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Synthesis, Crystal Structure, and Fluxional Behavior of $\text{Re}_3\text{H}_2(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$

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The oxidation reactions of the unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ with C_7H_9^+ are described. They imply, as the first step, abstraction of a H^- ligand, and when performed in the presence of donor species L , such as CO or RCN , they lead to the neutral derivatives $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}\text{L}_2$. In the absence of donor molecules, in inert solvents, the new species $\text{Re}_3\text{H}_2(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$ is readily obtained in high yields. It has been investigated by single-crystal X-ray analysis. The crystals are monoclinic, space group $\text{C}2/c$, with cell constants $a = 31.507(7) \text{ \AA}$, $b = 8.561(3) \text{ \AA}$, $c = 16.503(4) \text{ \AA}$, $\beta = 106.60(2)^\circ$, and $Z = 8$. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques, on the basis of 2677 significant independent counter data, up to a final R value of 0.027. The molecule contains a triangular arrangement of rhenium atoms. Two metals, $\text{Re}2$ and $\text{Re}3$, each bear four terminal CO groups, while $\text{Re}1$ is linked to two such ligands and to the η^5 -cycloheptadienyl ligand. The two hydrides have been indirectly located, one double-bridging the $\text{Re}2\text{-Re}3$ edge and the second one in a triple-bridging location. Rhenium-rhenium bond lengths are $\text{Re}1\text{-Re}2 = 3.160(1) \text{ \AA}$, $\text{Re}1\text{-Re}3 = 3.193(1) \text{ \AA}$, and $\text{Re}2\text{-Re}3 = 3.076(1) \text{ \AA}$. ^1H and ^{13}C NMR analyses at different temperatures indicate a fluxional behavior in solution of the C_7H_9 group, involving also the scrambling of the two CO groups bound to $\text{Re}1$. The apparent C_{2v} symmetry for the whole compound at room temperature has been interpreted as deriving from a complete interchange of the coordination sites of the ligands bound to $\text{Re}1$, accompanied by a concerted up and down movement of the $\mu_3\text{-H}$ ligand through the Re_3 plane. At -100°C the 10 CO groups and all the hydrogen atoms of the C_7H_9 ligand display different resonances, in accordance with the lack of symmetry of the solid-state structure.

Introduction

In our previous studies on the reactivity of the unsaturated hydrido-carbonyl cluster $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ (1),¹ we have observed that most of the processes imply at the first stage attack on the $\text{Re}(\mu\text{-H})_2\text{Re}$ system by an electrophile, which removes a H^- ligand. Acids HX ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$,² RCOO^- ,³ ArO^- ⁴) give H_2 evolution, and I_2 reacts with HI formation.⁵ We have therefore attempted the oxidation of the parent cluster with other electrophiles, and we report here its reactions with tropylium ion and the X-ray structure of the derivative $\text{Re}_3(\mu\text{-H})(\mu_3\text{-H})(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$ (2) containing a η^5 -cycloheptadienyl group. Compound 2 exhibits a fluxional behavior in solution, as shown by ^1H and ^{13}C NMR analyses at different temperatures.

Experimental Section

Reactions were performed under N_2 , using solvents deoxygenated and purified by standard methods. Compound 1 was prepared as previously described.^{1,5b} Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer in 0.1-mm CaF_2 cells and were calibrated with polystyrene film absorptions. NMR spectra were recorded by M. Bonfà on a Varian XL 200 FT spectrometer. The mass spectrum was obtained by P. Russo on a Varian MAT 112 instrument, with a direct inlet probe, at 100°C and 70 eV. Gas chromatographic analyses of the gases evolved in the reactions were performed on a Carlo Erba Fractovap M instrument, fitted with HWD and two 1-m columns in series (molecular sieves and silica gel), using Ar as carrier. Elemental analysis was performed by the Microanalytical Laboratory of the Milan University.

