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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates, experimental details of

the X-ray study, bond distances and angles (involving non-hydrogen and hydrogen atoms), selected least-squares planes, and interatomic distances (21 pages); a table of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

Insertion of Isocyanides into Metal-Hydrogen Bonds in Triangular Hydrido-Carbonyl Clusters of Rhenium. X-ray Crystal Structures of $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNR})(\text{CO})_{10}]^-$ ($\text{R} = p\text{-Tolyl}$) and of $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CHNR})(\text{CO})_9]^-$ ($\text{R} = \text{Cyclohexyl}$)

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The reaction of the unsaturated triangular cluster anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ with isocyanides CNR ($\text{R} = \text{cyclohexyl}$ or $p\text{-tolyl}$) gives in high yields $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNR})(\text{CO})_{10}]^-$, containing a formimidoyl group originated by the transfer of a hydride ligand to the C atom of the isocyanide. Upon heating, this complex loses one CO ligand, giving with good selectivity $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CHNR})(\text{CO})_9]^-$, in a reaction that can be reversed only under high CO pressure (50 atm). The structures of these two formimidoyl species have been elucidated by single-crystal X-ray analyses of their NEt_4^+ salts: $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_4\text{Me})(\text{CO})_{10}]^-$ gives monoclinic crystals, space group $P2_1/c$, with $a = 16.755(5)$ Å, $b = 12.705(5)$ Å, $c = 16.816(4)$ Å, $\beta = 117.5(2)^\circ$, $Z = 4$, and $R = 0.030$; $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_9]^-$ gives monoclinic crystals, space group $P2_1/a$, with $a = 14.589(7)$ Å, $b = 12.965(8)$ Å, $c = 16.843(9)$ Å, $\beta = 93.99(4)^\circ$, $Z = 4$, and $R = 0.039$. Variable-temperature ^1H NMR experiments showed that the triple-bridging formimidoyl group undergoes two types of dynamic processes, causing partial or total equalization of the hydrides and consisting presumably in rotations of this ligand on the Re_3 face, through the interchange of its three coordination modes ($\sigma\text{-C}$, $\sigma\text{-N}$, π) among the vertices of the triangle. Insertion reactions were observed also upon treatment of the unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ with two-electron-donor molecules, as CO (50 atm) or $\text{CNC}_6\text{H}_{11}$ itself. In the latter case, two isomers of the complex $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ are formed, likely differing in the coordination of the $\text{CNC}_6\text{H}_{11}$ ligand (axial syn or anti with respect to the bridging formimidoyl). In all the insertion reactions here reported, the H transfer is supposed to take place in intermediate $[\text{Re}_3(\mu\text{-H})_3\text{H}(\text{CO})_9(\text{CNR})]^-$ adducts, too reactive to be observed. The differences with respect to the analogous reactions of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ are discussed.

Introduction

Isocyanide molecules insert into M-H bonds much more easily than the isoelectronic carbon monoxide,¹ in a reaction that represents the first step of their hydrogenation to amines. In mononuclear complexes, terminally coordinated formimidoyl groups -C(H)=NR are formed and the two valence electrons lost by the metallic center in the insertion are provided by extra ligands,² by the increase in donicity of a ligand,³ or by dimerization:⁴ in polynuclear complexes, in fact, the formimidoyl group itself can provide

more electrons, assuming a bridging coordination. In a basic study,⁵ Adams and Golembeski demonstrated that, in the triangular osmium cluster $[\text{Os}_3(\mu\text{-H})\text{H}(\text{CO})_{10}(\text{CNR})]$, a hydride can be transferred to the isocyanide in two different ways. Upon heating in nondonor solvents, an intramolecular insertion process gives a $\mu\text{-}\eta^2$ -coordinated formimidoyl ligand, while, in donor solvents, a $\mu\text{-}\eta^1$ -iminyl =C=N(H)R group is obtained.⁶ The last reaction is base catalyzed, and a mechanism involving a proton dissociation step was assumed.⁷ Upon further heating, the form-

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(6) The formation of a dinuclear μ -formimidoyl complex was also reported by treatment with Me_3N of an intermediate μ -aminocarbene, formed by reaction of MeNC with $[\text{Co}_2(\mu\text{-PPh}_2)_2(\mu\text{-H})\text{Cp}_2]^+$; Zolk, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 577.

(7) Recently, studies on kinetic isotope effects have demonstrated that, for the methyl isocyanide derivative, the conversion to the $\mu\text{-}\eta^1$ -iminyl group occurs also in dry benzene, through an intramolecular reaction path, with a significant tunneling component. Upon addition of base, the intermolecular mechanism via proton transfer becomes the faster one; Roseberg, E. *Polyhedron* 1989, 8, 383.

imidoyl assumes a $\mu_3\text{-}\eta^2$ -coordination on the face of the cluster, expelling a CO molecule. The same type of coordination was suggested in analogous complexes of iron⁸ and ruthenium,⁹ while $\mu\text{-}\eta^2$ -formimidoyls were obtained in the reactions of isocyanides with the unsaturated complexes $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]^{10}$ and $[\text{Y}_2(\mu\text{-H})_2(\text{THF})_2(\text{C}_6\text{H}_4\text{R})_2]^{11}$. These species, as well as the starting material of the reactions studied by Adams, $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ (1), contain a reactive, formally unsaturated $\text{M}(\mu\text{-H})_2\text{M}$ moiety. This unit is also present in the triangular rhenium cluster anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ (2),¹² which is isoelectronic (46 valence electrons, ves) with $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$. We have previously performed the stepwise reduction of a CO ligand of 2 to methanol,¹³ and we are therefore interested in attempting a similar process on an isocyanide molecule.

Different methods have been used to anchor bielelectron-donor molecules L on the hydridic cluster 2. (i) The treatment of 2 with strong acids in the presence of the L ligands gave neutral $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}\text{L}_2]$ species (48 ves; L = CO, RCN, PR_3 , py).¹⁴ In the case of isocyanides, this reaction was hampered by the reactivity of the ligand itself toward strong acids. (ii) The treatment of 2 with Me_3NO , in the presence of the L ligands, led to the substitution of a carbonyl by L, allowing the synthesis of $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ derivatives (46 ves; L = RCN, PR_3 , py).¹⁵ We have already reported¹⁶ the obtainment of $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ through this pathway and the PMe_2Ph -promoted insertion of the coordinated isocyanide into a Re-H bond, to give the formimidoyl derivative $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})]^-$. (iii) The direct reaction between 2 and molecules L (CO, RCN, PR_3) resulted in the substitution of two hydrides by two L ligands, leading to $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}\text{L}_2]^-$ derivatives (48 ves).¹⁷

In the case of isocyanides the last approach leads to different results, which are discussed in this paper. Some differences with respect to the reactivity with isocyanides of the related osmium complex 1 have been established. Other examples of insertion reactions in $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ are also presented.

Results and Discussion

Reaction of $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ with Isocyanides. Treatment of compound 2 with cyclohexyl isocyanide (room temperature, large excess of ligand to increase the reaction rate) results in a reaction different from what was expected (see Introduction). Instead of the substitution of two isocyanides for two hydrogen atoms, spectroscopic monitoring shows the quantitative transformation of 2 into

a complex characterized as the anion $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_{10}]^-$ (3a, 48 valence electrons). Three signals (intensity 1:1:1) are present in the hydridic region of the ¹H NMR spectrum, while a resonance at δ 10.5 (a region characteristic of formimidoyl ligands)^{2-11,16} revealed that the fourth hydride had been transferred to the carbon atom of the isocyanide. The formulation of the complex has been confirmed by a single-crystal X-ray analysis (see below) of compound 3b, containing *p*-tolyl isocyanide (prepared on purpose, 3a being difficult to isolate as a solid at room temperature).

