Re1−C3	149.7(3)
Re1−Re2−C4	151.2(4)	Re1−Re2−C5	121.4(3)
Re1−Re2−C6	92.3(3)	Re3−Re1−C1	156.5(3)
Re3−Re1−C2	102.0(4)	Re3−Re1−C3	111.7(3)
Re3−Re2−C4	112.6(4)	Re3−Re2−C5	100.7(4)
Re1−H1−Re2	106(4)	Re1−H2−Re2	96(8)
Re1−H3−Re3	115(4)	Re2−H4−Re3	130(5)

1 quantitatively. The ^{1}H NMR spectrum indicates that there are four hydrides and three equivalent molecules of DMF in **1**. The hydride NMR pattern of −5.76 (3H) and −8.00 ppm (1H) is virtually the same as that reported for the product of the reaction of $H_4Re_4(CO)_{12}$ and methanol.[1c,d] This methanol product cannot be isolated because an attempt at isolation leads to decomposition. However, on the basis of the spectroscopic data, it was formulated as $[H_4Re_3(CO)_9]^-[Re(CO)_3(MeOH)_3]^+$. The ^{1}H NMR spectra as well as the elemental analysis results of **1** are consistent with a formula of $[H_4Re_3(CO)_9]^-[Re(CO)_3(DMF)_3]^+$.[1b] The X-ray structure of **1** confirms this formulation. The cation $[Re(CO)_3(DMF)_3]^+$ is in a facial conformation (see Supporting Information) as expected.

In the anionic cluster of **1** (Figure 1), the three rhenium atoms are on the vertices of a nearly isosceles triangle. The relevant bond distances and angles for this cluster are collected in Table 1. The distances of Re1−Re3 (3.244 Å) and Re2−Re3 (3.282 Å) are typical of a hydride bridged Re−Re single-bond distance. The hydrides bridging Re1−Re3 and Re2−Re3 are expected to be on the trirhenium plane. Comparing with the dihydride-bridged Re−Re double-bond distances in $H_2Re_2(CO)_8$ (2.976 Å),[8] $H_2Re_2(CO)_6(PPh_2CH_2PPh_2)$ (2.893 Å),[9] $H_4Re_3(CO)_{10}^-$ (2.821 Å),[4e] and $H_3Re_3(CO)_{10}^{2-}$ (2.797 Å),[10] the Re1−Re2 distance (2.8915 Å) indicates that it is a dihydride-bridged Re−Re double bond. The two hydrides between Re1−Re2 are expected to be located above and below the trirhenium triangular plane. In the difference-Fourier map, these four hydrides were found in the expected locations. The Re−H distances are in the range 1.57(8)−2.13(6) Å with a mean of 1.82 Å. The mean Re−H−Re angles are 122 and 101° for the long and short Re−Re edges, respectively. These values are comparable with the neutron diffraction results of $H_3Re_3(CO)_{11}(PPh_3)$ (Re−H, 1.78−1.83 Å; ∠Re−H−Re, 111−113°)[11] and $H_3Re_3(CO)_8\{(EtO)_2POP(OEt)_2\}_2$ (Re−H, 1.77−1.87 Å; ∠Re−H−Re, 125−136°)[12] and the X-ray diffraction results of $[H_4Re_3(CO)_9(PPh_3)]^-$ (Re−H, 1.65(7)−1.90(7) Å; mean Re−H−Re angles, 121 and 100° for the long and short edges, respectively).[4a] The distances of Re3−H1 (2.54 Å) and Re3−H2 (3.02 Å) indicate that there is a very weak (if any) interaction between Re3 and H1 or H2.

Re1, Re2, and Re3 are each coordinated by three carbonyl groups. Since there is double bond between Re1 and Re2, the coordination environment on Re3 appears to be unsaturated. The two carbonyl groups C8O8 and C9O9 are located closely on the trirhenium plane, and the third carbonyl group C7O7 is nearly perpendicular to the trirhenium plane. There is a vacant coordination site trans to C7O7. Therefore, the structure of the 44-e anionic cluster $[H_4Re_3(CO)_9]^-$ has a Re−Re double bond as well as an empty coordination site on Re3.