Preparation of $\text{Re}_3\text{H}_2(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$ (2). A 100-mg sample (0.103 mmol) of the NEt_4^+ salt of compound 1, dissolved in 2 mL of CH_2Cl_2 , was treated with a solution of $(\text{C}_7\text{H}_7)\text{BF}_4$ (25 mg, 0.141 mmol) in CH_2Cl_2 (40 mL), and the mixture was then stirred at room temperature. The color of the solution turned immediately from yellow to red-brown and then slowly to bright yellow. Gas and solution samples were taken at different times for GLC and IR analyses. Only traces of evolved H_2 were detected. IR analyses indicated that most of 1 had reacted after about 2 h. The mixture was stirred overnight to complete the reaction and then evaporated to dryness. The resulting solid was dissolved in a little volume of CH_2Cl_2 , and the solution was eluted over a PLC plate of silica gel 60 (2 mm), with $\text{CH}_2\text{Cl}_2/n\text{-C}_6\text{H}_{14}$ (2:3). Only a bright yellow band was eluted, which was extracted with CH_2Cl_2 ; the solution was evaporated to dryness, and the residue

was washed with a little volume of n -pentane and then dried under vacuum (72 mg, yield 75%). Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{O}_{10}\text{Re}_3$: C, 21.84; H, 1.18. Found: C, 21.10; H, 1.30. The compound is stable in the solid state and also in air, for several days, while in solution it decomposes, very slowly in CH_2Cl_2 , but much more rapidly in other solvents such as MeCN . Upon being heated, the solid compound decomposes at 125°C . IR (CH_2Cl_2) in the $\nu(\text{CO})$ region: 2108 w, 2084 mw, 2016 s, 2000 m, 1980 sh, 1968 m, 1955 sh, 1900 br, w cm^{-1} . ^1H NMR (200 MHz, CDCl_3 , standard Me_4Si) at 30°C : δ_{H} 6.57 (1, t, $J(\text{HH}) = 5.8 \text{ Hz}$), 5.05 (2, dd, $J(\text{HH}) = 5.8, 9.1 \text{ Hz}$), 4.55 (2, m), 2.35 (2, m), 2.05 (2, m), -14.20 (1, d, $J(\text{HH}) = 2.7 \text{ Hz}$), -15.60 (1, d, $J(\text{HH}) = 2.8 \text{ Hz}$). These values do not change significantly ($\leq 0.1 \text{ ppm}$) in $\text{C}_4\text{D}_8\text{O}$ solution. At -100°C (200 MHz, $\text{C}_4\text{D}_8\text{O}$, all signals broad unresolved multiplets): δ_{H} 7.1 (1), 5.6 (1), 5.0 (1), 4.5 (1), 4.3 (1), 2.4-1.5 (not integrable), -13.5 (1), -15.6 (1).

The ^{13}C spectrum was obtained from a sample prepared as described above, using as starting material compound 1 about 20% ^{13}CO enriched (made by exchange between the natural-abundance sample and ^{13}CO , about 50%, in acetone solution, for 3 days at room temperature). ^{13}C NMR at 30°C (50.3 MHz, CDCl_3 , standard Me_4Si): δ_{C} 196.3 (2), 184.2 (2), 183.9 (4), and 181.1 (2) for the carbonyls and 96.0 (2), 89.6 (1), 71.9 (2), and 33.0 (2) for the dienyl moiety (the number of carbon atoms and not the relative intensities are given in parentheses, the C_7H_9 moiety not being ^{13}C enriched). ^{13}C NMR at -100°C (50.3 MHz, $\text{CDCl}_3/\text{CHFCI}_2$ (1:5), all signals of equal intensity): δ_{C} 204.1, 192.2, 185.8, 185.5, 184.9, 184.3, 183.6, 182.9, 182.0, and 180.9, all due to carbonyls; the resonances of the C_7H_9 ligand could not be unambiguously assigned, due to the high noise and to the presence of strong bands of the solvents in the same region. The ^{13}C uncoupled spectrum, at room temperature, showed only a broadening of all the signals, but no resolved multiplets.

The mass spectrum shows the expected molecular ion multiplet centered at m/e 933 and the sequence of fragments $[\text{Re}_3\text{H}_n(\text{CO})_m(\text{C}_7\text{H}_9)]^+$ ($n = 0-2$, $m = 0-9$), those with $n = 0$ being dominant from $m = 6$. Also ions of type $[\text{Re}_3\text{H}_n(\text{CO})_m]^+$ ($n = 0-3$, $m = 0-12$) are present, arising by loss of the organic moiety from the molecular ion. Crystals, ranging in color from bright yellow to orange, suitable for

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X-ray analysis were obtained by slow evaporation, under N_2 , of a CH_2Cl_2 solution.