Due to the unsaturation of 2, it is likely that the reaction goes through the formation of an adduct, of formula $[\text{Re}_3(\mu\text{-H})_3\text{H}(\text{CO})_{10}(\text{CNC}_6\text{H}_{11})]^-$, analogous to the complex formed in the reaction of 1 with isocyanides and structurally characterized, both in solution (variable-temperature NMR)¹⁸ and in solid (X-ray analysis).¹⁹ While the osmium adducts are stable and thermal activation is required to promote the insertion, in the case of rhenium we have been unable to obtain any evidence of this intermediate, even by monitoring the reaction progress at low temperature. This difference can be rationalized by considering the negative charge of 2, which makes more difficult the nucleophilic attack of the isocyanide on the anion and at the same time favors the intramolecular nucleophilic attack of the hydrides (more negatively polarized) on the carbon of the coordinated isocyanide. The adduct therefore reacts with a rate higher than that of its formation. An intermediate situation (i.e. adduct stable only at low temperatures) was observed^{10b} in the case of the reaction with (*t*-Bu)NC of $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$, which, due to the presence of the basic diphosphine, is expected to have a polarization of the hydrides intermediate between the neutral compound 1 and the anion 2.

The above considerations also allow the explanation of a second remarkable difference in the reactivity of the rhenium complex with respect to the osmium one. In the reaction of 2 with isocyanides, the H atom is transferred to the carbon atom of CNR, also in a polar solvent like tetrahydrofuran and even in the presence of added NEt_3 . The formation of an iminyl group, $=\text{C}=\text{N}(\text{H})\text{R}$, which is base catalyzed in the osmium system, was not observed here. Likely, the negative charge of the rhenium complex and the hydridic polarization of its H ligands disfavor the deprotonation step, involved, according to the authors,⁵ in the transfer of H to the nitrogen atom of the isocyanide.

Upon heating, 3a loses one carbonyl ligand and gives, with good selectivity, $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_9]^-$ (4), as confirmed by an X-ray single-crystal structural characterization (see below). Similar transformations of double-bridging (trielelectron-donor) ligands into triple-bridging (penta-electron-donor) ones, via CO elimination, are well-known in the chemistry of triangular clusters of rhenium²⁰ and osmium.²¹ In particular, this reaction was also observed⁵ for the formimidoyl complexes $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-CHNR})(\text{CO})_{10}]$ (R = C_6H_5 , CH_3) and was easily reversed by treatment with 1 atm (1 atm = 1.013×10^5 Pa) of carbon monoxide. In compound 4, however, the coordination of the formimidoyl on three metallic centers is particularly stable: after about 2 days, under 50 atm of CO, only 65% ca. of 4 was transformed into 3a. The reaction was performed at room temperature, because 3a

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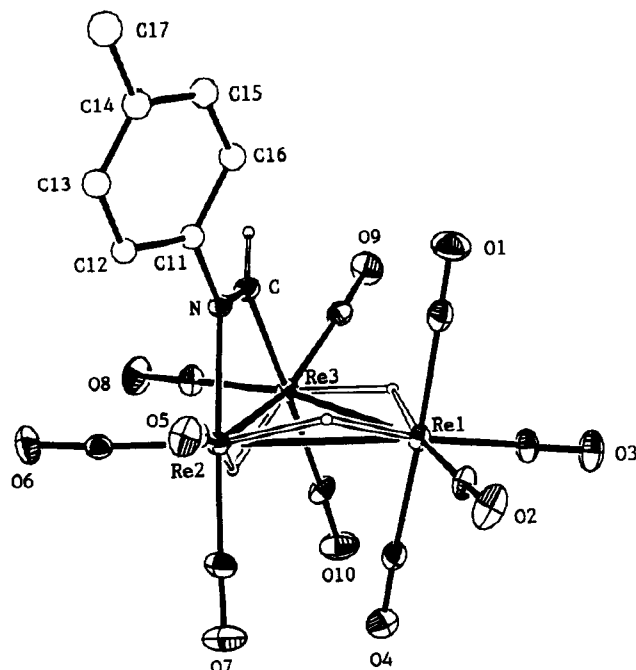


Figure 1. View of the anion $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_4\text{Me})\text{-(CO)}_{10}]^-$ (**3b**). The hydrogen atoms of the *p*-tolyl group have been omitted for clarity. The numbering of the carbonyl groups is indicated by the labels of their oxygen atoms.

transforms into **4** much easier than in the osmium case (2 h of reflux in *n*-butyl ether, bp 142 °C, for the Os complex but only 10 min in dioxane, bp 101 °C, for the Re compound). Slow formation of **4** was observed even at room temperature: for this reason the synthesis of **3a** is better performed at 10 °C.

We have also attempted to promote CO elimination from **3a** by using Me_3NO , instead of thermal activation. The reaction occurs but is exceedingly slow (less than 30% of conversion after 24 h, at room temperature in CD_2Cl_2). This is rather surprising, if we consider the easiness of the reaction of compound **2** with Me_3NO to give $[\text{Re}_3(\mu\text{-H})_4\text{-(CO)}_9\text{L}]^-$ derivatives.¹⁵

The ^1H NMR spectrum of **4** shows, at room temperature, only one hydridic resonance [δ -14.50 ppm, intensity three with respect to $-\text{C}(\text{H})\text{NR}$], instead of the three resonances expected from the solid-state structure. On lowering of the temperature, the hydridic signal collapses at 223 K, giving then rise to two resonances (intensity 1:2, 183 K) at δ -13.26 and -15.73 (whose barycenter is 0.4 ppm shifted with respect to -14.50 ppm, due to the high-field shift observed on lowering of the temperature). These data indicate that **4** in solution undergoes two types of dynamic processes, causing the equalization (partial at 183 K, complete at room temperature) of the hydrides. The slower process **a** consists presumably in the rotation of the formimidoyl ligand on the Re_3 face, through the interchange of its three coordination modes ($\sigma\text{-C}$, $\sigma\text{-N}$, π) among the three vertices of the cluster. For this process a $\Delta G^\ddagger_{223} = 41 \text{ kJ mol}^{-1}$ was estimated.²² The faster process **(b)**, still operative at 183 K, involves a 60° rotation of the ligand, the carbon atom remaining bound to its vertex and the nitrogen swinging between the other two vertices, creating a time-averaged plane of symmetry. Two dynamic processes analogous to **(a)** and **(b)** were observed for a $\mu_3\text{-}\eta^2\text{-C}_6\text{H}_4$ group coordinated on a Os_3 cluster.²³

Table I. Bond Distances (Å) and Angles (deg) within the Anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_4\text{Me})]^-$ (**3b**)

