Organometallics **1993,** *12,* 4863–4870

Ortho-Metalated Pyridine Derivatives of the Unsaturated Anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$. Syntheses and X-ray Crystal Structures of the Tetraethylammonium Salts of the Anions $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ and $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)]^-$

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Received July 14, 1993[⊗]

The unsaturated cluster anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**1**) reacts overnight in pyridine solution, at room temperature, giving the μ-pyridyl derivative $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ (**2**). The ortho-metalation proceeds with H_2 evolution, which derives from the elimination of two hydrides of the parent cluster, as shown on performing the reaction with NC_5D_5. When the above reaction, in pyridine solution, is accomplished at 85 °C, within 2 h another product is obtained, namely $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)]^-$ (**3**), containing the μ-pyridyl ligand and a pyridine molecule replacing a carbonyl ligand. On the contrary, in tetrahydrofuran solution, in the presence of only a moderate excess of pyridine (~5 equiv), the reaction at 85 °C gives the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_9(NC_5H_5)]^-$ (**4**), previously known. This species has been proven to be unable to further react with pyridine, and therefore the formation of **3** from compound **1** occurs *via* intermediate **2** and not **4**. Both complexes **2** and **3**, as their NEt_4^+ salts, have been investigated by X-ray analysis. Complex **2** gives orthorhombic crystals, space group *Pbca* (No. 61), with $a = 13.297\ (4)$ Å, $b = 18.343(7)$ Å, $c = 24.432(12)$ Å, and $Z = 8$; the structure was refined to $R = 0.028$ for 1829 significant observed reflections. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ (No. 14), with $a = 13.363(1)$ Å, $b = 13.143(1)$ Å, $c = 18.955(3)$ Å, $\beta = 100.09(1)°$, and $Z = 4$; the refinements, based on 3924 significant observed data, gave a final R value of 0.027. Both the anions contain an isosceles triangle of metal atoms, with the two longer edges bridged by a hydrido ligand and the shorter one by a hydride and a μ-pyridyl ligand. In **3** an axial carbonyl of the $Re(CO)_4$ unit of **2** has been substituted by a pyridine molecule whose aromatic ring faces that of the pyridyl group. ^1H NMR analysis of **2** in solution at different temperatures reveals a fluxional behavior, leading to the exchange of the two hydrides bridging the longer triangular edges ($E_a = 72 \pm 1$ kJ/mol).

Introduction

A number of ortho-metalated derivatives of pyridine, substituted pyridines, and related molecules within various polynuclear metal systems have been reported.[1] This type of C–H oxidative addition reaction has been more extensively investigated with trinuclear osmium and ruthenium carbonyl clusters but has also been reported for larger cluster species.[1c] The direct reactions of $[M_3(CO)_{12}]$ (M = Ru, Os) with pyridines require pyrolytic conditions and lead to mixtures of ortho-metalated products, with hydrogen transfer to the metallic framework.[2,3] In the case of osmium,[1a,2] carbonyl substitution is believed to occur in a first stage, leading to the intermediate (not directly observed) $[Os_3(CO)_{11}(NC_5H_5)]$, which then eliminates CO, giving $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]$. The thermal reaction of $[Re_2(CO)_8(NC_5H_5)_2]$ also leads to the μ-pyridyl derivative $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_8]$.[4]

The alternative use of activated or unsaturated clusters allows one to avoid the relatively high temperatures necessary to generate reactive species from saturated metal clusters. In fact, ortho-metalated derivatives have been easily obtained[1a] from species like $[Os_3(CO)_{10}L_2]$, containing labile L ligands as acetonitrile or olefins. However, no pyridine ortho-metalation product has been described, to our knowledge, on starting from the unsaturated hydrido carbonyl cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[5] The reaction with 2-ethenylpyridine[6] proceeds with C–H cleavage and metalation at the ethenyl function rather than at the heterocyclic ring, leading to a product, $[Os_3H(\mu\text{-}\eta^3\text{-}NC_5H_4\text{-}$

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1993.

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$CH{=}CH)(CO)_{10}]$, which contains an open Os–Os–Os trimetal array.

We are currently studying the reactivity of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (1),[7] isoelectronic with and structurally similar to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, and we have now found that it reacts in pyridine solution at room temperature, giving, instead of the expected addition product, an ortho-metalated derivative. When the temperature is raised, another ortho-metalated product is obtained. This reactivity is described here, together with the complete results of the single-crystal X-ray investigations of the two new compounds.

Results and Discussion

The unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (1, 46 valence electrons), as its tetraethylammonium salt, dissolved in pyridine under N_2 atmosphere and left at room temperature for one night, gives quantitatively a complex characterized as the saturated ortho-metalated derivative $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ (2). Gas chromatographic analysis has revealed H_2 evolution during the reaction process. The tetraethylammonium salt of 2 was recovered as a pale yellow powder upon precipitation with *n*-heptane from the pyridine solution.

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + NC_5H_5 \rightarrow [Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^- + H_2 \quad (1)$$

The ^1H NMR spectrum of 2 shows three signals (intensity 1:1:1, δ −12.26, −13.45, and −15.05 in acetone-d_6) in the hydridic region and four resonances, each of intensity 1, in the region of the pyridinic hydrogens, in agreement with the presence of a μ-pyridyl ligand. The formulation of 2 has been confirmed by a single-crystal X-ray determination (see below).

The three hydridic resonances have been assigned on the following grounds: (i) in all the related clusters of formula $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ (X = halide,[8] OR,[9] OPh,[10] etc.), the hydridic signal of intensity 2 always lies at higher field than that of intensity 1, which is due to the hydride bridging the same Re–Re interaction as the ligand X^-; (ii) in polynuclear rhenium compounds, an N-donor ligand causes a significant low-field shift of the resonances of the μ-H ligands bound to the same Re atom.[11] We can therefore assign the resonance at lower field (δ −12.26) to the hydride on the same edge bridged by the μ-pyridyl group (H23), the intermediate resonance (δ −13.45) to the hydride on the edge with the N-bonded rhenium atom (H13), and the higher field resonance (δ −15.05) to the remaining hydride (H12).

The decrease in the time of the integrated intensities of the hydridic resonances of complex 1 shows that the ortho-metalation proceeds cleanly to form 2, at 21 °C, with a pseudo-first-order rate constant of $(1.25 \pm 0.05) \times 10^{-4}\ s^{-1}$, corresponding to a $t_{1/2}$ of *ca.* 90 min. No addition product is obtained under these conditions; neither is one revealed as an intermediate species by NMR monitoring of the reaction in pyridine-d_5. The reaction of 1 with pyridine at room temperature also differs from those observed with other two-electron-donor ligands L, like CO (high pressure) or PR_3 (large excess);[12] see below for a discussion of this point.