Reaction of 1 with $C_7H_7^+$ under CO. A 20-mg sample (0.021 mmol) of the NEt_4^+ salt of 1, dissolved in 2 mL of CH_2Cl_2 under CO, was treated with 5 mg (0.028 mmol) of $(C_7H_7)BF_4$ dissolved in 8 mL of CH_2Cl_2 , and the solution was stirred at room temperature. The color of the solution turned immediately from yellow to red-brown and then slowly faded. The reaction progress was followed by IR analyses of different samples, which showed the complete disappearance of the bands due to reagent, substituted by those due to $Re_3H_3(CO)_{10}$,⁶ in about 2 h.

Reaction of 1 with $C_7H_7^+$ in MeCN Solution. A 20-mg sample (0.021 mmol) of the NEt_4^+ salt of 1, dissolved in 2 mL of MeCN, was treated with 5 mg (0.028 mmol) of $(C_7H_7)BF_4$, and the mixture was stirred at room temperature. The solution became colorless in about 2 h, and in the same time IR analysis and TLC of different samples showed the formation of $Re_3H_3(CO)_{10}(NCMe)_2$.⁷ No other product was revealed by the 1H NMR spectrum of the mixture evaporated to dryness at the end of the reaction. No H_2 evolution was detected by GLC analysis.

To clarify the fate of the organic oxidizing agent, the reaction was performed in a NMR tube by treating 20 mg (0.021 mmol) of the NEt_4^+ salt of 1, dissolved in 1 mL of CD_3CN , with 5 mg (0.028 mmol) of $(C_7H_7)BF_4$. The appearance of multiplets at 6.6, 6.2, and 5.0 ppm clearly indicates the formation of cycloheptatriene.

Reaction of 1 with $C_7H_7^+$ in the Presence of MeCN. A 20-mg sample (0.021 mmol) of the NEt_4^+ salt of 1, dissolved in 3 mL of CH_2Cl_2 , was treated with 3 mL of MeCN (0.073 mmol) and 5 mg (0.028 mmol) of $(C_7H_7)BF_4$, and the mixture was then stirred at room temperature. The color of the solution became red-brown and then progressively faded. IR analyses and TLC of samples at different times showed formation only of $Re_3H_3(CO)_{10}(NCMe)_2$. No other product was detected by 1H NMR analysis of the mixture evaporated to dryness after about 4 h.

X-ray Analysis of Compound 2. A multifaceted crystal of dimensions $0.17 \times 0.23 \times 0.27$ mm was mounted on a glass fiber and examined with an Enraf-Nonius CAD4 automated diffractometer. Graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was used. The setting angles of 25 random reflections ($16^\circ < 2\theta < 25^\circ$) were used to determine by least-squares fit accurate cell constants and an orientation matrix. The crystal is monoclinic with cell parameters $a = 31.507(7) \text{ \AA}$, $b = 8.561(3) \text{ \AA}$, $c = 16.503(4) \text{ \AA}$, $\beta = 106.60(2)^\circ$, and $V = 4265.9 \text{ \AA}^3$. The space group, from observed extinctions and successful refinements, is $C2/c$ (No. 15). For $Z = 8$ and a molecular weight of 933.9, the calculated density is 2.91 g-cm^{-3} . $F(000) = 3344$; $\mu(\text{Mo } K\alpha) = 172.7 \text{ cm}^{-1}$.

The data collection was performed by the ω -scan method, within the limits $3^\circ < \theta < 25^\circ$, using a variable scan speed (from 2 to $20^\circ/\text{min}$) and a variable scan range of $(0.9 + 0.35 \tan \theta)^\circ$, with a 25% extension at each end for background determination. The total number of collected data was 3734. The intensities of three standard reflections were measured every 2 h of X-ray exposure, and no significant crystal decay was observed.