Distances			
Re1-Re2	3.237 (1)	C11-C12	1.40 (1)
Re1-Re3	3.235 (1)	C11-C16	1.40 (2)
Re2-Re3	3.160 (1)	C12-C13	1.38 (2)
Re2-N	2.178 (9)	C13-C14	1.37 (2)
Re3-C	2.151 (12)	C14-C15	1.37 (2)
N-C	1.300 (13)	C15-C16	1.38 (2)
Re1-C1	2.00 (2)	C14-C17	1.53 (2)
Re1-C2	1.95 (1)	C1-O1	1.13 (2)
Re1-C3	1.93 (1)	C2-O2	1.11 (1)
Re1-C4	1.99 (2)	C3-O3	1.14 (1)
Re2-C5	1.93 (1)	C4-O4	1.14 (1)
Re2-C6	1.92 (1)	C5-O5	1.15 (1)
Re2-C7	1.90 (1)	C6-O6	1.16 (1)
Re3-C8	1.91 (1)	C7-O7	1.16 (1)
Re3-C9	1.93 (1)	C8-O8	1.16 (1)
Re3-C10	1.97 (1)	C9-O9	1.15 (1)
N-C11	1.45 (1)	C10-O10	1.13 (1)
Angles			
Re2-Re1-C1	98.1 (4)	Re1-Re3-C8	164.5 (4)
Re2-Re1-C2	101.4 (3)	Re1-Re3-C9	107.8 (4)
Re2-Re1-C3	162.7 (4)	Re1-Re3-C10	90.3 (4)
Re2-Re1-C4	80.2 (3)	Re1-Re3-C	86.3 (3)
Re3-Re1-C1	94.1 (4)	Re2-Re3-C8	104.6 (4)
Re3-Re1-C2	159.4 (4)	Re2-Re3-C9	151.8 (4)
Re3-Re1-C3	106.8 (4)	Re2-Re3-C10	111.2 (4)
Re3-Re1-C4	81.8 (4)	Re2-Re3-C	83.6 (3)
C1-Re1-C2	93.1 (6)	C8-Re3-C9	87.6 (5)
C1-Re1-C3	91.6 (6)	C8-Re3-C10	90.7 (6)
C1-Re1-C4	175.8 (6)	C8-Re3-C	91.5 (5)
C2-Re1-C3	92.3 (5)	C9-Re3-C10	93.7 (5)
C2-Re1-C4	90.9 (6)	C9-Re3-C	91.3 (5)
C3-Re1-C4	89.1 (6)	C10-Re3-C	174.7 (5)
Re1-Re2-C5	107.7 (3)	Re1-C1-O1	179 (2)
Re1-Re2-C6	160.8 (4)	Re1-C2-O2	178 (1)
Re1-Re2-C7	91.3 (4)	Re1-C3-O3	177 (1)
Re1-Re2-N	86.3 (2)	Re1-C4-O4	178 (1)
Re3-Re2-C5	157.2 (4)	Re2-C5-O5	174 (1)
Re3-Re2-C6	100.8 (4)	Re2-C6-O6	176 (1)
Re3-Re2-C7	111.9 (4)	Re2-C7-O7	174 (1)
Re3-Re2-N	65.5 (2)	Re3-C8-O8	176 (1)
C5-Re2-C6	91.4 (5)	Re3-C9-O9	177 (1)
C5-Re2-C7	86.7 (6)	Re3-C10-O10	178 (1)
C5-Re2-N	95.6 (5)	Re2-N-C	112.1 (8)
C6-Re2-C7	91.1 (6)	Re2-N-C11	127.7 (7)
C6-Re2-N	90.6 (4)	Re2-C-N	118.8 (9)
C7-Re2-N	177.1 (4)	C-N-C11	120 (1)
Re1-Hy1-Re2 ^a	122.4	Re1-Hy2-Re3 ^a	122.3
Re2-Hy3-Re3 ^a	117.3		

^aHydrides in calculated positions.

The mobility of $\mu_3\text{-}\eta^2$ -formimidoyl ligands is probably a general feature, which could not be observed in the osmium analogue due to the lack of suitable spectroscopic probes (the three hydrides). In $[\text{Fe}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-CHNPr}^i)(\text{CO})_9]^{8b}$, the two methyl group of the Pr^i ligand allowed the recognition of a fluxionality quite similar to the above process **(b)**, involving not only the twisting of the $\text{CH}=\text{NPr}^i$ group but also the concurrent flipping of the bridging hydride ligand. This likely accounts for the significantly higher kinetic barrier in this iron system (52 kJ mol^{-1}).

Description of the Structures of the Anions **3b and **4**.** The structure of the anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_4\text{Me})]^-$ (**3b**), in its NET_4^+ salt, is illustrated in Figure 1, and bond distances and angles are reported in Table I. The anion contains an isosceles Re_3 triangle, with two long, hydrogen-bridged metal-metal edges [$\text{Re1-Re2} = 3.237$ (1) Å, $\text{Re1-Re3} = 3.235$ (1) Å] and a shorter one

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Table II. Main Structural Parameters Involving Double-Bridging Formimidoyl Ligands in Isocyanide Complexes (Distances in Å, Angles in deg)

compd	M-C	M-N	C-N	M-C-N	M-N-C
[Os ₃ H(CO) ₉ (μ ₃ -S)(μ-η ² -CHN-p-C ₆ H ₄ F)] ^a	2.051 (13)	2.205 (11)	1.213 (14)	136.1 (12)	118.5 (10)
[Co(μ-PMe ₂)(C ₆ H ₅) ₂ (μ-η ² -CHNMe)] ^{+b}	1.910 (14)	1.958 (12)	1.26 (2)	123.8 (13)	116.2 (11)
[Os ₃ H ₃ (CO) ₉ (μ-η ² -C ₆ H ₄)(μ-η ² -CHNC ₆ H ₅)] ^c	2.082 (14)	2.186 (9)	1.274 (14)	113.3 (8)	112.4 (7)
[Pt(μ-η ² -CHNBu ^t)(SiMePh ₂)(CNBu ^t) ₂] ^d	2.028 ^e	2.173 ^e	1.277 ^e	117.6 ^e	112.4 ^e
[Re ₃ (μ-H) ₃ (CO) ₉ (μ-η ² -CHNC ₆ H ₁₁)(PMe ₂ Ph)] ^{-f}	2.13 (2)	2.19 (2)	1.29 (3)	119 (2)	113 (2)
[Re ₃ (μ-H) ₃ (CO) ₁₀ (μ-η ² -CHNC ₆ H ₄ Me)] ^{-g}	2.151 (12)	2.178 (9)	1.300 (13)	118.8 (9)	112.1 (8)
[Os ₃ (μ-H)(CO) ₉ (μ-η ² -C(H)=NC ₆ H ₅)P(OMe) ₃] ^h	2.075 (9)	2.150 (6)	1.320 (10)	116.0 (6)	109.8 (6)

^a Adams, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* 1981, 103, 6510. ^b Reference 6. ^c Adams, R. D.; Golembeski, N. M. *J. Organomet. Chem.* 1979, 172, 239. ^d Reference 4. ^e Mean value. ^f Reference 15. ^g Compound 3b, this work. ^h Reference 5.

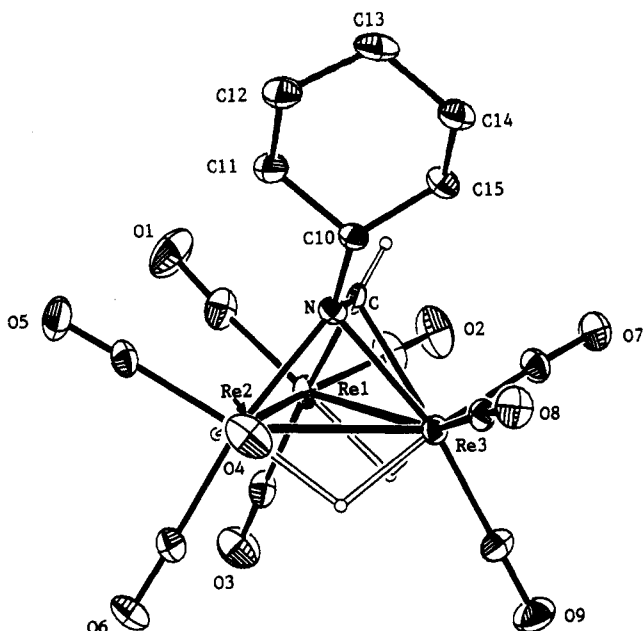


Figure 2. View of the anion [Re₃(μ-H)₃(μ₃-η²-CHNC₆H₁₁)(CO)₉]⁻ (4). The hydrogen atoms of the cyclohexyl group have been omitted for clarity. The numbering of the carbonyl groups has been indicated by the labels of their oxygen atoms.