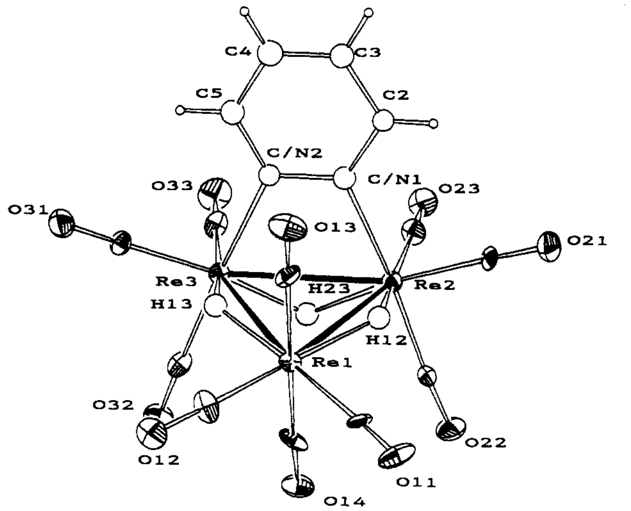

Figure 1. ORTEP drawing of $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ (2). For clarity the numbering of the carbonyl groups is indicated only by the labels of their oxygen atoms.

When the reaction of 1 in pyridine is performed at higher temperature (85 °C), a different product is obtained, namely the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)]^-$ (3). According to its solid-state structure (see below), it contains a μ-pyridyl ligand and an N-bonded pyridine molecule which replaces an axial CO ligand of the $Re(CO)_4$ unit of 2, *syn* coordinated with respect to the other heterocyclic ring. The reaction leads to a unique isomer.

The ^1H NMR spectrum of 3 shows three hydridic signals (intensity 1:1:1; δ −9.30, −10.99, −11.95 in acetone-d_6), all downfield-shifted with respect to 2, due to the presence of the novel pyridine ligand. It has been previously observed for related triangular clusters of rhenium that the replacement of a carbonyl by a pyridine ligand downfield-shifts, about 4.1 ppm, the resonances of the bridging hydrides bound to the same vertex.[11] On this basis, the resonance at δ −9.30 should be attributed to H13 (corresponding δ for 2: −13.45), that at δ −11.00 to H12 (δ −15.05 for 2) and that at δ −11.95 to H23 (δ −12.26 for 2).

Description of the Structures of Complexes 2 and 3. The crystal structures of both complexes consist of the packing of discrete cluster anions and tetraethylammonium cations in the ratio 1:1, separated by normal van der Waals contacts. The structures of the anions $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ (2) and $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)]^-$ (3) are illustrated in Figures 1 and 2, respectively; bond distances and angles are given in Tables I and II.

Both anions contain an isosceles triangle of rhenium atoms with two longer hydrogen-bridged edges and one shorter edge doubly bridged by the μ-pyridyl ligand and by the third hydrido ligand. In anion 2 it was not possible to differentiate the N and C metal-bonded atoms of the pyridyl group, probably due to disorder in the solid state; it exhibits, therefore, an idealized C_s symmetry. Its ligand

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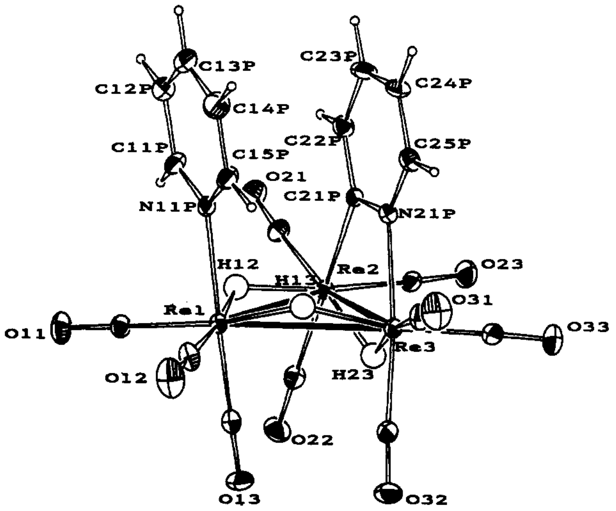

Figure 2. ORTEP drawing of $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)]^-$ (**3**). For clarity the numbering of the carbonyl groups is indicated only by the labels of their oxygen atoms.

Table I. Distances and Angles within $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ (2)

	Distances (Å)		
Re1–Re2	3.238(1)	C12–O12	1.16(3)
Re1–Re3	3.230(1)	C13–O13	1.12(2)
Re2–Re3	3.116(1)	C14–O14	1.12(2)
Re1–C11	1.96(2)	C21–O21	1.14(2)
Re1–C12	1.91(2)	C22–O22	1.14(2)
Re1–C13	2.02(2)	C23–O23	1.14(2)
Re1–C14	1.99(2)	C31–O31	1.14(2)
Re2–C21	1.91(2)	C32–O32	1.15(3)
Re2–C22	1.96(2)	C33–O33	1.14(2)
Re2–C23	1.91(2)	C/N1–C/N2	1.35(2)
Re2–C/N1	2.19(2)	C/N1–C2	1.37(3)
Re3–C31	1.90(2)	C2–C3	1.41(3)
Re3–C32	1.95(2)	C3–C4	1.28(3)
Re3–C33	1.92(2)	C4–C5	1.37(4)
Re3–C/N2	2.18(2)	C5–C/N2	1.38(3)
C11–O11	1.12(2)		
	Angles (deg)		
Re2–Re1–C11	106.1(6)	C31–Re3–C32	90.0(8)
Re3–Re1–C11	161.7(6)	Re1–Re3–C33	157.7(6)
Re2–Re1–C12	160.4(7)	Re2–Re3–C33	97.0(6)
Re3–Re1–C12	103.7(7)	C31–Re3–C33	92.9(9)
C11–Re1–C12	91.3(8)	C32–Re3–C33	90.3(9)
Re2–Re1–C13	96.9(5)	Re1–Re3–C/N2	84.9(5)
Re3–Re1–C13	96.6(5)	Re2–Re3–C/N2	66.0(5)
C11–Re1–C13	93.5(8)	C/N2–Re3–C31	93.2(8)
C12–Re1–C13	90.8(9)	C/N2–Re3–C32	176.5(7)
Re2–Re1–C14	78.7(5)	C/N2–Re3–C33	91.0(8)
Re3–Re1–C14	79.0(7)	Re1–C11–O11	178(2)
C11–Re1–C14	90(1)	Re1–C12–O12	174(2)
C12–Re1–C14	93(1)	Re1–C13–O13	178(2)
C13–Re1–C14	175.0(7)	Re1–C14–O14	177(2)
Re1–Re2–C21	112.1(7)	Re2–C21–O21	177(2)
Re3–Re2–C21	158.1(5)	Re2–C22–O22	176(2)
Re1–Re2–C22	93.5(6)	Re2–C23–O23	177(2)
Re3–Re2–C22	109.2(5)	Re3–C31–O31	177(2)
C21–Re2–C22	91.4(7)	Re3–C32–O32	177(2)
Re1–Re2–C23	157.0(7)	Re3–C33–O33	178(2)
Re3–Re2–C23	96.3(7)	Re2–C/N1–C/N2	113(2)
C21–Re2–C23	90(1)	Re2–C/N1–C2	126(1)
C22–Re2–C23	90.3(8)	Re3–C/N2–C/N1	115(2)
Re1–Re2–C/N1	84.9(5)	Re3–C/N2–C5	126(2)
C/N1–Re2–C21	93.1(7)	C/N2–C/N1–C2	120(2)
C/N1–Re2–C22	175.5(7)	C/N1–C2–C3	117(2)
C/N1–Re2–C23	89.6(8)	C2–C3–C4	124(3)
Re1–Re3–C31	109.1(6)	C3–C4–C5	118(3)
Re2–Re3–C31	156.9(6)	C4–C5–C/N2	121(3)
Re1–Re3–C32	92.6(6)	C5–C/N2–C/N1	119(2)
Re2–Re3–C32	110.6(6)		