The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied, on the basis of Ψ -scans (Ψ 0–360°; every 10°) of suitable reflections with χ values close to 90°; the maximum, minimum, and average relative transmission values were 1.0, 0.79, and 0.89, respectively. A set of 2677 independent significant reflections, with $I > 3\sigma(I)$, was used in the structure solution and refinements.

The coordinates of the rhenium atoms were obtained from a three-dimensional Patterson function. Successive difference Fourier maps showed the positions of all the remaining non-hydrogen atoms. The refinements were carried out by full-matrix least-squares methods, with all atoms treated anisotropically. Weights were assigned according to the formula $W = 1/\sigma_F^2$, where the σ 's of the reflections were modified by a p "ignorance factor" of 0.03. Attempts were made to directly locate the hydrogen atoms by means of difference Fourier maps. These showed residual peaks not exceeding ca. 1.1 e/\AA^3 . Two residues (ca. 0.9 and 0.8 e/\AA^3) were found, which could be assigned to the two hydrides, one bridging the Re2–Re3 edge and the second

Table I. Final Positional Parameters for $Re_3H_3(CO)_{10}(\eta^5-C_7H_9)$

atom	x	y	z
Re1	0.15996 (1)	0.24110 (5)	0.16188 (2)
Re2	0.06680 (1)	0.09195 (5)	0.15150 (2)
Re3	0.10001 (1)	0.36374 (5)	0.27529 (2)
C11	0.1704 (3)	0.028 (1)	0.2021 (7)
O11	0.1792 (3)	−0.0986 (9)	0.2223 (6)
C12	0.2027 (3)	0.307 (1)	0.2658 (6)
O12	0.2298 (3)	0.349 (1)	0.3222 (5)
C21	0.0791 (4)	−0.054 (1)	0.0721 (7)
O21	0.0877 (3)	−0.144 (1)	0.0259 (5)
C22	0.0104 (3)	0.002 (1)	0.1416 (7)
O22	−0.0241 (3)	−0.048 (1)	0.1351 (6)
C23	0.0373 (4)	0.240 (1)	0.0574 (7)
O23	0.0184 (3)	0.317 (1)	0.0037 (5)
C24	0.0904 (3)	−0.056 (1)	0.2482 (6)
O24	0.1007 (3)	−0.1435 (9)	0.3019 (5)
C31	0.1443 (3)	0.522 (1)	0.3277 (6)
O31	0.1700 (3)	0.6133 (9)	0.3558 (6)
C32	0.0646 (4)	0.410 (1)	0.3491 (7)
O32	0.0433 (3)	0.435 (1)	0.3939 (6)
C33	0.0674 (4)	0.523 (1)	0.1958 (7)
O33	0.0485 (4)	0.619 (1)	0.1527 (7)
C34	0.1362 (4)	0.213 (1)	0.3588 (6)
O34	0.1578 (4)	0.133 (1)	0.4078 (6)
C1	0.2165 (3)	0.232 (2)	0.1018 (6)
C2	0.1777 (4)	0.167 (2)	0.0465 (7)
C3	0.1387 (4)	0.255 (2)	0.0161 (7)
C4	0.1340 (4)	0.406 (2)	0.0506 (7)
C5	0.1648 (4)	0.494 (1)	0.1075 (7)
C6	0.2114 (4)	0.527 (2)	0.1110 (9)
C7	0.2345 (4)	0.390 (2)	0.0841 (8)

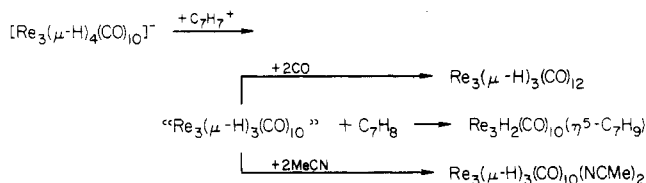
one triply bridging the metallic triangle. These locations are reasonable on the basis of steric hindrance considerations and have been confirmed also by potential energy calculations, using a program by Orpen.⁸ The Re–H distances assumed were ca. 1.82 Å for the double-bridging hydride (Hy1) and ca. 1.89 Å for the triple-bridging one (Hy2).