It is well-known that a compound with a coordinative unsaturation site is extremely reactive. There is no reason to expect that this structure can be formed in the presence of DMF, which is a moderately strong coordinating ligand. Searched beyond a distance of 3.4 Å, the distance expected for a Re−Re bonding interaction, another $[H_4Re_3(CO)_9]^-$ was found as shown in Figure 1. The relevant bond distances and angles between the two monomeric clusters are summarized in Table 2. The two trirhenium units are in an antiprismatic arrangement and are related by an inversion symmetry. The distances of Re1−Re3a (3.482 Å) and Re2−Re3a (3.453 Å) are much longer then that of Re−Re single bond in $R_2(CO)_{10}$ (3.041 Å).[13] These intercluster distances are also longer than that of hydride-bridged Re−Re single bond. Therefore the formation of single bond between Re1−Re3a and Re2−Re3a is highly unlikely. However, there must be some interaction between the two anionic $[H_4Re_3(CO)_9]^-$ clusters because some carbonyl groups on each cluster are

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[8] Masciocchi, N.; Sironi, A.; D'Alfonso, G. *J. Am. Chem. Soc.* **1990**, *112*, 9395.

[9] Prest, D. W.; Mays, M. J.; Orpen, A. G.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 737.

[10] Bertolucci, A.; Freni, M.; Romiti, P.; Ciani, G.; Albano, V. G. *J. Organomet. Chem.* **1976**, *113*, C61.

[11] Wei, C. Y.; Garlaschelli, L.; Bau, R.; Kowtzle, T. F. *J. Organomet. Chem.* **1981**, *213*, 61.

[12] Prest, D. W.; Mays, M. J.; Mcmullan, R. K.; Orpen, A. G. *J. Organomet. Chem.* **1982**, *240*, 395.

[13] Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

Table 2. Significant Bond Distances (Å) and Angles (deg) between the Two Monomers of $[H_4Re_3(CO)_9]^-$ in Figure 1

Bond Distances			
Re1−Re3a	3.4823(11)	Re2−Re3a	3.4530(12)
Re3−H1a	2.27(9)		
Bond Angles			
Re2−Re1−Re3a	64.83(4)	Re1−Re2−Re3a	65.89(4)
Re1−Re3a−Re2	49.28(3)	Re3−Re1−Re3a	77.75(4)
Re3−Re2−Re3a	78.49(5)	Re1−Re3−Re2a	80.43(4)
Re2−Re3−Re1a	80.30(4)	Re1−H1−Re3a	110(4)
Re2−H1−Re3a	123(5)		

pushed away from the other cluster to facilitate the interaction. For example ∠Re2−Re1−C3 (149.7°) and ∠Re1−Re2−C4 (151.2°) are ca. 30° larger than ∠Re2−Re1−C2 (121.4°) and ∠Re1−Re2−C5 (121.4°). Furthermore, the dihedral angles between the Re1−Re2−Re3 plane and the Re3−C8−C9 and Re1−Re2−C1−C6 planes are 4.6 and 0.8°, respectively, away from the other cluster.

The distances between Re3a−C3 (3.83 Å) and Re3a−C4 (3.81 Å) are about 2 Å longer than a normal Re−CO distance (1.8−1.9 Å). The distances of Re3a−O3 (4.46 Å) and Re3a−O4 (4.46 Å) are also longer than expected for a bonding interaction. Furthermore, ∠Re1−C3−O3 (174°) and ∠Re2−C4−O4 (175°) are close to linearity. On the basis of these bond distances and angles, it is obvious that the interaction of Re3a with carbonyl groups on the other cluster is negligible.