stereochemistry and bond parameters within the $[Re_3(\mu\text{-}H)_3(CO)_{10}]$ frame are similar to those observed in the other related complexes containing a $\mu\text{-}\eta^2$ ligand, listed in Table III. All these compounds possess quite similar Re–Re bond lengths, the doubly bridged edge, Re2–Re3, being always the shorter one. This bond is longer than an unsupported Re–Re bond, *e.g.* 3.0413(11) Å in $[Re_2(CO)_{10}]$,[13] due to the lengthening effect of the bridging hydride. The lengthening however is contrasted by the steric requirements of the other bridging group. This is confirmed by the fact that the presence of $\mu\text{-}\eta^1$-X ligands causes markedly shorter Re–Re bond distances [X = $OCHMe_2$,[9a] 2.930(1) Å; X = OC_6F_5,[10] 2.975(1) Å; X = Cl,[8] 2.995(2) Å]. Anion **3**, in which one of the axial CO ligands of the $Re(CO)_4$ unit is replaced by the N-bonded pyridine molecule, exhibits Re–Re bonds only slightly longer than those of **2**.

Re–Re interactions doubly bridged by a hydride and a μ-pyridyl ligand are present also in the dinuclear species $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_8]$ [Re–Re = 3.2088(4) and 3.1956(5) Å for two independent molecules] and $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_7(Me_3NO)]$ [Re–Re = 3.2324(5) Å].[4b] These longer metal–metal bonds are related to the presence of four CO ligands (or three CO's and the amine oxide) on the Re atoms, *vs* three CO ligands on the corresponding metal atoms of **2** and **3**; a similar bond length relationship holds for the $Re(\mu\text{-}H)_2Re$ interactions in **1** and in $[Re_2(\mu\text{-}H)_2(CO)_8]$ [Re–Re = 2.789(1) *vs* 2.876(1) Å].[14]

In both anions the geometry about each rhenium atom is best described as distorted octahedral, taking into account also the hydrido ligands. All the hydridic hydrogens were indirectly located, on the basis of the stereochemistry of the other ligands and by use of potential energy calculations. The two hydrogen atoms bound on the longer Re–Re edges show a moderate displacement out of the Re_3 plane, by the same side of the μ-pyridyl ligand (0.37 and 0.45 Å in **2**; 0.24 and 0.54 Å in **3**); the third hydrido ligand is more markedly displaced in the opposite direction with respect to the same plane, with a dihedral angle between the Re_3 plane and the relevant Re–H–Re plane of 106.0° in **2** and 108.1° in **3**.

The μ-pyridyl ligands display bonding parameters similar to those found in $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_8]$ [two molecules: Re–N = 2.184(7), 2.185(7) Å; Re–C = 2.181(8), 2.197(7) Å] and in $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_7(Me_3NO)]$ [Re–N = 2.165(7) Å; Re–C = 2.156(9) Å].[4b] These groups show some outward folding around the Re2–Re3 axis, the dihedral angles between the Re_3 plane and the Re2–N–C–Re3 best plane being 97.6(3)° for **2** and 97.1(1)° for **3**.

In **3** the pyridine ligand is bound by the same side of the metal atom plane bearing the μ-pyridyl ligand. The two aromatic rings are almost parallel, exhibiting a dihedral angle of 10.5(3)° and a distance between their centroids of *ca.* 3.5 Å. The slight divergence of the two planes indicates however that the interaction between the two groups cannot be attractive. An explanation of the *syn* coordination of the two heterocyclic ligands and of the finding of one isomer only is not simple. The observed stereochemistry is probably favored by lower steric interligand repulsions. For the related $\mu\text{-}\eta^2$-formimidoyl

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Table II. Distances and Angles within $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)]^-$ (3)

Distances (Å)

Re1–Re2	3.2570(5)	C21–O21	1.15(1)
Re1–Re3	3.2682(5)	C22–O22	1.15(1)
Re2–Re3	3.1528(5)	C23–O23	1.16(1)
Re1–C11	1.93(1)	C31–O31	1.16(1)
Re1–C12	1.92(1)	C32–O32	1.14(1)
Re1–C13	1.91(1)	C33–O33	1.14(1)
Re1–N11P	2.236(7)	N11P–C11P	1.34(1)
Re2–C21	1.920(9)	C11P–C12P	1.41(1)
Re2–C22	1.94(1)	C12P–C13P	1.37(2)
Re2–C23	1.894(9)	C13P–C14P	1.36(2)
Re2–C21P	2.171(8)	N11P–C15P	1.33(1)
Re3–C31	1.91(1)	C14P–C15P	1.40(2)
Re3–C32	1.94(1)	N21P–C21P	1.37(1)
Re3–C33	1.91(1)	C21P–C22P	1.38(1)
Re3–N21P	2.176(7)	C22P–C23P	1.38(1)
C11–O11	1.15(1)	C23P–C24P	1.38(1)
C12–O12	1.16(1)	N21P–C25P	1.37(1)
C13–O13	1.14(1)	C24P–C25P	1.37(1)

Angles (deg)