[Re2-Re3 = 3.160 (1) Å], doubly bridged by the μ-η²-formimidoyl ligand and by the third hydride (the hydrides were located indirectly). The Re-Re bond lengths are similar to those of the recently reported [Re₃(μ-H)₃(CO)₉(μ-η²-CHNC₆H₁₁)(PMe₂Ph)]⁻ analogue [mean value of the two longer edges 3.255 Å, shorter edge 3.164 (1) Å].¹⁶

The formimidoyl group is σ-C bonded to Re3 and σ-N bonded to Re2; therefore, each Re atom attains a distorted octahedral coordination when also the Re-H interactions are included.

The bond parameters involving the μ-η²-CHNR ligand are compared in Table II with those of other related compounds structurally characterized. Common features are the slightly longer M-N vs M-C bond lengths and slightly larger M-C-N vs M-N-C angles. The C-N bond length in 3b, 1.300 (13) Å, falls inside the range of values (ca. 1.21-1.32 Å) found for these interactions, which can be formally considered CN double bonds.

The dihedral angle between the Re₃ plane and the Re2,Re3,N,C best plane has a value of 100.6°. This angle is increased to 106.1° in [Re₃(μ-H)₃(CO)₉(μ-η²-CHNC₆H₁₁)(PMe₂Ph)]⁻ due to the presence of the bulky phosphine bound to the third Re atom in axial direction, on the same side of the Re₃ triangle with respect to the formimidoyl ligand.

The Re-C(carbonyl) bond lengths are in the range 1.90(1)-2.00 (2) Å, the longer bonds being associated with the two mutually trans CO bound to Re1 (mean 1.99 Å vs 1.93 Å for the other ones).

Table III. Bond Distances (Å) and Angles (deg) within the Anion [Re₃(μ-H)₃(CO)₉(μ₃-η²-CHNC₆H₁₁)]⁻ (4)

Distances			
Re1-Re2	3.167 (1)	N-C10	1.52 (1)
Re1-Re3	2.978 (1)	C10-C11	1.53 (2)
Re2-Re3	2.947 (1)	C10-C15	1.50 (2)
Re1-C	2.118 (12)	C11-C12	1.53 (2)
Re2-N	2.170 (8)	C12-C13	1.48 (2)
Re3-C	2.353 (11)	C13-C14	1.49 (2)
Re3-N	2.312 (9)	C14-C15	1.49 (2)
C-N	1.286 (13)	C1-O1	1.16 (2)
Re1-C1	1.89 (2)	C2-O2	1.14 (2)
Re1-C2	1.89 (2)	C3-O3	1.16 (1)
Re1-C3	1.93 (1)	C4-O4	1.14 (1)
Re2-C4	1.90 (1)	C5-O5	1.13 (2)
Re2-C5	1.92 (1)	C6-O6	1.14 (1)
Re2-C6	1.92 (1)	C7-O7	1.12 (1)
Re3-C7	1.92 (1)	C8-O8	1.15 (1)
Re3-C8	1.90 (1)	C9-O9	1.15 (1)
Re3-C9	1.89 (1)		
Angles			
Re2-Re1-C1	102.7 (5)	Re2-Re3-C7	147.7 (4)
Re2-Re1-C2	153.7 (4)	Re2-Re3-C8	95.5 (3)
Re2-Re1-C3	108.5 (4)	Re2-Re3-C9	119.5 (4)
Re2-Re1-C	63.9 (3)	Re2-Re3-C	66.2 (3)
Re3-Re1-C1	143.9 (4)	Re2-Re3-N	46.8 (2)
Re3-Re1-C2	98.8 (5)	C7-Re3-C8	93.9 (5)
Re3-Re1-C3	121.0 (4)	C7-Re3-C9	91.2 (6)
Re3-Re1-C	51.7 (3)	C7-Re3-C	81.7 (5)
C1-Re1-C2	91.1 (7)	C7-Re3-N	103.0 (5)
C1-Re1-C3	92.9 (6)	C8-Re3-C9	90.2 (5)
C1-Re1-C	93.3 (5)	C8-Re3-C	112.4 (5)
C2-Re1-C3	92.8 (6)	C8-Re3-N	87.3 (4)
C2-Re1-C	93.5 (5)	C9-Re3-C	156.6 (5)
C3-Re1-C	171.2 (5)	C9-Re3-N	165.7 (5)
Re1-Re2-C4	156.8 (3)	C-Re3-N	32.0 (3)
Re1-Re2-C5	102.6 (4)	Re1-C1-O1	174 (1)
Re1-Re2-C6	107.6 (4)	Re1-C2-O2	176 (1)
Re1-Re2-N	64.0 (2)	Re1-C3-O3	178 (1)
Re3-Re2-C4	100.6 (4)	Re2-C4-O4	178 (1)
Re3-Re2-C5	147.7 (4)	Re2-C5-O5	179 (1)
Re3-Re2-C6	118.6 (4)	Re2-C6-O6	176 (1)
Re3-Re2-N	51.0 (3)	Re3-C7-O7	177 (1)
C4-Re2-C5	91.3 (5)	Re3-C8-O8	177 (1)
C4-Re2-C6	90.5 (5)	Re3-C9-O9	177 (1)
C4-Re2-N	95.9 (4)	Re1-C-Re3	83.4 (4)
C5-Re2-C6	90.9 (6)	Re1-C-N	118.2 (8)
C5-Re2-N	98.3 (5)	Re3-C-N	72.3 (6)
C6-Re2-N	168.7 (5)	Re2-N-Re3	82.2 (3)
Re1-Re3-C7	95.1 (4)	Re2-N-C	113.8 (7)
Re1-Re3-C8	153.6 (4)	Re3-N-C	75.7 (7)
Re1-Re3-C9	114.4 (4)	Re2-N-C10	124.0 (7)
Re1-Re3-C	44.9 (3)	Re3-N-C10	120.6 (7)
Re1-Re3-N	66.5 (2)	C-N-C10	121.0 (9)
Re1-Hy1-Re2 ^a	117.8	Re1-Hy2-Re3 ^a	107.2
Re2-Hy3-Re3 ^a	105.5		

^a Hydrides in calculated positions.

The structure of the anion [Re₃(μ-H)₃(CO)₉(μ₃-η²-CHNC₆H₁₁)]⁻ (4), in its NET₄⁺ salt, is shown in Figure 2; bond distances and angles are reported in Table III. The Re₃ triangle is again isosceles but exhibits two short edges,

Re1-Re3 = 2.978 (1) Å and Re2-Re3 = 2.947(1) Å, and one longer edge, Re1-Re2 = 3.167 (1) Å. All the metal-metal edges are supposed to be hydrogen-bridged (the hydrides have been located only indirectly). Each Re atom bears three terminal CO groups, and the formimidoyl group is σ -C bonded to Re1, σ -N bonded to Re2, and π -bonded to Re3. Taking into account also the Re-H interactions, the three metal atoms again display distorted octahedral environments.