The nature of the interaction between the two anionic clusters of $[H_4Re_3(CO)_9]^-$ is not obvious from the X-ray structure. We believe that the two hydrides H1 and H1a in between the two trirhenium units play a key role in the interaction. In $[HM_2(CO)_{10}]^-$ (M = Cr, W),[14] the 3c−2e M−H−M bonding leads to M−M distances in the range of 3.33−3.53 Å which is the range for Re1−Re3a and Re2−Re3a. The unusually long Re−Re distances in $HRe_3(CO)_{14}$ (3.34 Å),[15] $HMnRe_2(CO)_{14}$ (3.39 Å),[16] and $H_4Re_4(CO)_{12}(HC(PPh_2)_3)$ (3.435 Å)[1e] can also be attributed to the same type of Re−H−Re 3c−2e bonding interaction. But, there is no hydride bridging Re1−Re3a and Re2−Re3a. Alternatively, it is possible to view the 3c−2e M−H−M bonding as a donor−acceptor interaction. The electrons of the M−H 18-e species are donated to the empty orbital of the 16-e species M to form a donor−acceptor complex. Using this concept of donor−acceptor interaction, then it is likely that the electrons of the Re1−H1−Re2 bridging bond are donated to the empty coordination site on Re3a. Likewise, the electrons of Re1a−H1a−Re2a are donated to Re3. These two donor−acceptor interactions are responsible for the stability of the dimeric cluster $[H_4Re_3(CO)_9{}^-]_2$ in the solid state. However, there is a noticeable difference with the hydride bonding in $[HM_2(CO)_{10}]^-$. In $[HM_2(CO)_{10}]^-$,[14] the hydrides are midway between the metal centers either linearly or bent. In $[H_4Re_3(CO)_9{}^-]_2$, the hydrides responsible for the adduct formation are much farther away from the coordinatively unsaturated metal centers than the rhenium atoms bridged by these hydrides.

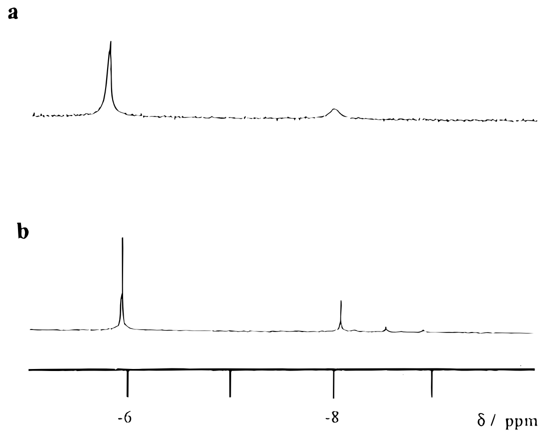

Figure 2. Hydride NMR spectra of $[H_4Re_3(CO)_9]^-$ in CD_2Cl_2 in the presence of a very small amount of DMF at (a) 293 K and (b) 183 K.

Since the conductivity data of the solution of $[H_4Re_3(CO)_9]^-[Re(CO)_3(MeOH)_3]^+$ indicates that $[H_4Re_3(CO)_9]^-$ exists as a monomer in solution,[1b] the dimer of **1** in the solid state must dissociate completely into a monomer in solution. It indicates that the interaction between the two anionic $[H_4Re_3(CO)_9]^-$ clusters is weak and/or $[H_4Re_3(CO)_9]^-$ is somewhat stable in solution.