C11–Re1–Re2	109.8(3)	C33–Re3–C31	89.6(4)
C11–Re1–Re3	166.3(3)	C33–Re3–C32	91.8(4)
C12–Re1–Re2	158.8(3)	N21P–Re3–Re1	85.0(2)
C12–Re1–Re3	101.6(3)	N21P–Re3–Re2	65.8(2)
C12–Re1–C11	90.0(4)	N21P–Re3–C31	95.1(4)
C13–Re1–Re2	83.6(3)	N21P–Re3–C32	173.9(3)
C13–Re1–Re3	82.7(3)	N21P–Re3–C33	92.9(3)
C13–Re1–C11	90.3(4)	Re1–N11P–C11P	120.5(6)
C13–Re1–C12	89.2(5)	Re1–N11P–C15P	122.2(7)
N11P–Re1–Re2	91.5(2)	Re2–C21P–N21P	114.6(5)
N11P–Re1–Re3	96.4(2)	Re2–C21P–C22P	127.4(6)
N11P–Re1–C11	89.5(3)	Re3–N21P–C21P	113.8(5)
N11P–Re1–C12	96.1(4)	Re3–N21P–C25P	126.3(6)
N11P–Re1–C13	174.7(4)	Re1–C11–O11	177.6(9)
C21–Re2–Re1	111.8(3)	Re1–C12–O12	179(1)
C21–Re2–Re3	157.0(3)	Re1–C13–O13	178.8(9)
C22–Re2–Re1	91.9(3)	Re2–C21–O21	177.9(9)
C22–Re2–Re3	110.2(3)	Re2–C22–O22	179.7(5)
C22–Re2–C21	91.4(4)	Re2–C23–O23	176.7(9)
C23–Re2–Re1	158.5(3)	Re3–C31–O31	179(1)
C23–Re2–Re3	97.4(3)	Re3–C32–O32	175.9(9)
C23–Re2–C21	88.9(4)	Re3–C33–O33	177.9(9)
C23–Re2–C22	93.5(4)	C15P–N11P–C11P	117.3(9)
C21P–Re2–Re1	83.3(2)	C12P–C11P–N11P	123(1)
C21P–Re2–Re3	65.6(2)	C13P–C12P–C11P	118(1)
C21P–Re2–C21	92.3(4)	C14P–C13P–C12P	120(1)
C21P–Re2–C22	174.8(3)	C15P–C14P–C13P	119(1)
C21P–Re2–C23	90.2(4)	C14P–C15P–N11P	123(1)
C31–Re3–Re1	109.7(3)	C25P–N21P–C21P	119.7(8)
C31–Re3–Re2	158.5(3)	C22P–C21P–N21P	118.0(8)
C32–Re3–Re2	109.5(3)	C23P–C22P–C21P	122.6(9)
C32–Re3–C31	88.8(4)	C24P–C23P–C22P	118.6(9)
C33–Re3–Re1	160.7(3)	C25P–C24P–C23P	118.3(9)
C33–Re3–Re2	100.8(3)	C24P–C25P–N21P	122.7(9)

anions $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}CH{=}NC_6H_{11})(CO)_9L]^-$ (L = PMe_2Ph, CNC_6H_{11}) two isomers were obtained, supposedly the *syn* and *anti* axial complexes.[15]

The Re–N(pyridine) bond length of 2.236(7) Å compares well with the corresponding bond in the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_9(NC_5H_5)]^-$ [Re–N = 2.21(1) Å][11] and in $[Re_3(\mu\text{-}H)_3(CO)_{10}(NC_5H_5)_2]$ [mean Re–N = 2.22 Å],[16] both containing axially bonded pyridine molecules.

As to the metal–carbonyl interactions, the groups bound to Re2 and Re3 exhibit quite similar bond contacts in the two anions, the Re–C bond lengths *trans* to the pyridyl C and N atoms being longer than the other ones, those *trans* to the hydrides (mean values 1.96 *vs* 1.91 Å in **2** and 1.94 *vs* 1.91 Å in **3**). The CO groups bound to Re1 occupy equatorial and axial coordination sites; in **2** the latter ones show, as expected, longer Re–C contacts (mean values 2.00 *vs* 1.94 Å), due to the mutual competition for π back-donation. In **3** the axial CO *trans* to the pyridine molecule exhibits a Re–C bond length, 1.91(1) Å, comparable to those of the equatorial groups (mean 1.92 Å).

Table III. Comparison of Mean Bond Lengths (Å) in the Known $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}X)(CO)_9L]^-$ Clusters, with L = CO or a Two-Electron-Donor Ligand Axially Bound to Re1

L	X	Re1–Re2,3	Re2–Re3	Re–X (bridge)	ref
CO	HCO_2	3.246	3.181	2.170	*a*
CO	CF_3CO_2	3.239	3.181	2.18	*a*
CO	PhC(NH)O	3.281	3.153	2.13	*b*
CO	NO	3.201	3.097	2.133	*c*
CO	$CH{=}NC_6H_4Me$	3.236	3.160	2.164	15b
CO	NC_5H_4	3.234	3.116	2.18	this work
PMe_2Ph	$CH{=}NC_6H_{11}$	3.255	3.164	2.16	15a
NC_5H_5	NC_5H_4	3.262	3.153	2.174	this work

[a] Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Organomet. Chem.* **1982**, *233*, C46. [b] Beringhelli, T.; Cesarotti, E.; Ciani, G.; D'Alfonso, G.; Sironi, A. *J. Organomet. Chem.* **1984**, *268*, C18. [c] Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1327.

The ortho-Metalation Reaction. We have previously reported that compound **1** reacts with two-electron-donor ligands L in a different way with respect to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, which gives stable monoaddition products of formula $[Os_3H(\mu\text{-}H)(CO)_{10}L]$ (L = CO, phosphines, isocyanides, etc.).[17] Compound **1** undergoes substitution of two H ligands by two L molecules, according to reaction 2.

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + 2L \rightarrow [Re_3(\mu\text{-}H)_2(CO)_{10}L_2]^- + H_2 \quad (2)$$

$$L = CO, PR_3{}^{12}$$

The first step of reaction 2 is likely the formation of addition products $[Re_3H(\mu\text{-}H)_3(CO)_{10}L]^-$, containing one terminal hydride and similar to the corresponding triosmium addition products. These adducts are believed to be too reactive to be observed (no evidence for them was obtained even on monitoring the reactions by NMR): they lose H_2 and add a second L molecule according to reaction 2. Also, the insertion of isocyanides into **1** to give $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}CHNR)(CO)_{10}]^-$ is supposed[15] to proceed *via* a similar unstable intermediate species $[Re_3H(\mu\text{-}H)_3(CO)_{10}(CNR)]^-$, in which H transfer from the cluster to the isocyanide C atom occurs.

It seems therefore reasonable to assume also for the ortho-metalation reaction (1) the preliminary formation of an unstable adduct $[Re_3H(\mu\text{-}H)_3(CO)_{10}(NC_5H_5)]^-$ (see Scheme I). After elimination as H_2 of two hydrides (likely the terminal hydride and one of the two adjacent bridging hydrides), oxidative addition of the C_2–H bond of the coordinated pyridine occurs toward the electron-poor Re atom, which has lost two hydrides.