The difference Fourier maps also showed the positions of the hydrogens of the C_7H_9 moiety. However, attempts to refine all the hydrogen atoms led to rather scattered bond parameters and oscillations for some of them. We have therefore preferred to use computed parameters both for the hydrides (with B thermal factors of 3.0 \AA^2) and for the hydrogens of the cycloheptadienyl group ($C-H$ 0.95 Å, B thermal factors of 5.0 \AA^2). These atoms were included in our model but not refined.

The final values of the conventional R and R' factors were 0.027 and 0.035, respectively, and the error in an observation of unit weight was 1.24. The final positional parameters for the refined atoms are reported in Table I. All computations were performed on a PDP 11/34 computer, using the Enraf-Nonius structure-determination package (SDP) and the physical constants therein tabulated.

Results and Discussion

The reaction of $[Re_3(\mu-H)_4(CO)_{10}]^-$ with $C_7H_7^+$ strictly resembles the analogous oxidation by a strong acid, such as CF_3SO_3H ,⁷ in that the first step of the process implies abstraction of H^- from the unsaturated cluster, with C_7H_8 formation instead of H_2 evolution. In both reactions the hydride elimination leads to the hypothetical superunsaturated " $Re_3(\mu-H)_3(CO)_{10}$ " unit, which further reacts with the available substrate, giving saturated compounds:



When the tropylium ion is reacted, in CH_2Cl_2 , in the presence of donor species L, such as CO or RCN, the neutral derivatives

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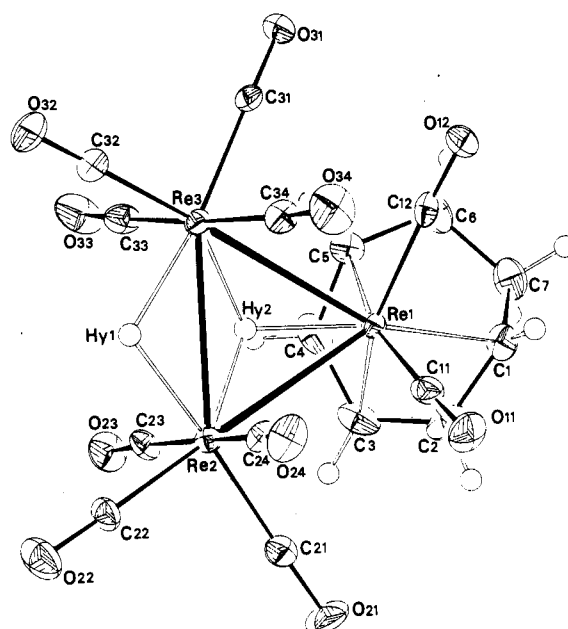
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Table II. Selected Bond Parameters for Re₃(μ-H)(μ₃-H)(CO)₁₀(η⁵-C₇H₉)

Distances (Å)					
Re1-Re2	3.160 (1)	Re2-C23	2.012 (10)	C31-O31	1.126 (11)
Re1-Re3	3.193 (1)	Re2-C24	2.005 (11)	C32-O32	1.150 (13)
Re2-Re3	3.076 (1)	Re3-C31	1.960 (10)	C33-O33	1.137 (13)
Re1-C11	1.933 (13)	Re3-C32	1.915 (11)	C34-O34	1.127 (12)
Re1-C12	1.936 (11)	Re3-C33	1.965 (11)	C1-C2	1.41 (2)
Re1-C1	2.275 (10)	Re3-C34	1.991 (10)	C1-C7	1.52 (2)
Re1-C2	2.224 (10)	C11-O11	1.148 (13)	C2-C3	1.41 (2)
Re1-C3	2.309 (10)	C12-O12	1.129 (12)	C3-C4	1.44 (2)
Re1-C4	2.277 (11)	C21-O21	1.168 (13)	C4-C5	1.37 (2)
Re1-C5	2.367 (11)	C22-O22	1.145 (12)	C5-C6	1.48 (2)
Re2-C21	1.930 (12)	C23-O23	1.128 (12)	C6-C7	1.51 (2)
Re2-C22	1.900 (10)	C24-O24	1.136 (12)		
Angles (deg)					
C11-Re1-C12	87.8 (4)	C22-Re2-C23	88.4 (4)	Re2-C23-O23	175 (1)
C11-Re1-C1	92.4 (4)	C22-Re2-C24	86.5 (5)	Re2-C24-O24	175 (1)
C11-Re1-C2	88.1 (5)	C23-Re2-C24	174.2 (4)	Re3-C31-O31	178 (1)
C11-Re1-C3	112.2 (5)	C31-Re3-C32	92.6 (4)	Re3-C32-O32	178 (1)
C11-Re1-C4	148.0 (5)	C31-Re3-C33	89.2 (4)	Re3-C33-O33	177 (1)
C11-Re1-C5	165.8 (4)	C31-Re3-C34	87.0 (4)	Re3-C34-O34	177 (1)
C12-Re1-C1	87.8 (4)	C32-Re3-C33	89.5 (5)	C2-C1-C7	122 (1)
C12-Re1-C2	123.9 (5)	C32-Re3-C34	91.0 (4)	C1-C2-C3	122 (1)
C12-Re1-C3	146.0 (4)	C33-Re3-C34	176.2 (5)	C2-C3-C4	121 (1)
C12-Re1-C4	122.3 (5)	Re1-C11-O11	174 (1)	C3-C4-C5	129 (1)
C12-Re1-C5	88.1 (4)	Re1-C12-O12	174 (1)	C4-C5-C6	129 (1)
C21-Re2-C22	92.6 (5)	Re2-C21-O21	178 (1)	C5-C6-C7	113 (1)
C21-Re2-C23	91.2 (5)	Re2-C22-O22	178 (1)	C1-C7-C6	113 (1)
C21-Re2-C24	91.8 (4)				