When $[H_4Re_3(CO)_9]^-[Re(CO)_3(DMF)_3]^+$ reacts with equimolar coordinating ligand L (L = CO, PPh_3, CH_3CN, and Py) in chloroform solution, a rapid clean reaction was observed.

$$[H_4Re_3(CO)_9]^- + L \rightarrow [H_4Re_3(CO)_9L]^-$$

The chemical shifts (ppm) of the hydrides of $[H_4Re_3(CO)_9L]^-$ in $CDCl_3$ are as follows: for L = PPh_3, −7.90 (1H), −8.82 (1H), −12.25 (2H); for L = CH_3CN, −8.40 (1H), −8.50 (1H), −10.51 (2H); for L = pyridine, −8.15 (1H), −8.81 (1H), −9.49 (2H); for L = CO, −8.50 (2H), −13.57 (2H). These hydride chemical shifts are virtually the same as those reported in literature[4a,b] In the structure of $[H_4Re_3(CO)_9L]^-$, L is occupying the coordinated unsaturation site in the monomeric structure of the anion in Figure 1.[4a,b]

From the X-ray structure of **1**, the NMR spectra of the anionic cluster cannot be understood. One would expect a hydride NMR intensity pattern of 1:1:2 instead of 3:1 (Figure 2). The ^{13}C NMR intensity pattern of the carbonyl groups in **1** is expected to be 1:2:2:2:2:3 instead of the observed 6:3:3 measured with ^{13}CO-enriched sample under the condition of quantitative ^{13}C NMR at 193 K. Both ^1H and ^{13}C NMR spectra clearly indicate that either there are fluxional motions of the hydrides and carbonyl groups leading to the observed patterns or the structure of $[H_4Re_3(CO)_9]^-$ is different from the monomeric structure in the solid state shown in Figure 1. In Figure 2, it is clear that the hydride NMR peaks remain sharp down to 183 K. Likewise, the ^{13}C NMR peaks of carbonyl groups are also sharp down to 183 K. At 193 K, $\Delta\nu_{1/2}$'s for the three peaks of carbonyl groups are within the range of 5.0 ± 0.2 Hz when measured with a 600 MHz instrument. All this line width information is consistent with the absence of fluxional motions of hydrides and carbonyl groups in $[H_4Re_3(CO)_9]^-$ at low temperature. However, the presence of rapid fluxional motion cannot be ruled out completely on the

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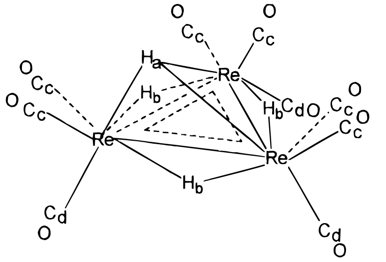
[14] (a) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176. (b) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

[15] Kaesz, H. D.; Bau, R.; Churchill, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 2775.

[16] Yang, C. S.; Cheng, C. P.; Kuo, L. W.; Wang, Y. *J. Chin. Chem. Soc.* **1985**, *32*, 17.

basis of these low-temperature NMR spectra alone. In order to have rapid fluxional motions, hydrides, the double bond, and carbonyl groups in the structure in Figure 1 have to move rapidly to lead to the observed spectral patterns. These movements involve so many structural elements in $[H_4Re_3(CO)_9]^-$; such fluxional motions cannot be low activation energy processes and are expected to be slow at 183 K. In agreement with this expection, the slow fluxional motion of the hydrides shows up in the broadness of the hydride NMR peaks at 293 K (Figure 2). Therefore, we conclude that the observed NMR spectra at 183 K cannot be due to the fluxional motions of hydrides and carbonyl groups in $[H_4Re_3(CO)_9]^-$; the structure of $[H_4Re_3(CO)_9]^-$ in solution is different from that in solid state. This is further supported by the IR data of **1**, which exhibits different spectra in the solid state and in solution. We propose that the structure of $[H_4Re_3(CO)_9]^-$ in solution is $[Re_3(\mu_3\text{-}H)(\mu_2\text{-}H)_3(CO)_9]^-$, shown as follows:



To make up the shortage in electron count in $[H_4Re_3(CO)_9]^-$, two double bonds are delocalized over the triangular rhenium plane making the three rhenium atoms equivalent as in the structure of $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$.[17] In the proposed structure, there are three hydrides in the edge-bridging (H_b) positions and one in the face-bridging (H_a) position, yielding the observed 3:1 intensity pattern in hydride NMR. The six carbonyl groups labeled C_cO are equivalent and on the same side of the trirhenium plane as that of H_a, whereas the other three carbonyl groups labeled C_dO are also equivalent and located on the other side of the trirhenium plane opposite to H_a. With this structure, the ^{13}C NMR intensity pattern of this anionic cluster is expected to be 6:3, as observed experimentally.