To gain better insight into the above reaction mechanism, we have performed reaction 1 in an NMR tube, at 300 K, using NC_5D_5. The results confirm the proposed

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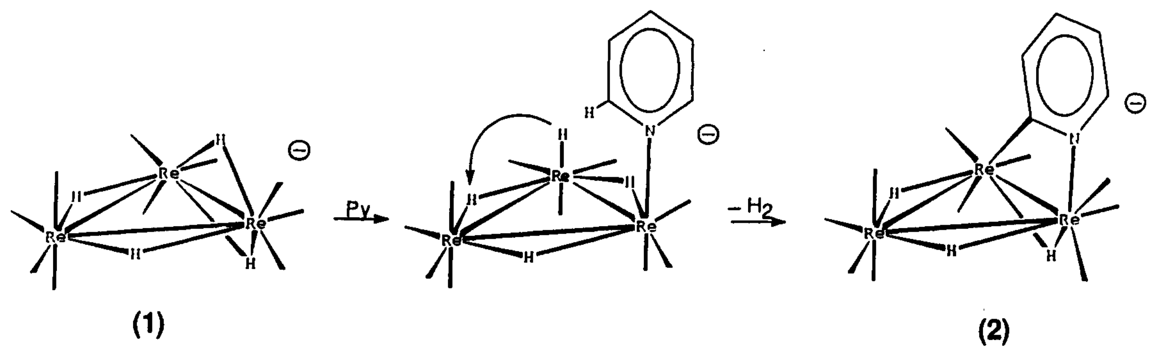
[15] (a) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Moret, M.; Sironi, A. *J. Organomet. Chem.* **1990**, *399*, 291. (b) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P.; Ciani, G.; Moret, M.; Sironi, A. *Organometallics* **1991**, *10*, 3131.

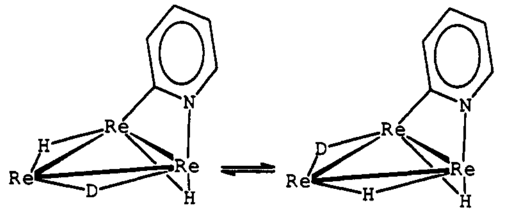
[16] Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1980**, *186*, 353.

[17] Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304 and references therein.

Scheme I



Scheme II



intramolecular hydrogen elimination, preceding the pyridine oxidative addition. In fact, gas chromatographic analysis of the gas evolved in the reaction has shown only the presence of H_2 and the absence of HD. Moreover, the ^{1}H NMR spectra showed the clean formation of 2, *the intensities of its hydridic signals being in the ratio 1:0.5: 0.5* at any time. This indicates the presence of a deuterium atom equally distributed on the two bridging sites spanning the two longer triangular edges (see Scheme II). This presence cannot arise from a selective H/D exchange of these hydridic sites, the 1:0.5:0.5 ratio being notably constant at all times (moreover, significant H/D exchange, at room temperature and in the reaction time, can be ruled out for any hydridic site of compounds 1 and 2, on the basis of the ratio of the hydridic *vs* cationic resonances). Since the site corresponding to the higher field resonance (H12) seems the more probable candidate for the initial addition (see the sequence outlined in Scheme I), the even distribution of the deuterium atom between the two sites can be explained on the basis of the fluxional behavior of 2.

Indeed, when the temperature of a toluene-d_8/acetone-d_6 (*ca.* 4:1) solution of complex 2 is raised, the two high-filed hydridic signals broaden and are almost collapsed at 81 °C, while the low-field resonance remains unchanged. This supports the idea that a dynamic process interchanges the two hydrides on the edges unbridged by the pyridine. Computer simulation of the spectra allowed the estimate of the rate constants and the activation parameters accordingly (E_a = 72 ± 1 kJ/mol, $\Delta H^{\ddagger}$ = 70 ± 1 kJ/mol, $\Delta S^{\ddagger}$ = −21 ± 3 J/(mol K)).

When the temperature is raised, a moderate broadening is observed also for the lowest and the highest field resonances of complex 3 (at −8.73 and −11.44 ppm in a toluene-d_8/acetone-d_6 mixture). However, this does not seem related to dynamic phenomena, since, when variable-temperature experiments performed at two different fields are compared, the bandwidths of the resonances are always greater at higher fields than at lower fields. This is in contrast with what is expected for a dynamic process and could possibly be related to changes in the relaxation time of the nitrogen atom of the ortho-metalated pyridine.[18]

Within the chemistry of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, the oxidative addition of ethylene to give the μ-ethenyl derivative occurs after the preliminary elimination of the two hydrides, not with H_2 formation but by migration to an ethylene molecule, previously added to the cluster, to give ethane.[19] In fact, on using $[Os_3(\mu\text{-}D)_2(CO)_{10}]$ 1 mol of ethane-d_2/mol of product was recovered. This outlines another difference in reactivity between 1 and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$: while the different polarizations of the hydrides of 1 allows the intramolecular hydrogen elimination, the osmium compound, to undergo oxidative addition, needs the presence of a species able to uptake its two hydrides.

As to the formation of 3, two pathways could be supposed, according to the ortho-metalation reaction preceding or following the pyridine substitution for CO on the $Re(CO)_4$ vertex. It is already known that the two mutually *trans* CO ligands of the $Re(CO)_4$ unit of 1 are particularly labile, due to their competition for π back-donation.[7] This allows the selective substitution of one of these ligand with two-electron-donor ligands L, either thermally activated or promoted by $(CH_3)_3NO$, leading to derivatives of formula $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ (including L = NC_5H_5, complex 4),[11] which maintain the unsaturated $Re(\mu\text{-}H)_2Re$ moiety of the parent anion.

The 1 → 3 conversion could therefore proceed *via* intermediate 2 or *via* intermediate 4, or through both pathways (Scheme III).

NMR monitoring has revealed that 4, dissolved in pyridine-d_5, does not react at all, for a period of days, not only at room temperature but also at temperatures as high as 50 °C. No reaction was observed even at 80 °C, for 2 h, which is the time of formation of 3 from 1. This implies that the substitution on the apical vertex of the triangle of the π-acidic CO with the good σ-donor pyridine dramatically decreases the susceptibility of the adjacent unsaturated moiety "$Re(\mu\text{-}H)_2Re$" toward nucleophilic attack.

NMR monitoring in pyridine-d_5 has also revealed that compound 2 converts cleanly to 3, also at temperatures as low as 50 °C (even if quite slowly at this temperature). The 1 → 2 → 3 pathway is therefore definitely ascertained.