Re₃(μ-H)₃(CO)₁₀L₂ are readily and selectively formed. Analogously, when the reaction is performed in nitrile solutions, Re₃(μ-H)₃(CO)₁₀(NCR)₂ is obtained. This provides a synthetic route for obtaining many substituted derivatives of Re₃(μ-H)₃(CO)₁₂, alternative to the route previously described using strong acids with a noncoordinating anion.⁷ In the absence of donor molecules, in an inert solvent, the reaction with tropylium ion could be expected to lead to coordination on the cluster of the just formed cycloheptatriene. However, a species of this type, if formed, is not stable: the only isolated product, in fact, contains a cycloheptadienyl C₇H₉ group, implying the transfer of a second hydride from the cluster to the organic moiety, probably through a complex intramolecular process, which also requires the migration of one CO group to an adjacent metal. This latter fact is particularly noteworthy since CO migration at room temperature usually occurs via intermediate bridging coordination, a type of coordination quite unusual in polynuclear compounds of rhenium. A similar carbonyl migration has been observed in one of the products obtained by the reaction of Os₃(μ-H)₂(CO)₁₀ with 1,3-butadiene, namely Os₃(CO)₁₀(η⁴-C₄H₆).⁹

The structure of Re₃(μ-H)(μ₃-H)(CO)₁₀(η⁵-C₇H₉) is illustrated in Figure 1. Bond distances and angles are reported in Table II. The metallic triangle exhibits a coordination geometry unusual for Re₃ clusters; two rhenium atoms bear four terminal carbonyl groups, while the third metal bears two such ligands plus the five-electron-donor η⁵-cycloheptadienyl ligand. One of the two hydrides, Hy1, is supposed to be bridging on the Re2-Re3 edge, in accordance with the geometry of the adjacent CO groups and in spite of the value of the subtended metal-metal bond length, 3.076 (1) Å, which is intermediate between the usual values of Re-Re unbridged and Re(μ-H)Re interactions. The second hydride, Hy2, has been indirectly located in a triple-bridging position (see Experimental Section). In the chemistry of rhenium clusters, μ₃-H ligands were previously found only in Re₄(μ₃-H)₄(CO)₁₂¹⁰ and in [Re₆(μ₃-H)₂C(CO)₁₈]²⁻.¹¹ The simultaneous presence

Figure 1. View of the complex Re₃(μ-H)(μ₃-H)(CO)₁₀(η⁵-C₇H₉).

of μ-H and μ₃-H ligands in a triangular cluster is rather unusual and was previously assumed, on the basis of NMR data, in the cation [Ir₃H₃(μ-H)₃(μ₃-H)(Ph₂P(CH₂)₃PPh₂)₃]²⁺.¹²

The two hydrides give rise in the ¹H NMR spectrum to two high-field doublets; coupling between hydrides in rhenium cluster compounds is rarely observed and in the present case may be due to the proximity of the two ligands. The Re-C(carbonyl) bonds are significantly longer when the CO groups are mutually trans (four groups, mean 1.993 Å) than those for the other ones (six groups, mean 1.929 Å).

