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New Synthesis, Reinvestigation of the Solid-State Structure, and NMR Analysis of the Unsaturated Anion Tetrakis(μ-hydrido)decacarbonyl-*triangulo*-trirhenate(1−)

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The unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ has been synthesized by reaction of $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ under high pressure of H_2; the reaction is reversed under CO pressure. The solid-state structure of the anion has been reinvestigated on its bis(triphenylphosphine)nitrogen(1+), PPN^+, salt. This salt crystallizes in the monoclinic space group $P2_1/c$, with cell constants $a = 11.327$ (3) Å, $b = 12.672$ (2) Å, $c = 32.183$ (6) Å, $\beta = 95.08$ (2)°, and $Z = 4$. The structure, solved by Patterson and Fourier methods, has been refined by least squares, on the basis of 4622 significant counter data, to a final R value of 0.042. The anion, of idealized C_{2v} symmetry, contains an isosceles triangle of rhenium atoms, with two longer hydrogen-bridged edges of 3.189 (1) and 3.190 (1) Å and one shorter edge (formally a Re–Re double bond), bridged by two hydrides, of 2.789 (1) Å. Each rhenium atom exhibits an almost octahedral coordination geometry, one with four carbonyls and two hydrides and the other two with three CO groups and three hydrides. NMR analysis at variable temperatures (−90 to +50 °C) has shown that the solid-state structure is retained in solution and the four carbonyl resonances (intensity ratio 2:1:1:1) have been unambiguously assigned. Selective population transfer experiments have pointed out the absence of any scrambling of the ligands. The two carbonyls mutually trans in the $Re(CO)_4$ moiety are selectively enriched under ^{13}CO exchange.

Introduction

Unsaturated carbonyl compounds containing a $M(\mu\text{-}H)_2M$ system[2] are quite interesting because of the reactivity of this moiety; known examples are $Os_3(\mu\text{-}H)_2(CO)_{10}$,[3] $Re_2(\mu\text{-}H)_2(CO)_8$,[4] $Re_2(\mu\text{-}H)_2(CO)_6(dppm)$,[5] and $[W_2(\mu\text{-}H)_2(CO)_8]^{2-}$.[6] Brief accounts of the synthesis and characterization of two other members of this class, $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$[7] and $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$,[8] have been previously reported. In particular, the monoanion gives a variety of derivatives with alcohols,[9] mercaptans,[10] halogen acids,[11] carboxylic acids,[12] iodine,[13] $C_7H_7^+$,[14] and NO^+.[15]

Our interest in this versatile cluster compound has led us to a new synthetic route giving better yields. Moreover, we needed more accurate bond parameters since those previously obtained[8] from the solid-state structure of its NEt_4^+ salt were unreliable due to the poor quality of the X-ray data.

This paper describes a new synthesis of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ from $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ under high pressure of H_2, the results of an X-ray analysis of its PPN^+ salt, and the investigation of the behavior of the anion in solution by ^1H and ^{13}C NMR analysis at variable temperature.

Results and Discussion

In the 1960s Kaesz and co-workers reported the synthesis of the family of triangular hydrido–carbonyl clusters $[Re_3(\mu\text{-}H)_{3-n}(CO)_{12}]^{n-}$ (n = 0, 1, 2),[16-18] through the reduction of $Re_2(CO)_{10}$ with Na/Hg or $NaBH_4$. Since the two unsaturated species $[Re_3(\mu\text{-}H)_{5-n}(CO)_{10}]^{n-}$ (n = 1, 2) can be formally derived from the corresponding members of the above family by substitution of two carbonyls with two hydrides, we have investigated the possibility of interconversion between the two series. Indeed, this occurs for the two species with $n = 1$. By treatment of $[Re_3(\mu\text{-}H)_2(CO)_{12}](NEt_4)$, in tetrahydrofuran, with H_2 (100 atm) at 100 °C for 24 h, the salt $[Re_3(\mu\text{-}H)_4(CO)_{10}](NEt_4)$ is obtained in good yields and can be isolated quite pure by crystallization from CH_2Cl_2/Et_2O. In turn, the latter species, under 50 atm of CO, converts slowly into the saturated compound, according to the equation

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + 2CO \underset{100\ ^\circ C,\ H_2\ (100\ atm)}{\overset{room\ temp,\ CO\ (50\ atm)}{\rightleftharpoons}} [Re_3(\mu\text{-}H)_2(CO)_{12}]^- + H_2$$

$Os_3(\mu\text{-}H)_2(CO)_{10}$ was similarly obtained by hydrogenation of $Os_3(CO)_{12}$ at atmospheric pressure of H_2.[19]

The novel synthesis of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ avoids the difficult isolation of the unstable species $[NEt_4][ReH_2(CO)_4]$, which is the first intermediate of our previous preparation (see Experimental Section).