It is interesting to note that the reaction of 1 with a moderate excess of pyridine (5 equiv), in tetrahydrofuran at 85 °C, gives only the unsaturated anion 4 and not complex 3. This different behavior, with respect to the reaction in pyridine solution, can be understood by assuming that CO substitution proceeds *via* a dissociative

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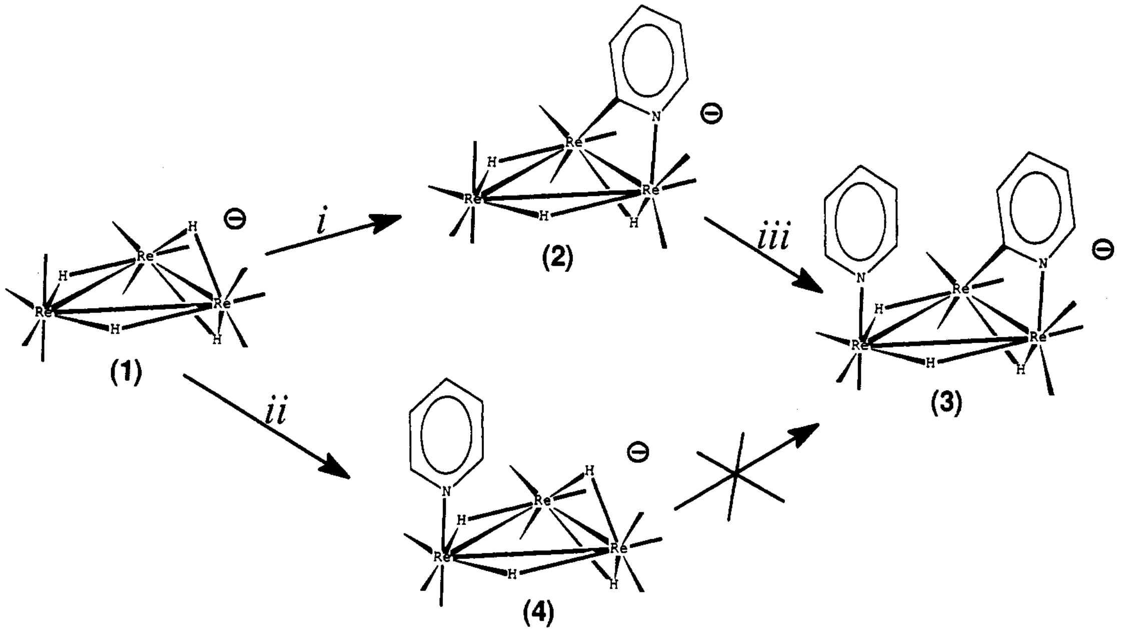
[18] In these spectra is observable also a signal at −10.9 ppm whose intensity increases reversibly with the temperature, from *ca.* 7% (25 °C) to 80% (81 °C) of the intensity of each resonance of 3. At present, there are no sound arguments to support a characterization of this species.

[19] Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29.

Scheme III[a]



[a]Key: (i) in pyridine, room temperature; (ii) in THF, few equivalents of pyridine, 85 °C; (iii) in pyridine, 85 °C.

mechanism and is therefore independent of the concentration of pyridine (being mainly affected by the temperature), while the rate of ortho-metalation increases with pyridine concentration (in line with a rate-determining pyridine addition). In pyridine solution, therefore, the rate of the latter process can overcome the rate of CO substitution, the pyridine concentration increasing by more than 2 orders of magnitude.

Experimental Section

The reactions were performed under N_2, and solvents were dried and deoxygenated by standard methods. $[Re_3(\mu\text{-}H)_4(CO)_{10}][NEt_4]$ and $[Re_3(\mu\text{-}H)_4(CO)_9(NC_5H_5)][NEt_4]$ were prepared as previously published.[7,11] Pyridine was distilled over KOH under reduced pressure just before the reaction. Pyridine-d_5 (Merck) was simply distilled immediately before use. The IR spectra were recorded in 0.1-mm CaF_2 cells on a Perkin-Elmer 781 grating spectrophotometer, equipped with a data station using PE780 software. The NMR spectra were obtained on Bruker WP80 and AC200 spectrometers. Elemental analyses were performed by the microanalytical laboratory of our department. The analysis of the evolved gas was performed on a Carlo Erba HR gas chromatograph, interfaced to a VGM quadrupole mass spectrometer and equipped with a capillary column (fused silica, 25 m × 0.32 mm, 30 μm of PLOT Molsieve 5 Å, Chrompack).

Synthesis of $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}][NEt_4]$ (2-[NEt₄]). A solution of $[Re_3(\mu\text{-}H)_4(CO)_{10}][NEt_4]$ (50 mg, 0.051 mmol) dissolved in pyridine (3 mL *ca.* 37 mmol) was stirred at room temperature for 19 h. The addition of *n*-heptane gave a cream-colored precipitate of pure (on the basis of spectroscopic and elemental analyses) $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}][NEt_4]$ (45 mg, 0.043 mmol, isolated yield 83%, after washing and drying under vacuum). Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a concentrated dichloromethane solution. IR (tetrahydrofuran): ν(CO) 2093 w, 2018 m, 1995 s, 1983 sh, 1939 mw, 1911 m, 1895 m cm^{-1}. ^{1}H NMR of the anion (acetone-d_6): δ 8.25 (m, 1), 7.45 (m, 1), 7.10 (m, 1), 6.65 (m, 1), −12.26 (s, 1), −13.45 (s, 1), −15.05 (s, 1), with the correct integrated intensity with respect to the cationic signals. Selective irradiation of the signals in the aromatic region allowed the assignment of the resonances and the estimate of the following coupling constants (the labeling starts from the hydrogen ortho to the nitrogen atom): H_α 8.25 ppm ($J_{\alpha\beta}$ = 5.2 Hz, $J_{\alpha\gamma}$ = 1.7 Hz, $J_{\alpha\delta}$ = *ca.* 1 Hz), H_β 6.63 ppm ($J_{\beta\gamma}$ = 7.5 Hz, $J_{\beta\delta}$ = 1.6 Hz), H_γ 7.06 ppm ($J_{\gamma\delta}$ = 7.7 Hz), H_δ 7.43 ppm. Anal. Calcd for $C_{23}H_{27}N_2O_{10}Re_3$: C, 26.30; H, 2.57; N, 2.67. Found: C, 26.5; H, 2.8; N, 2.4.

Synthesis of $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)][NEt_4]$ (3[NEt₄]). A solution of $[Re_3(\mu\text{-}H)_4(CO)_{10}][NEt_4]$ (20 mg, 0.021 mmol) in pyridine (4 mL, *ca.* 50 mmol) was stirred in an oil bath at 85 °C for 2 h, while a H_2 stream was passed through the solution to remove the evolved CO. The addition of a large excess of *n*-heptane (about 30 mL) gave a light brown precipitate of pure (on the basis of spectroscopic and elemental analyses) $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)][NEt_4]$ (12 mg, 0.011 mmol, isolated yield 52%, after washing and drying under vacuum). Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a concentrated dichloromethane solution. IR (tetrahydrofuran): ν(CO) 2030 ms, 2000 s, 1990 s, 1920 ms, 1905 vs, 1890 sh cm^{-1}. Selective irradiation experiments allowed the assignment of the resonances in the aromatic region of the ^{1}H NMR spectrum of the anion (acetone-d_6). The H atoms are labeled with numbers for the terminal pyridine and with Greek letters for the ortho-metalated pyridine: δ 8.6 (m, 2, H1–H1′), 7.8 (m, 1, H_α), 7.6 (m, 1, H3, $J_{3\text{-}2}$ = 7.6 Hz), 7.1 (m, 2, H2–H2′), 7.0 (m, 1, H_δ), 6.5 (m, 1, H_γ), 6.2 (m, 1, H_β), −9.30 (s, 1), −10.99 (s, 1), −11.95 (s, 1), with the correct integrated intensity with respect to the cationic signals. Anal. Calcd for $C_{27}H_{32}N_3O_9Re_3$: C, 29.44; H, 2.91; N, 3.82. Found: C, 29.6; H, 3.1; N, 3.6.