The bonding mode of the cycloheptadienyl group is similar to that observed in Ru₃(CO)₆(C₇H₇)(C₇H₉),¹³ and the bonding

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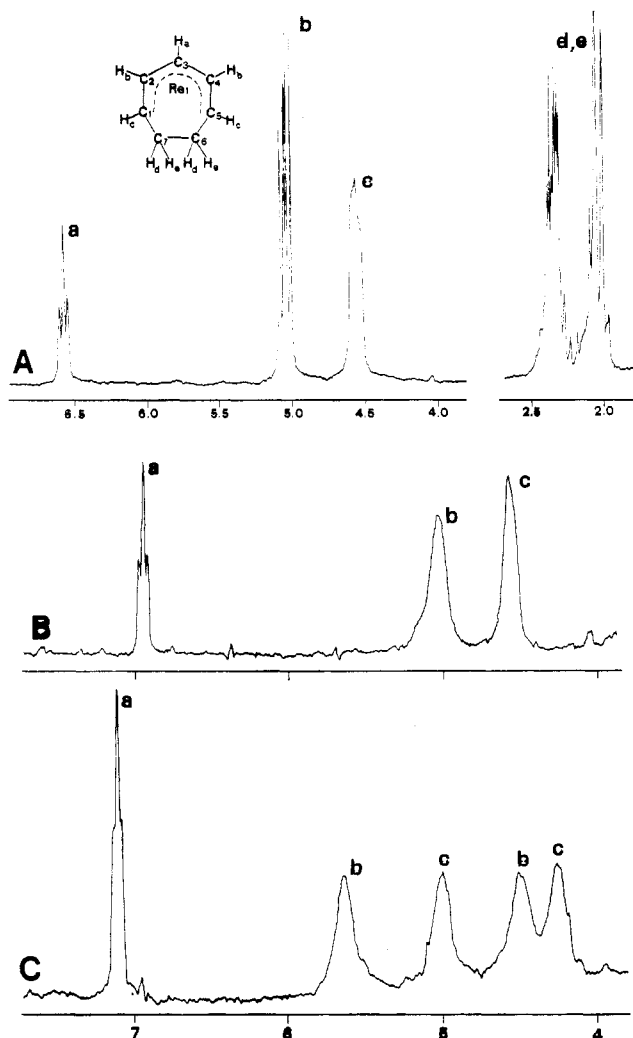


Figure 2. Variable-temperature ^1H NMR spectra of $\text{Re}_3(\mu_3\text{-H})(\mu_3\text{-H})(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$ in the low-field region, showing the signals due to the cycloheptadienyl ligand: (A) at 30°C , in CDCl_3 , with assignments confirmed by selective irradiation experiments, which showed also a long-range coupling between H_a and H_c ; (B) at -60°C , in $\text{C}_4\text{D}_8\text{O}$, with only the signals due to the hydrogens of type a, b, and c shown; (C) at -100°C , in $\text{C}_4\text{D}_8\text{O}$, same range as spectrum B, with assignments confirmed by selective irradiations, which showed (1) narrowing of the signal at δ 7.1 and disappearance of both signals at δ 5.6 and 4.5 upon irradiation at δ 5.6 and (2) disappearance of both signals at δ 5.0 and 4.25 upon irradiation at δ 5.0. These experiments indicate the persistence at -100°C of a fluxional behavior, slow on the NMR time scale.

parameters within the C_7H_9 moiety, as well as the Re1-C (dienyl) bonds (range 2.224 (10)–2.367 (11) Å), are as expected. The atoms from C1 to C5 are almost exactly coplanar (maximum out-of-plane displacement of 0.05 Å), while the two methylenic carbons show somewhat different displacements from the plane (0.83 Å for C6 and 1.13 Å for C7).