At 293 K, the line widths of the hydride NMR (Figure 2), $\Delta\nu_{1/2}$'s, are 15 and 46 Hz for the −5.76 and −8.00 ppm signals, respectively. It indicates the presence of exchange process between hydrides attributed to these two signals. The exchange rate constants is 190 s^{-1}. At 223 K and up, the ^{13}C NMR peaks at 193.5 and 196.7 ppm broaden visibly whereas the peak at 197.8 ppm remains sharp. At 293 K, the 193.5 ppm peak is broadened and shifted to 193.9 ppm and the peak at 196.7 ppm is too broad to be seen. Therefore, we assign the broadened peaks to CO groups in $[H_4Re_3(CO)_9]^-$ and the sharp peak at 197.8 ppm to the CO groups in $[Re(CO)_3(DMF)_3]^+$. These NMR data indicate the carbonyl groups on $[H_4Re_3(CO)_9]^-$ are exchanging at temperature above 223 K. According to our proposed structure of $[H_4Re_3(CO)_9]^-$ in solution, these exchange process are the exchange between H_a and H_b and between C_cO and C_dO, respectively. This proposed explanation is consistent with our assertion that in solution the exchange of hydrides and carbonyl groups is not a low activation energy process and there is no fluxional motions of hydrides and carbonyl groups in $[H_4Re_3(CO)_9]^-$ at 183 K.

Table 3. Crystal Data for the Structural Analysis of 1, $[H_4Re_3(CO)_9]^-[Re(CO)_3(DMF)_3]^+$

emp formula	$Re_4O_{15}N_3C_{21}H_{25}$
fw	1340.26
cryst system	triclinic
lattice params	
a, Å	11.394(7)
b, Å	11.913(3)
c, Å	13.144(8)
α, deg	72.94(4)
β, deg	74.77(4)
γ, deg	82.92(4)
V, Å^3	1643.7(15)
space group	$P\bar{1}$ (No. 2)
Z	2
D_{calc}, g/cm^{-3}	2.635
F_{000}	1174
μ(Mo Kα), cm^{-1}	149.514
temp, K	298
$2\theta_{max}$, deg	45.0
no. measd reflns	4382
no. obsns ($I > 2\sigma(I)$)	3647
no. variables	405
R, R_w	0.029, 0.029
max, min in *D*-map, e Å^{-3}	−1.640, 1.760

The structures of $[H_3Re_3(CO)_9(\mu\text{-}OEt)]^-$ [18] and $[H_3Re_3(CO)_9(\mu\text{-}SBu)]^-$ [19] consist of a face-bridging OEt^- and SBu^-, respectively. In each of these two structures, six equivalent carbonyl groups are located on the same side of the trirhenium plane containing the face-bridging group. It seems that the $H_3Re_3(CO)_9$ fragment has a tendency to take on a face-bridging ligand. In our proposed structure, a hydride H^- is taking the place of OEt^- and SBu^-. However, there is an obvious difference that OEt^- and SEt^- are 6-e donors and hydride H^- is only a 2-e donor. To make up the difference in electron count, there must be two double bonds delocalized in the proposed structure of $[H_4Re_3(CO)_9]^-$.