The longer Re1-Re2 edge in 4 corresponds to the Re2-Re3 edge in 3b. This metal-metal bond is substantially unaffected by the π interaction of the formimidoyl ligand with the third metal atom, Re3. On the other hand, the other two Re-Re bonds show a conspicuous shortening (more than 0.2 Å), which is due to the different arrangement of the three assembled octahedral units centered at the metals, imposed by the μ_3 -coordination of the organic ligand. Comparable short Re(μ -H)Re bond lengths were observed in $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-O})(\text{CO})_9]^{2-}$ (mean 2.968 Å).²⁴

The interaction of the formimidoyl group with the triangular cluster is similar to that found for $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHNC}_6\text{H}_5)]$,⁵ the unique example, to our knowledge, of a $\mu_3\text{-}\eta^2$ -coordination for such a ligand previously characterized by X-ray analysis. The Re-C and Re-N σ -bond lengths and the related Re-C-N and Re-N-C angles compare well with those found in 3b. The π contacts, Re3-C = 2.353 (11) Å and Re3-N = 2.312 (9) Å, exhibit normal values. The C-N bond length, 1.286 (13) Å, is surprisingly shorter than expected. The value in fact is close to what expected for a double bond and is essentially the same as in 3b, while a lengthening should arise from its π interaction with Re3, as found in the case of $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHNC}_6\text{H}_5)]$, exhibiting a C-N bond length of 1.415 (11) Å, on line with a predictable trend of decreasing bond order with increasing metal-ligand interactions. There seems to be no chemical reason to justify our value. However the difference between the two values (ca. 0.13 Å) should not be overemphasized, considering their relatively high uncertainties and taking into account that also the C-N bonds in double-bridging formimidoyl species (see Table II) are scattered in a range of ca. 0.11 Å. Moreover, the values of the C-N interaction in two strictly related compounds containing triple-bridging acetimidoyl ligands, $[\text{Os}_3\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-HNCCF}_3)]$ ²⁵ and $[\text{Fe}_3\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-HNCCCH}_3)]$,²⁶ are 1.403 (23) and 1.344 (2) Å, respectively, and lie in between the values of the two bond lengths discussed above. It is worth noting that, as previously observed for $[\text{Fe}_3\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-HNCCCH}_3)]$,²⁶ the bond angles at the C and N atoms in 4 are close to the values expected for an sp^2 hybridization.

The nine Re-C(carbonyl) bond lengths are similar, in the range 1.89 (2)-1.93 (1) Å, with a mean value of 1.91 Å.

Insertion Reactions in $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$. We have recently reported¹⁶ that the unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ (46 valence electrons, compound 5), in spite of the presence of an isocyanide bound to a rhenium atom bearing also hydrides, is quite stable in solution and no insertion reaction was observed, also upon heating. This is particularly surprising, since the formimidoyl group formed in the insertion could coordinate μ_3 on the " $\text{Re}_3(\mu\text{-H})_3(\text{CO})_9$ " moiety, to give the stable compound 4.

The insertion reaction, however, occurred when 5 was treated with a bielelectron-donor molecule, like PMe_2Ph .¹⁶ The addition of 1 equiv of phosphine, at room temperature, caused the fast formation of two isomers 6a and 6b. A single-crystal X-ray analysis¹⁶ established for 6b the formula $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_9(\text{PMe}_2\text{Ph})]^-$, with the phosphine axially coordinated on the Re atom not bearing the bridging formimidoyl, syn with respect to this group. An axial anti location was suggested for 6a, on the basis of the NMR data and of the number of isomers observed.

Since compound 5 is an unsaturated species, as 1 and 2, the above reaction likely proceeds through an unstable adduct $[\text{Re}_3(\mu\text{-H})_3\text{H}(\text{CO})_9(\text{CNC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})]^-$, analogous to that postulated in the formation of 3a. In this case the isocyanide molecule is already coordinated on the cluster and this demonstrates the intramolecular nature of the insertion reaction.

This has been further confirmed by the transformation of 5 into 3a, by addition of carbon monoxide. In fact, according to the above mechanism, the addition of CO gives the same $[\text{Re}_3(\mu\text{-H})_3\text{H}(\text{CO})_{10}(\text{CNC}_6\text{H}_{11})]^-$ adduct formed by addition of $\text{CNC}_6\text{H}_{11}$ to 2. No reaction is observed, for a time of several days, by using 1 atm of CO ,¹⁶ but under 50 atm of CO , 3a forms slowly (in competition with the replacement of the isocyanide by CO , to give 2). Because 3a can be thermally decarbonylated to 4, the sequence of reactions $5 \rightarrow 3a \rightarrow 4$ demonstrates the kinetic nature of the barrier preventing the direct $5 \rightarrow 4$ transformation.

The insertion can be promoted also by the addition of cyclohexyl isocyanide itself, as a two-electron-donor species. The reaction is significantly slower than in the case of PMe_2Ph (12 h with a 10-fold excess of isocyanide), but also in this case two isomers, 7a and 7b, are formed, of formula $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$, containing a terminal isocyanide (as shown by the ν_{CN} band at 2183 cm^{-1} in the IR spectrum) and a bridging formimidoyl (resonances at δ 10.35 and 10.30, for the two isomers 7a and 7b, respectively). Differently from the phosphine derivatives 6,¹⁶ in this case the isomers 7a:7b ratio was notably constant (1:2.5) from the very beginning of the reaction. As to the structure of these isomers, we remark that isocyanide ligands are usually found in the electronically preferred axial location in triangular osmium clusters.^{21,27} Even the bulky CNBu^t ligand was axially coordinated in the adduct $[\text{Os}_3(\mu\text{-H})\text{H}(\text{CO})_{10}(\text{CNBu}^t)]$.⁵ Taking into account the more stringent steric requirements of the axial location in Os_3 clusters with respect to the rhenium analogues²⁸ (due to the longer M-M distances in the Re case, for the presence of bridging hydrides), it is reasonable to assume that the isocyanide ligands in both isomers 7a and 7b are in axial locations. The similarity of the pattern of the hydridic resonances²⁹ for the two couples a and b of isomers of 6 and 7 suggests similar structural features. The dominant isomer 7b should therefore have the syn

(27) Mays, M. J.; Gavens, P. D. *J. Chem. Soc., Dalton Trans.* 1980, 911.

(28) This is evidenced, for instance, by the axial coordination of PMe_2Ph observed in compound 6b,¹⁶ while phosphines in Os_3 clusters are always found in equatorial locations.²¹

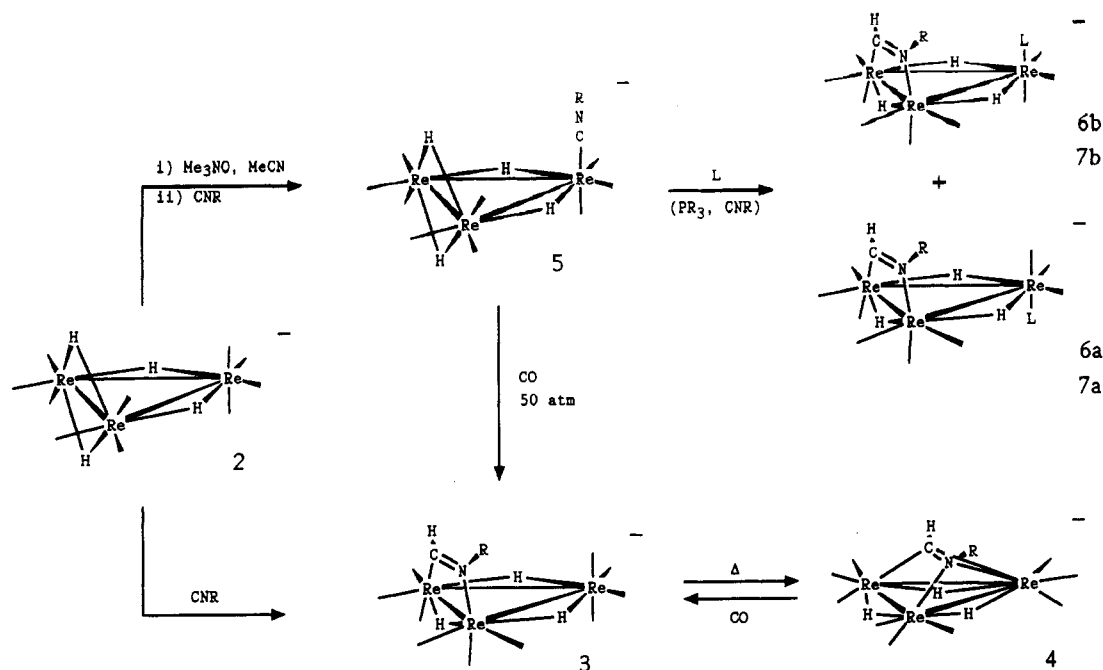
(29) Data from ref 16 are as follows. ¹H NMR resonances of the hydrides of 6a: δ -12.9 (s broad, unresolved H-H and H-P couplings with $J < 2$ Hz), -13.5 (d, $J_{\text{HP}} = 10$ Hz), -14.6 (d, $J_{\text{HP}} = 15$ Hz). ¹H NMR resonances of the hydrides of 6b: δ -12.1 (d, $J_{\text{HP}} = 18$ Hz), -13.1 (broad, unresolved H-H and H-P couplings with $J < 2$ Hz), -13.9 (d, $J_{\text{HP}} = 19$ Hz). The resonance due to the basal hydride is that at lowest field in the isomer 6a and at intermediate field in 6b: the same order is observed in the isomers 7a and 7b, according to the attribution discussed in the Experimental Section.