An attempt to obtain the title compound by irradiation of $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ under H_2 atmosphere, parallel to the synthesis of $Re_2(\mu\text{-}H)_2(CO)_8$ from $Re_2(CO)_{10}$,[20] was unsuccessful; only

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Table I. Bond Distances and Angles within $[Re_3(\mu\text{-}H)_4(CO)_{10}](PPN)$

Distances (Å)

Re(1)-Re(2)	3.189 (1)	Re(3)-C(32)	1.905 (11)	C(33)-O(33)	1.174 (13)
Re(1)-Re(3)	3.190 (1)	Re(3)-C(33)	1.896 (13)	P(1)-N	1.579 (8)
Re(2)-Re(3)	2.789 (1)	C(11)-O(11)	1.128 (13)	P(2)-N	1.580 (8)
Re(1)-C(11)	1.961 (14)	C(12)-O(12)	1.144 (13)	P(1)-C(111)	1.805 (9)
Re(1)-C(12)	1.932 (13)	C(13)-O(13)	1.135 (13)	P(1)-C(121)	1.788 (9)
Re(1)-C(13)	1.985 (13)	C(14)-O(14)	1.132 (15)	P(1)-C(131)	1.807 (9)
Re(1)-C(14)	2.015 (15)	C(21)-O(21)	1.140 (12)	P(2)-C(211)	1.801 (10)
Re(2)-C(21)	1.919 (11)	C(22)-O(22)	1.139 (12)	P(2)-C(221)	1.809 (9)
Re(2)-C(22)	1.928 (12)	C(23)-O(23)	1.132 (11)	P(2)-C(231)	1.787 (9)
Re(2)-C(23)	1.907 (9)	C(31)-O(31)	1.149 (14)	C-C(phenyl)	1.342 (16)-1.415 (13)
Re(3)-C(31)	1.913 (13)	C(32)-O(32)	1.140 (12)		

Angles (deg)

Re(2)-Re(1)-Re(3)	51.86 (1)	Re(3)-Re(1)-C(12)	106.7 (3)	C(22)-Re(2)-C(23)	92.3 (4)
Re(1)-Re(2)-Re(3)	64.09 (1)	Re(3)-Re(1)-C(13)	81.9 (3)	Re(1)-Re(3)-C(31)	160.6 (3)
Re(1)-Re(3)-Re(2)	64.06 (1)	Re(3)-Re(1)-C(14)	91.5 (4)	Re(1)-Re(3)-C(32)	98.2 (4)
Re(1)-C(11)-O(11)	177.5 (11)	C(11)-Re(1)-C(12)	91.6 (5)	Re(1)-Re(3)-C(33)	106.1 (3)
Re(1)-C(12)-O(12)	177.1 (12)	C(11)-Re(1)-C(13)	90.9 (4)	Re(2)-Re(3)-C(31)	97.3 (3)
Re(1)-C(13)-O(13)	176.8 (10)	C(11)-Re(1)-C(14)	93.7 (5)	Re(2)-Re(3)-C(32)	136.0 (3)
Re(1)-C(14)-O(14)	178.0 (12)	C(12)-Re(1)-C(13)	91.3 (5)	Re(2)-Re(3)-C(33)	132.3 (3)
Re(2)-C(21)-O(21)	175.9 (10)	C(12)-Re(1)-C(14)	95.5 (5)	C(31)-Re(3)-C(32)	91.8 (5)
Re(2)-C(22)-O(22)	178.5 (8)	C(13)-Re(1)-C(14)	171.6 (5)	C(31)-Re(3)-C(33)	90.3 (5)
Re(2)-C(23)-O(23)	173.9 (9)	Re(1)-Re(2)-C(21)	161.3 (3)	C(32)-Re(3)-C(33)	90.4 (5)
Re(3)-C(31)-O(31)	176.9 (11)	Re(1)-Re(2)-C(22)	102.9 (3)	P(1)-N-P(2)	140.1 (5)
Re(3)-C(32)-O(32)	178.7 (11)	Re(1)-Re(2)-C(23)	101.4 (3)	N-P(1)-C(111)	110.9 (4)
Re(3)-C(33)-O(33)	173.8 (11)	Re(3)-Re(2)-C(21)	97.2 (3)	N-P(1)-C(121)	116.8 (4)
Re(2)-Re(1)-C(11)	109.8 (4)	Re(3)-Re(2)-C(22)	134.8 (3)	N-P(1)-C(131)	109.3 (4)
Re(2)-Re(1)-C(12)	158.6 (3)	Re(3)-Re(2)-C(23)	131.7 (3)	N-P(2)-C(211)	114.3 (4)
Re(2)-Re(1)-C(13)	87.1 (3)	C(21)-Re(2)-C(22)	89.9 (5)	N-P(2)-C(221)	111.8 (4)
Re(2)-Re(1)-C(14)	84.8 (4)	C(21)-Re(2)-C(23)	91.5 (4)	N-P(2)-C(231)	108.6 (4)
Re(3)-Re(1)-C(11)	160.4 (4)				