Experimental Section

$H_4Re_4(CO)_{12}$ was prepared from the reaction of $Re_2(CO)_{10}$ (from Strem Chemical Co.) with H_2 at elevated temperature according to the literature method.[1e] *N*,*N*-dimethylformamide and chloroform were obtained from Aldrich Chemical Co. and purified according to the standard procedure.[20] ^{13}C-enriched $H_4Re_4(CO)_{12}$ was prepared from enriched $Re_2(^{13}CO)_{10}$, which was obtained from photolysis of $Re_2(CO)_{10}$ (using a 450 W medium-pressure mercury lamp) under ^{13}CO atmosphere in toluene solution. The enriched sample was used to obtain high-quality ^{13}C NMR spectra.

Physical Measurements. NMR spectra were measured on Bruker AM-400, Varian Unity-400, or Bruker AMX-600 spectrometers. IR spectra were recorded on a Jasco FTIR-300E spectrometer. UV−vis spectra were measured on a Perkin-Elmer Lamda-5 spectrometer.

Reaction of $H_4Re_4(CO)_{12}$ with DMF. DMF was added dropwisely to a chloroform solution (2 mL) of $H_4Re_4(CO)_{12}$ (50 mg, 46 μmol) until the characteristic red color of $H_4Re_4(CO)_{12}$ disappeared. When hexane was added to the reaction mixture,

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[17] Hoffman, D. M.; Lappas, D.; Putilina, E. *Inorg. Chem.* **1992**, *31*, 79.

[18] Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1981**, *219*, C23.

[19] Bonfichi, R.; Ciani, G.; D'Alfonso, G.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1982**, *231*, C35.

[20] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

yellow precipitate **1** (53 mg) was obtained quantitatively (based on rhenium). ^{1}H NMR (CD_2Cl_2): δ 7.90 (s, 3H, H in DMF), 2.96 (s, 9H, CH_3 in DMF), 3.13 (s, 9H, CH_3 in DMF), −5.76 (s, 3H), −8.00 (s, 1H) ppm. ^{13}C NMR (CD_2Cl_2, 193 K): δ 33.7, 33.9, 167.3, 193.5 (6CO), 196.7 (3CO) and 197.8 (3CO) ppm. IR (ν(CO), CH_2Cl_2): 2048 (w), 2034 (m), 2008 (s), 1930 (s), 1915 (s) cm^{-1}. IR (ν(CO), KBr pellet): 2034 (m), 2025 (m), 2016 (s), 2007 (s), 1946 (sh), 1921 (s), 1907 (s), 1887 (s) cm^{-1}. UV−vis ($CHCl_3$): 370 nm (ϵ = 9400 M^{-1} cm^{-1}). Anal. Calcd for $C_{21}H_{25}N_3O_{15}Re_4$ ($[H_4Re_3(CO)_9]^-[Re(CO)_3(DMF)_3]^+$): C, 19.34; H, 1.93; N, 3.22. Found: C, 19.47; H, 1.83; N, 3.16.

Recrystallization of **1** from chloroform solution failed because **1** decomposed. However, instead of addition of hexane, if the reaction mixture was stored at −10 °C, X-ray-quality crystal were obtained.

X-ray Crystallography. A single crystal of **1** was sealed in epoxy resin. Diffraction intensity data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer using monochromatic Mo Kα radiation (0.7107 Å) from a graphite single crystal at 25 °C. The general data collection and results are summarized in Table 3. The structure was solved by the heavy-atom method. All non-hydrogen atoms were subsequently located from a Fouier map and then anisotropically refined by full-matrix least squares. In the difference-Fourier map, four charge density peaks (assigned to hydrides H1, H2, H3, and H4; see labeling in Figure 1) with intensities in the range 0.53−0.80 e Å^{-3} were found besides the heavy-atom ripples near the rhenium atoms. The positions of these four hydrides were refined isotropically. All other hydrogen atoms were placed in ideal positions in structure factor calculations. All calculations were performed on a Micro VAX III computer with the NRCC-SDP-VAX program.

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Supporting Information Available: ORTEP drawings and tables of crystal data, bond distances and bond angles, atomic coordinates, and thermal parameters for **1** (9 pages). Ordering information is given on any current masthead page.

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