(24) Ciani, G.; Sironi, A.; Albano, V. G. *J. Chem. Soc., Dalton Trans.* 1977, 1667.

(25) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* 1981, 219, 103.

(26) Andrews, M. A.; van Buskirk, G.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* 1979, 101, 7245.

Scheme I



structure of **6b** and the constant **7a:7b** ratio could reflect the anti:syn ratio of the two isocyanides in the adduct $[\text{Re}_3(\mu\text{-H})_3\text{H}(\text{CO})_9(\text{CNC}_6\text{H}_{11})_2]^-$ formed in the rate-determining step.

Conclusions

Scheme I summarizes the reactions here presented. The results refer to the first step of the hydrogenation of the CN triple bond of isocyanides. For the first time, the insertion of isocyanides into M-H bond has been studied in anionic complexes. The comparison with the reactivity of the related cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ suggests a stronger hydridic nature of the H ligands in the rhenium anions, causing the lack of H transfer to the nitrogen atom of the isocyanide and an easier nucleophilic attack on the carbon atom. The formimidoyl group so formed adopts a bridging coordination on two or three metallic centers, the latter coordination being particularly stable, more than in the osmium system.

The presence of hydrides on each cluster edge of compound **4** has allowed us to recognize the existence of two dynamic processes, both involving rotations of the triple-bridging formimidoyl group about the Re₃ face. Such fluxionality is likely a general feature for $\mu_3\text{-}\eta^2$ -formimidoyls.

The stability of complex **5** demonstrates that the contemporary coordination on the same metallic center of the substrate isocyanide and of the potential reducing agent H does not suffice to cause the insertion. This is possibly related to the bridging coordination of all the H ligands in complex **5**, because, as already observed,⁵ H atoms bound to two metallic centers have a reduced tendency to engage in the insertion. In all the insertion reactions here reported, the H transfer is believed to occur in adducts, too reactive to be observed, of formula $[\text{Re}_3(\mu\text{-H})_3\text{H}(\text{CO})_9(\text{CNR})\text{L}]^-$ (L = CO, CNR, PMe₂Ph), containing one terminally bound hydride. In the osmium adducts $[\text{Os}_3(\mu\text{-H})\text{H}(\text{CO})_9\text{L}]$, bridging and terminal hydrides are rapidly exchanging (at room temperature) through a $\text{Os}(\mu\text{-H})_2\text{Os}$ intermediate.¹⁸ This mechanism, if operating also in the rhenium case, would make heptacoordinate the metal

center bearing the isocyanide (three H, three CO, one CNR). This anomalous coordination could be the driving force of the insertion, overcoming the barrier to insertion due to the bridging coordination of the hydride ligand candidate.

Experimental Section

The reactions were performed under N₂, in solvents deoxygenated and dried by standard methods. The IR spectra were recorded in 0.1-mm CaF₂ cells on a Perkin-Elmer 781 grating spectrophotometer, equipped with a data station using PE780 software. The NMR spectra were performed on Bruker WP80 and AC200 spectrometers. $[\text{NET}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]$ and $[\text{NET}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{C}_6\text{H}_{11}\text{CN})]$ were prepared as previously described.^{9,16} C₆H₁₁CN (Merck-Schuchardt) was used as received.

Synthesis of $[\text{Net}_4][\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNR})(\text{CO})_{10}]$. (a) **R** = C₆H₁₁. A 50-mg (0.0515-mmol) sample of $[\text{NET}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]$, dissolved in 5 mL of THF, was treated in an ice bath with 500 μL (4.1 mmol, 80 equiv) of CNC₆H₁₁. After 24 h at 10 °C, the volume was reduced and *n*-heptane was added, giving a pale yellow oily precipitate (about 40 mg, 0.037 mmol, 72% yield). Even by repeated dissolutions in CH₂Cl₂ and precipitations with *n*-heptane it was impossible to reduce the product to a powder: no elemental analysis could therefore be performed. The relative intensities of the hydridic and cationic resonances in the ¹H NMR spectra indicated a purity higher than 80%, and the product was used as such in the subsequent reactions. No significant change was observed on performing the reaction in the presence of NET₃ (20 equiv). IR (ν_{CO} , THF): 2091 w, 2015 m, 1994 vs, 1938 m, 1909 s, 1893 ms cm⁻¹. ¹H NMR of the anion **3a** (CD₂Cl₂): δ 10.33 (d, *J* = 2 Hz, 1, CHNR), 2.1 (s br, 1, NCH), 1.6–1.2 (m, 10, CH₂), -12.95 (s, 1, ReH), -13.36 (s, 1, ReH), -15.44 (s, 1, ReH). The resonances of the cyclohexyl group extensively overlap with that of the cationic methyl group. Irradiation experiments showed that the lower field hydridic resonance ($\Delta\nu_{1/2}$ 4.5 Hz) is coupled with the formimidoylic hydrogen. We can attribute this resonance to the basal hydride (i.e., that bridging the Re-Re interaction bridged by the formimidoyl), by comparison with what observed for compounds **6a** and **6b**, where the values of *J*_{HP} allowed us to unambiguously identify the resonance of the basal hydride as that broadened by an unresolved coupling with the formimidoylic hydrogen.

(b) **R** = *p*-C₆H₄CH₃. The reaction was performed as above, giving a pale yellow microcrystalline precipitate. Mp: 145 °C dec. IR (ν_{CO} , THF): 2090 w, 2020 m, 1990 vs, 1940 m, 1915 s,

Table IV. Crystal Data for $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11}\text{Me})]$ ($[\text{NEt}_4]3\text{b}$) and $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})]$ ($[\text{NEt}_4]4$)

	$[\text{NEt}_4]3\text{b}$	$[\text{NEt}_4]4$
formula	$\text{C}_{26}\text{H}_{31}\text{N}_2\text{O}_{10}\text{Re}_3$	$\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_9\text{Re}_3$
fw	1094.14	1054.15
cryst sys	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14 nonstandard)
<i>a</i> , Å	16.755 (5)	14.589 (7)
<i>b</i> , Å	12.705 (5)	12.965 (8)
<i>c</i> , Å	16.816 (4)	16.843 (9)
β , deg	117.5 (2)	93.99 (4)
<i>V</i> , Å ³	3185.2	3178.1
<i>Z</i>	4	4
ρ (calc), g cm ⁻³	2.273	2.203
<i>F</i> (000)	2024	1960
radn (graphite monochr)	Mo K α	Mo K α
λ , Å	0.71073	0.71073
μ (Mo K α), cm ⁻¹	115.8	116.0
2θ range, deg	3–50	3–50
scan method	ω	ω
scan interval, deg	$0.9 + 0.35 \tan \theta$	$1.0 + 0.35 \tan \theta$
scan speed, deg min ⁻¹	2–20	2–20
collected octants	$\pm h, k, l$	$\pm h, k, l$
no. of data collected (at room temp)	5767	5843
no. of data used ($I > 3\sigma(I)$)	2937	3430
no. of variable params	290	312
cryst decay, %	8	18
no. of azimuth reflns for abs corr	3	3
max–min trans factors	0.43–1.00	0.31–1.00
cryst size, mm	$0.05 \times 0.15 \times 0.23$	$0.05 \times 0.20 \times 0.30$
weighting fudge <i>p</i> factor	0.040	0.050
ESD ^a	1.086	1.504
<i>R</i> ^b	0.030	0.039
<i>R</i> _w ^c	0.033	0.051