While many mononuclear cyclopentadienyl complexes of rhenium are known and a cycloheptadienyl species has also been isolated, namely $\text{Re}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)$,¹⁴ this is the first example of a rhenium cluster bearing a π -bonded unsaturated hydrocarbon moiety, representing therefore an entry into the organic chemistry of Re_3 cluster species.

The NMR analysis of the complex (Figures 2 and 3) indicates a fluxional behavior of the C_7H_9 group, involving also

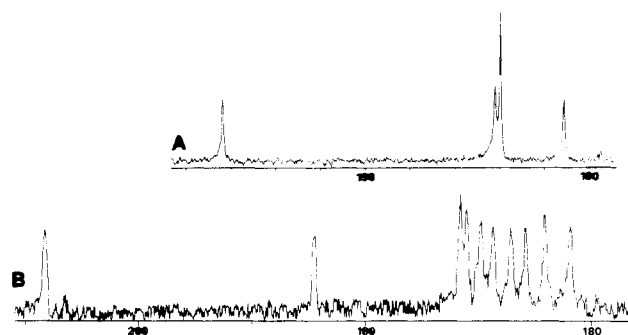


Figure 3. Variable-temperature ^{13}C NMR spectra of $\text{Re}_3(\mu_3\text{-H})(\mu_3\text{-H})(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$ in the carbonyl region: (A) at 30°C , in CDCl_3 ; (B) at -100°C , in $\text{CDCl}_3/\text{CH}_2\text{Cl}_2$.

a scrambling of the two CO groups bound to the same Re atom. At room temperature, both the ^1H and ^{13}C NMR spectra show for the cycloheptadienyl group an apparent C_3 symmetry, which does not agree with its solid-state conformation and its coordination mode on the cluster. This behavior and similar values of chemical shift are observed in many other complexes of the same ligand.^{13–17}

The ^{13}C NMR of the carbonyls provides a better insight into the dynamic process. The four signals shown by the spectrum at room temperature (apart from the possibility of the accidental overlap of two two-carbonyl resonances) can be rationalized by assuming nonfluxional behavior of the CO groups bound to Re2 and Re3 and an apparent C_{2v} symmetry for the whole complex. This requires a complete interchange of the coordination sites for the ligands bound to Re1 and also implies that, in a concerted way, the triple-bridging hydride moves up and down through the plane of the metallic triangle (computed out-of-plane displacement of $\text{Hy}2$ 0.53 Å, by the same side of the C_7H_9 ligand). This unusual mechanism seems the only reasonable explanation for the magnetic equivalence of four carbonyls (183.9 ppm, Figure 3A) that can be only the axial ones.

As the temperature is lowered, the spectrum changes. In $\text{CDCl}_3/\text{CH}_2\text{Cl}_2$, at ca. -70°C the lowest field signal appears collapsed and at ca. -85°C it gives rise to two signals whose large $\Delta\nu$ (ca. 600 Hz) suggests assignment to the carbonyls bound to Re1. At this temperature the other signals are almost collapsed, and at -100°C the overall spectrum (Figure 3B) displays a pattern of 10 resonances, consistent with the complete lack of symmetry observed in the solid-state structure. Analogously, the signals of hydrogens b and c of the C_7H_9 moiety (Figure 2), in $\text{C}_4\text{D}_8\text{O}$, collapse between -80 and -90°C , and at -100°C all the H atoms appear inequivalent (Figure 2C). A similar splitting was observed in $\text{Ru}_3(\text{C-O})_6(\text{C}_7\text{H}_7)(\text{C}_7\text{H}_9)$.¹³ Investigation is in progress in order to elucidate the reactivity of the coordinated dienyl.

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Registry No. 1- NEt_4 , 64478-51-9; 2, 88314-58-3; $(\text{C}_7\text{H}_7)\text{BF}_4$, 27081-10-3; $\text{Re}_3\text{H}_3(\text{CO})_{12}$, 12146-47-3; $\text{Re}_3\text{H}_3(\text{CO})_{10}(\text{NCMe})_2$, 87526-42-9.

Supplementary Material Available: Listings of structure factor moduli, thermal parameters, and computed hydrogen atom positions (21 pages). Ordering information is given on any current masthead page.

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