NMR Monitoring of the Reaction Processes. Proper amounts of the NEt_4 salts of complexes 1, 2, and 4 (typically *ca.* 15 mg) were each dissolved in 0.5 mL of pyridine-d_5 in a 0.5-mm NMR tube, and spectra were recorded at different times.

Reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}][NEt_4]$(1[NEt₄]) with Pyridine in Tetrahydrofuran. A sample of $[Re_3(\mu\text{-}H)_4(CO)_{10}][NEt_4]$ (20 mg, 0.019 mmol), dissolved in tetrahydrofuran (3 mL), was treated with pyridine (9 μL, ~5 equiv), and the mixture was heated in a sealed vessel at 85 °C for 2.5 h. The solvent was removed, and NMR analysis showed that the main hydridic product was 4 [NEt₄], the other hydridic components of the mixture being unreacted 1[NEt₄] (about 20% of 4[NEt₄]) and uncharacterized species, responsible for signals of lower intensity, at δ −11.7 (likely $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OH)(CO)_9]^-$, originating from some water in the solvent) and at δ −17.2. No signal due to 3 was detected.

Variable-Temperature NMR Analysis. A sample of compound 2[NEt₄] (0.015 mmol) was dissolved in a mixture of toluene

Table IV. Summary of Crystal Data

	2[NEt$_4$]	3[NEt$_4$]
formula	$C_{23}H_{27}N_2O_{10}Re_3$	$C_{27}H_{32}N_3O_9Re_3$
fw	1050.1	1101.2
crystal system	orthorhombic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a, Å	13.297(4)	13.363(1)
b, Å	18.343(7)	13.143(1)
c, Å	24.432(12)	18.955(3)
β, deg	90.00	100.09(1)
V, Å^3	5959.1	3277.6
Z	8	4
D_{calcd}, g cm^{-3}	2.341	2.231
F(000)	3872	2048
λ (Mo Kα), Å	0.710 73	0.710 73
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
μ, cm^{-1}	123.8	112.6
θ range, deg	3–25	3–25
scan method	ω	ω
scan range, deg	0.90 + 0.35 tan θ	0.90 + 0.35 tan θ
max scan time, s	60	60
collected octants	+*h*,+*k*,+*l*	±*h*,+*k*,+*l*
no. of collected reflns	5767	5990
no. unique obsd reflns ($I > 3\sigma(I)$)	1829	3924
min transm factors	0.27	0.74
crystal dimens, mm	0.06 × 0.18 × 0.28	0.10 × 0.14 × 0.39
no. of ref variables	272	339
R	0.028	0.027
R_w	0.030	0.029

Table V. Final Positional Parameters for $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}](NEt_4)$ (2[NEt$_4$])

atom	*x*	*y*	*z*	*B*,[a] Å^2
Re1	0.13344(4)	0.19394(3)	0.12304(3)	3.16(1)*
Re2	0.25015(5)	0.32523(4)	0.06124(3)	3.15(2)*
Re3	0.24310(5)	0.32445(4)	0.18871(3)	3.14(2)*
C11	0.063(1)	0.139(1)	0.0659(9)	4.0(5)*
O11	0.020(1)	0.108(1)	0.0345(9)	6.9(6)*
C12	0.066(2)	0.140(1)	0.179(1)	5.2(6)*
O12	0.024(2)	0.114(1)	0.2159(9)	6.3(5)*
C13	0.250(1)	0.123(1)	0.125(1)	4.4(4)*
O13	0.316(1)	0.0856(8)	0.1258(9)	7.6(4)*
C14	0.028(1)	0.2703(9)	0.121(1)	4.2(5)*
O14	–0.0342(9)	0.3117(7)	0.1178(7)	5.8(4)*
C21	0.292(1)	0.298(1)	–0.0109(9)	3.9(5)*
O21	0.314(1)	0.284(1)	–0.0545(7)	6.8(5)*
C22	0.126(1)	0.368(1)	0.0329(8)	3.6(5)*
O22	0.057(1)	0.394(1)	0.0137(8)	6.5(6)*
C23	0.317(2)	0.417(1)	0.0540(9)	4.4(6)*
O23	0.357(1)	0.4717(9)	0.0521(6)	5.8(4)*
C31	0.274(1)	0.292(1)	0.2608(9)	3.6(5)*
O31	0.294(1)	0.276(1)	0.3045(7)	6.0(5)*
C32	0.116(2)	0.364(1)	0.2149(9)	4.0(5)*
O32	0.042(2)	0.390(2)	0.2292(9)	7.1(5)*
C33	0.307(2)	0.417(1)	0.1997(8)	4.1(5)*
O33	0.346(1)	0.4722(9)	0.2057(6)	7.0(5)*
C/N1	0.385(1)	0.280(1)	0.0993(7)	3.8(4)
C/N2	0.381(1)	0.280(1)	0.1545(7)	3.5(3)
C2	0.468(2)	0.2527(9)	0.073(1)	3.6(7)
C3	0.551(2)	0.233(1)	0.1053(9)	4.4(5)
C4	0.547(2)	0.228(1)	0.158(1)	5.0(5)
C5	0.463(2)	0.254(1)	0.184(1)	4.5(8)
N1T	0.247(1)	0.5097(7)	–0.1199(9)	3.9(3)
C1T	0.248(2)	0.511(2)	–0.061(1)	7.9(8)
C2T	0.146(1)	0.534(1)	–0.1466(7)	5.0(4)
C3T	0.276(2)	0.433(1)	–0.1418(9)	6.3(6)
C4T	0.321(1)	0.566(1)	–0.1465(8)	5.2(5)
C5T	0.221(3)	0.585(2)	–0.036(1)	11(1)
C6T	0.056(2)	0.487(1)	–0.126(1)	8.1(6)
C7T	0.278(3)	0.418(2)	–0.202(1)	10.0(9)
C8T	0.429(2)	0.554(1)	–0.126(1)	6.6(5)

[a] An asterisk indicates an equivalent isotropic *B* factor.