^aESD = $(\sum w(|F_o| - k|F_c|)^2 / (N_{\text{obs}} - N_{\text{var}}))^{1/2}$; $w = 4|F_o|^2 / \sigma^2(|F_o|)^2$, where $\sigma(|F_o|)^2 = (\sigma^2(I) + (pI)^2)^{1/2} / LP$. ^b $R = \sum ||F_o| - k|F_c|| / \sum |F_o|$. ^c $R_w = (\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|)^{1/2}$.

1900 ms cm⁻¹. ¹H NMR of the anion **3b** (CD_2Cl_2): δ 10.69 (d, $J = 2$ Hz, 1, CHNR), 6.8–7.2 (m, 4, C_6H_4), 2.25 (s, 3, CH_3), –12.74 (1, ReH), –13.07 (1, ReH), –15.38 (1, ReH) (all the hydridic resonances are unresolved multiplets with $J_{\text{HH}} < 2$ Hz).

Synthesis of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_9]$. (a) A sample of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_{10}]$, obtained as above from 0.04 mmol of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}]$, was refluxed in THF for 3 h (with dioxane, the reaction time was only 10 min). The solution was concentrated under vacuum, and addition of ethanol/*n*-hexane gave a white microcrystalline precipitate (about 20 mg, 0.019 mmol, yield ca. 50% based on the starting compound 2). Mp: 151 °C dec. IR (ν_{CO} , THF): 2042 w, 2006 s, 1995 s, 1938 sh, 1917 s, 1890 sh cm⁻¹. ¹H NMR of the anion 4 (CD_2Cl_2 , room temperature): δ 10.18 (s, 1, CHNR), 2.1 (s br, 1, NCH), 1.6–1.2 (m, 10, CH_2), –14.47 (s, 3, ReH). NMR ($\text{CD}_2\text{Cl}_2/\text{CDCl}_3$ (2:1), 183 K, 200 MHz): 9.85 (s, 1), –13.26 (s, 1), –15.73 (s, 2). The resonances of the cyclohexyl group extensively overlap with that of the cationic methyl group. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{O}_9\text{N}_2\text{Re}_3$: C, 27.32; H, 3.32; N, 2.66. Found: C, 27.5; H, 3.5; N, 2.4.

(b) A sample of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_{10}]$, obtained as above from 0.01 mmol of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}]$, dissolved in an NMR tube in CD_2Cl_2 , was treated with ca. 1 mg (0.013 mmol) of anhydrous Me_3NO . Spectra taken at different times showed the slow formation of 4.

Reaction of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})(\text{CO})_9]$ with CO. (a) A solution of 4 in THF was saturated with CO and kept under CO atmosphere for 6 days, without spectroscopic evidences of the formation of 3a. (b) A solution of 4 in acetone-*d*₆ in a NMR tube was kept under 50 atm of CO for 40 h, giving a mixture of 3a (65%) and unreacted 4 (35%).

Reactions of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\text{CNC}_6\text{H}_{11})]$ with Two-Electron-Donor Molecules. (a) **Reaction with CO.** A sample of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\text{CNC}_6\text{H}_{11})]$ (21 mg, 0.02 mmol) dissolved in acetone-*d*₆ in a NMR tube was kept in an autoclave at room temperature under 50 atm of CO for 48 h. ¹H NMR spectra showed the presence mainly of compounds 3a, 2, and unreacted 5, about equimolar.

Table V. Final Atomic Coordinates for $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CHNC}_6\text{H}_4\text{Me})]$ ($[\text{NEt}_4]3\text{b}$)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Re1	0.39937 (3)	–0.12965 (4)	0.19205 (3)
Re2	0.18413 (3)	–0.16156 (4)	0.10166 (3)
Re3	0.30773 (3)	–0.35612 (4)	0.11677 (3)
O1	0.4146 (6)	–0.073 (1)	0.0184 (6)
O2	0.4169 (6)	0.1002 (7)	0.2517 (7)
O3	0.6027 (5)	–0.1629 (7)	0.2971 (7)
O4	0.3818 (6)	–0.2025 (9)	0.3615 (6)
O5	0.0965 (5)	0.0561 (7)	0.0456 (7)
O6	0.0011 (5)	–0.2728 (8)	0.0260 (6)
O7	0.1821 (6)	–0.1045 (9)	0.2778 (6)
O8	0.1827 (6)	–0.5480 (8)	0.0543 (7)
O9	0.4281 (5)	–0.4825 (7)	0.0576 (6)
O10	0.3949 (6)	–0.4495 (8)	0.3087 (6)
C1	0.4093 (7)	–0.093 (1)	0.0813 (9)
C2	0.4113 (7)	0.0162 (9)	0.2315 (9)
C3	0.5269 (7)	–0.153 (1)	0.2576 (9)
C4	0.3866 (7)	–0.177 (1)	0.2985 (8)
C5	0.1291 (6)	–0.026 (1)	0.0624 (8)
C6	0.0689 (7)	–0.229 (1)	0.0561 (7)
C7	0.1830 (7)	–0.132 (1)	0.2122 (8)
C8	0.2273 (7)	–0.4732 (9)	0.0758 (9)
C9	0.3852 (7)	–0.4330 (9)	0.0810 (8)
C10	0.3646 (7)	–0.414 (1)	0.2392 (8)
C	0.2414 (7)	–0.2813 (9)	–0.0119 (7)
N	0.1920 (5)	–0.1989 (7)	–0.0210 (5)
C11	0.1473 (6)	–0.1462 (9)	–0.1064 (7)
C12	0.0628 (7)	–0.1006 (9)	–0.1324 (8)
C13	0.0203 (7)	–0.049 (1)	–0.2137 (8)
C14	0.0593 (7)	–0.037 (1)	–0.2695 (9)
C15	0.1418 (7)	–0.081 (1)	–0.2432 (8)
C16	0.1871 (7)	–0.134 (1)	–0.1633 (8)
C17	0.0107 (9)	0.020 (1)	–0.359 (1)
NT	0.7542 (6)	–0.2399 (9)	0.1234 (7)
CT1	0.7694 (8)	–0.199 (1)	0.215 (1)
CT2	0.8411 (9)	–0.289 (1)	0.130 (1)
CT3	0.737 (1)	–0.141 (1)	0.065 (1)
CT4	0.684 (1)	–0.319 (1)	0.091 (1)
CT5	0.797 (1)	–0.276 (1)	0.287 (1)
CT6	0.924 (1)	–0.226 (1)	0.172 (1)
CT7	0.721 (1)	–0.164 (2)	–0.028 (1)
CT8	0.592 (1)	–0.276 (2)	0.067 (1)
Hy1 ^a	0.2840	–0.0831	0.1205
Hy2 ^a	0.4038	–0.2648	0.1539
Hy3 ^a	0.2320	–0.2899	0.1536

^aCalculated positions.

(b) **Reaction with $\text{CNC}_6\text{H}_{11}$.** A sample of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\text{CNC}_6\text{H}_{11})]$ (0.02 mmol) dissolved in CD_2Cl_2 in a NMR tube was treated with 28 μL (0.23 mmol) of $\text{CNC}_6\text{H}_{11}$. The progress of the reaction (295 K) was monitored by ¹H NMR spectroscopy, showing the disappearance of 5 in ca. 12 h and the formation of a couple of species 7a and 7b (average ratio, on 13 spectra: 2.59 ± 0.03), each characterized by four resonances of equal intensity: 7a, δ 10.35 (d, $J_{\text{HH}} = 2$ Hz), –12.79 (d, $J_{\text{HH}} = 2$ Hz), –13.23 (s), –15.49 (s); 7b, δ 10.30 (d, $J_{\text{HH}} = 2$ Hz), –12.54 (s, 1), –13.00 (d, $J_{\text{HH}} = 2$ Hz), –14.96 (s). For both isomers, the resonances of CH of the cyclohexyl groups were at δ 3.8 for the terminal isocyanides and δ 2.6 for the bridging formimidoyls. The other resonances of the cyclohexyl groups (δ 1.6–1.2) extensively overlapped with that of the cationic methyl group. As above discussed for compound 3, in both isomers the resonance coupled with the low-field signal is attributable to the basal hydride.

X-ray Analysis of 3b and 4. Intensity Measurements. Crystal data are reported in Table IV. The crystal samples were mounted on glass fibers in the air. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromatized Mo K α radiation. The setting angles of 25 random intense reflections ($16^\circ < 2\theta < 25^\circ$) were used in both cases to determine by least-squares fit accurate cell constants and orientation matrices. The collections were performed by the ω -scan method, within the limits $6^\circ < 2\theta < 50^\circ$. A variable scan speed and a variable scan range were used, with a 25% extension at each end of the scan range for background determination. Three standard intense reflections, monitored

Table VI. Final Atomic Coordinates for
 $[\text{NEt}_4][\text{Re}_2(\mu\text{-H})_2(\text{CO})_8(\mu_2\text{-}\eta^2\text{-CHNC}_6\text{H}_{11})] ([\text{NEt}_4]4)$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Re1	0.20873 (4)	-0.15027 (4)	0.25373 (4)
Re2	0.18849 (3)	0.08918 (4)	0.28535 (3)
Re3	0.09945 (4)	-0.01098 (4)	0.14303 (3)
O1	0.214 (1)	-0.236 (1)	0.4223 (8)
O2	0.149 (1)	-0.3586 (9)	0.1867 (9)
O3	0.4123 (8)	-0.196 (1)	0.2275 (9)
O4	0.1008 (7)	0.3015 (8)	0.2734 (8)
O5	0.2104 (9)	0.102 (1)	0.4665 (7)
O6	0.3792 (6)	0.1828 (9)	0.2755 (7)
O7	-0.0281 (8)	-0.1771 (9)	0.0726 (7)
O8	-0.0382 (7)	0.1611 (8)	0.1014 (7)
O9	0.1812 (8)	0.014 (1)	-0.0167 (7)
C1	0.217 (1)	-0.206 (1)	0.358 (1)
C2	0.169 (1)	-0.278 (1)	0.210 (1)
C3	0.336 (1)	-0.180 (1)	0.2385 (9)
C4	0.1323 (8)	0.221 (1)	0.2786 (8)
C5	0.202 (1)	0.097 (1)	0.3992 (9)
C6	0.307 (1)	0.151 (1)	0.278 (1)
C7	0.019 (1)	-0.117 (1)	0.100 (1)
C8	0.0138 (9)	0.097 (1)	0.1189 (8)
C9	0.149 (1)	0.008 (1)	0.0432 (9)
N	0.0615 (7)	0.0017 (8)	0.2737 (7)
C	0.0731 (9)	-0.095 (1)	0.2629 (7)
C10	-0.0311 (8)	0.044 (1)	0.2933 (8)
C11	-0.034 (1)	0.043 (1)	0.3839 (9)
C12	-0.122 (1)	0.094 (1)	0.409 (1)
C13	-0.205 (1)	0.052 (2)	0.364 (1)
C14	-0.199 (1)	0.047 (1)	0.277 (1)
C15	-0.1147 (9)	-0.008 (1)	0.255 (1)
NT1	0.500	0.000	0.500
CT1A	0.537 (3)	-0.005 (3)	0.594 (3)
CT1B	0.424 (3)	0.036 (3)	0.545 (2)
CT2	0.463 (2)	0.035 (2)	0.646 (1)
CT3A	0.590 (3)	0.070 (3)	0.513 (2)
CT3B	0.468 (3)	0.107 (3)	0.477 (2)
CT4	0.557 (2)	0.187 (2)	0.498 (2)
NT2	0.500	0.000	0.000
CT5A	0.588 (3)	0.038 (3)	0.059 (3)
CT5B	0.535 (4)	0.101 (4)	-0.015 (3)
CT6	0.373 (2)	-0.131 (2)	-0.054 (2)
CT7A	0.477 (3)	-0.032 (3)	0.088 (2)
CT7B	0.419 (3)	0.094 (3)	0.011 (2)
CT8	0.401 (2)	0.061 (2)	0.109 (2)
Hy1 ^a	0.2572	-0.0303	0.2987
Hy2 ^a	0.2019	-0.0958	0.1522
Hy3 ^a	0.1875	0.0860	0.1755

^a Calculated positions.

every 2 h, showed some crystal decay, of ca. 8% (3b) and 18% (4) at the end of the collections. The intensities were corrected for Lorentz, polarization, and decay effects. An empirical absorption correction was applied to the data, on the basis of ψ -scans

(ψ 0–360° every 10°) of suitable reflections with χ values close to 90°. Two sets of 2937 (3b) and 3430 (4) significant [$I > 3\sigma(I)$] independent reflections were used in the structure solutions and refinements.

Structure Solution and Refinements. All computations were performed on a PDP 11/73 computer, using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.

Both structures were solved by Patterson and Fourier methods, which revealed the locations of all the non-hydrogen atoms.

The tetraethylammonium cations in 4 were found to be disordered, lying on two classes of inversion centers and exhibiting, as usual, the NC_4 tetrahedra doubled to give approximate cubes with vertices of half-carbon atoms.

The refinements were carried out by full-matrix least squares. Anisotropic thermal parameters were assigned to all atoms except those of the *p*-tolyl (3b) and those of the cationic atoms.

The hydrogen atoms of the formimidoyl ligands in both structures and the cationic hydrogens in 3b were located in ideal positions ($\text{C-H} = 0.95 \text{ \AA}$, with $B = 5.0 \text{ \AA}^2$ in 3b and 6.0 \AA^2 in 4) after each cycle of refinement, and their contribution to the structure factors was kept into account.

In both structures the final difference-Fourier maps showed only some residual peaks, not exceeding ca. 1 e \AA^{-3} , close to the metal atoms. Though some peaks could be ascribed to the bridging hydride ligands, we decided to locate these atoms using the Orpen energy-minimization program,³⁰ with a mean Re-H bond length of 1.85 \AA . They were included in the structure factors calculations ($B = 5.0 \text{ \AA}^2$ in 3b and 6.0 \AA^2 in 4) but not refined.

Weights were assigned according to the formula $w = 4F_o^2 / \sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2} / Lp$ (I and Lp being the integrated intensity and the Lorentz-polarization correction, respectively); p was optimized to 0.040 (3b) and to 0.050 (4). The final values of the conventional agreement indices are reported in Table IV. The final positional parameters are given in Tables V (3b) and VI (4).

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Supplementary Material Available: Complete lists of bond lengths and angles and tables of the calculated coordinates of the hydrogen atoms and of anisotropic and isotropic thermal factors (4 pages); listings of observed and calculated structure factor moduli (44 pages). Ordering information is given on any current masthead page.