Table VI. Final Positional Parameters for $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5)](NEt_4)$ (3[NEt$_4$])

atom	*x*	*y*	*z*	*B*,[a] Å^2
Re1	0.32864(3)	0.11651(3)	0.22475(2)	2.799(8)*
Re2	0.13228(3)	0.18596(3)	0.10760(2)	2.684(8)*
Re3	0.26595(3)	0.35534(3)	0.19669(2)	2.892(8)*
C11	0.3496(7)	–0.0280(7)	0.2179(5)	3.6(2)*
O11	0.3644(7)	–0.1138(5)	0.2161(4)	5.9(2)*
C12	0.4543(8)	0.1280(8)	0.2909(6)	4.8(3)*
O12	0.5311(7)	0.1335(7)	0.3299(5)	7.9(3)*
C13	0.4006(8)	0.1394(7)	0.1479(6)	4.2(2)*
O13	0.4433(7)	0.1548(6)	0.1017(5)	6.2(2)*
N11P	0.2314(5)	0.0879(5)	0.3074(4)	3.3(2)*
C11P	0.1603(8)	0.0148(8)	0.2975(6)	4.5(3)*
C12P	0.0996(9)	–0.0100(9)	0.3486(6)	5.3(3)*
C13P	0.115(1)	0.0437(9)	0.4112(7)	6.1(4)*
C14P	0.186(1)	0.1179(9)	0.4223(7)	6.5(4)*
C15P	0.2428(9)	0.1394(7)	0.3684(6)	4.9(3)*
C21	0.0323(7)	0.0799(7)	0.0893(5)	3.8(2)*
O21	–0.0300(6)	0.0187(6)	0.0782(4)	5.6(2)*
C22	0.1957(7)	0.1411(7)	0.0284(5)	4.0(2)*
O22	0.2338(6)	0.1147(6)	–0.0186(4)	5.7(2)*
C23	0.0406(7)	0.2741(7)	0.0494(5)	3.6(2)*
O23	–0.0171(6)	0.3302(6)	0.0166(4)	5.8(2)*
C31	0.3242(8)	0.4347(8)	0.2779(6)	4.4(3)*
O31	0.3601(7)	0.4839(7)	0.3266(5)	7.7(3)*
C32	0.3889(8)	0.3761(7)	0.1575(6)	4.1(2)*
O32	0.4583(6)	0.3932(6)	0.1323(5)	5.8(2)*
C33	0.2054(8)	0.4756(8)	0.1512(6)	4.6(3)*
O33	0.1716(7)	0.5479(7)	0.1228(6)	8.1(3)*
N21P	0.1296(5)	0.3149(5)	0.2384(4)	3.3(2)*
C21P	0.0751(6)	0.2375(6)	0.2019(4)	2.6(2)*
C22P	–0.0073(7)	0.2004(7)	0.2281(5)	3.8(2)*
C23P	–0.0359(8)	0.2376(8)	0.2899(5)	4.8(3)*
C24P	0.0198(7)	0.3163(8)	0.3260(5)	4.3(3)*
C25P	0.1004(8)	0.3538(8)	0.2987(5)	4.2(2)*
N1T	–0.3213(5)	0.2275(6)	0.0130(4)	3.4(1)
C1T	–0.2697(9)	0.2399(9)	–0.0525(6)	5.6(2)
C2T	–0.245(1)	0.232(1)	0.0791(7)	7.1(3)
C3T	–0.376(1)	0.125(1)	0.0099(8)	7.0(3)
C4T	–0.402(1)	0.308(1)	0.0096(7)	6.6(3)
C5T	–0.1938(9)	0.1550(9)	–0.0608(7)	5.7(3)
C6T	–0.2872(9)	0.239(1)	0.1479(7)	6.7(3)
C7T	–0.454(1)	0.109(1)	–0.0535(8)	8.0(4)
C8T	–0.362(1)	0.416(1)	0.0188(8)	7.8(3)

[a] An asterisk indicates an equivalent isotropic *B* factor.

and acetone-d_6. The spectra were recorded in the range 300–354 K on a Bruker 80 SY spectrometer operating at 80.13 MHz. The same experiments were performed on a sample of **3**[NEt$_4$] (0.011 mmol) at 80.13 and 200.13 MHz (Bruker AC200) in the same range of temperature. The temperature was controlled by the B VT-1000 unit of the spectrometer and calibrated with an ethylene glycol solution. Computer simulations were performed using a modified version of the QCPE program MSEX.[20]

X-ray Analyses of the NEt$_4^+$ Salts of Anions 2 and 3. Intensity Measurements. Crystal data for both compounds 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 Kα radiation. The setting angles of 25 random intense reflections (16° <2θ< 25°) were used in both cases to determine by least-squares fits accurate cell constants and orientation matrixes. The collections were performed by the ω-scan method, within the limits 6° <2θ< 50°. 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 every 2 h, showed no crystal decay upon X-ray exposure for **2** and a small crystal decay for **3**, of *ca.* 8% at the end of the collection. The intensities were corrected for Lorentz and polarization effects; in the case of **3**, the data were also corrected for the decay. An empirical absorption correction was applied to the data of both structures, based on ψ scans (ψ 0–360° every 10°) of three suitable reflections with χ values close to 90°. The numbers of significant [$I > 3\sigma(I)$] independent reflections used in the structure solutions and refinements were 1829 and 3924 for **2** and **3**, respectively.

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(20) Chan, S. O.; Reeves, L. W. *J. Am. Chem. Soc.* **1973**, *95*, 673.

Structure Solutions and Refinements. The data reductions were performed on a PDP 11/73 computer, using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein. All other crystallographic computations were carried out by using the SHELX programms.

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

The refinements were carried out by full-matrix least-squares procedures, minimizing the function $\sum w(F_o - k|F_c|)^2$. Anisotropic thermal parameters were assigned to the rhenium atoms and to the carbonyl atoms in **2** and to all atoms of the anion **3**. In **2** it was not possible to recognize, on the basis of the thermal parameters, the metal-bonded C and N atoms of the pyridyl ligand. A statistically disordered molecular model was therefore refined, each of the two atoms being treated as 0.5 C + 0.5 N.

The hydrogen atoms of the aromatic rings and of the cations were located in ideal positions (C–H = 0.95 Å) after each cycle of refinement; their thermal parameters were refined isotropically in groups, assigning a unique factor to all the aromatic ring hydrogens, a second factor to the cationic methyl hydrogens, and a third one to the methylene hydrogen atoms. Since no direct evidence was obtained from the difference Fourier maps, all the hydrido ligands were located using Orpen's HYDEX program,[21] assuming Re-H interactions of 1.85 Å. Their positional parameters were not refined; a fixed thermal factor (B = 4.0 Å^2) was assigned in the case of **2**, while a unique isotropic thermal parameter was refined in the case of **3**.

The final difference Fourier maps were flat, showing only some residual peaks not exceeding *ca.* 1.0 e Å^{-3} in both cases.

Weights were assigned according to the formula $w = k/[\sigma^2(F_o) + gF_o^2]$, with k = 0.8848 and g = 8.96 × 10^{-4} for **2** and k = 0.9908 and g = 6.33 × 10^{-4} for **3**. The final values of the conventional agreement indices R and R_w are reported in Table IV. The final positional parameters are given in Tables V and VI.

Supplementary Material Available: Tables S1–S5, listing anisotropic thermal factors, calculated fractional coordinates of the hydrogen atoms, and complete bond distances and angles (6 pages). Ordering information is given on any current masthead page.

OM930481D

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[21] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.