traces of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ were detected.

Description of the Structure. The crystal structure consists of the packing of discrete $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ anions and PPN^+ cations, in the ratio 1:1, separated by normal van der Waals contacts.

The structure of the anion, of overall idealized C_{2v} symmetry, is shown in Figure 1. Bond distances and angles are reported in Table I. The anion contains an isosceles Re_3 triangle bearing 10 terminal CO ligands and four edge-bridging hydrido ligands. Unfortunately, it was not possible to locate directly these hydrides and they were placed in computed positions (see Experimental Section). If the direct metal–metal interactions are neglected, each rhenium atom exhibits an almost octahedral coordination.

The metal–metal bond lengths are similar to those found in the structure of the NEt_4^+ salt of the same anion,[8] while the bond parameters involving the carbonyl ligands show some differences and are much more accurate in the present case, since in our previous study, due to the poor quality of the X-ray data, the CO groups were constrained to linearity with a fixed C–O bond distance of 1.18 Å.

The two long hydrogen-bridged Re–Re bonds, 3.189 (1) and 3.190 (1) Å, fall into the range usually found for Re(μ-H)Re interactions, 3.12–3.39 Å.[21]

The Re(μ-H)$_2$Re formal double bond, 2.789 (1) Å, is comparable with the corresponding bond in the NEt_4^+ salts of this anion, 2.821 (7) Å,[8] and of the related $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$, 2.797 (4) Å.[7a] These bond lengths are ca. 0.2 Å shorter than a normal unbridged Re–Re single bond, as, for instance, in $Re_2(CO)_{10}$, 3.041 (1) Å.[22] Analogous Re(μ-H)$_2$Re systems are known to be present in two dinuclear compounds, $R_2(\mu\text{-}H)_2(CO)_8$[4] and $Re_2(\mu\text{-}H)_2(CO)_6(dppm)$,[5] with Re–Re bonds of 2.896 (3) and 2.893 (2) Å, respectively, ca. 0.1 Å longer than in the trinuclear species. This is very likely due to the higher nonbonding repulsions involving the ligands normal to the Re(μ-H)$_2$Re plane in the Re_2 compounds.

In the saturated derivatives $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$, where a three-electron-donor X group has replaced a hydride, the Re(μ-H)(μ-X)Re bond lengths become quite longer than the Re(μ-H)$_2$Re ones (X = Cl,[11] 2.995 (2) Å; X = O_2CH,[12] 3.181 (1) Å).

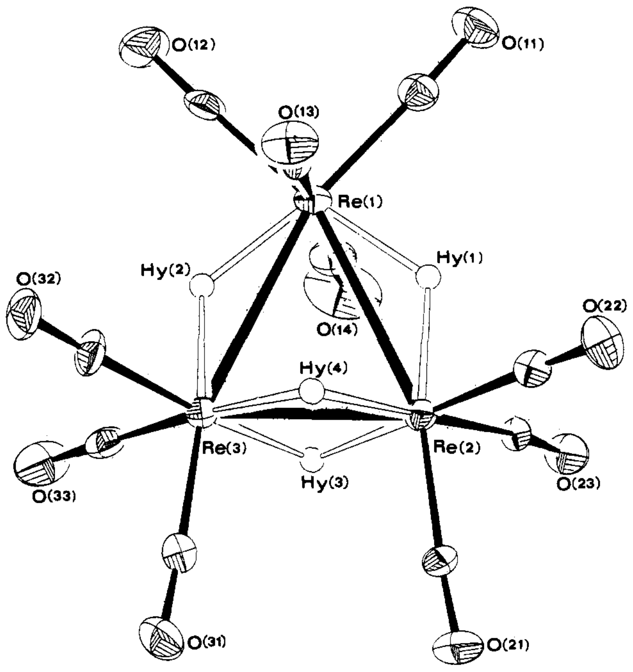

Figure 1. View of the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$, with the calculated hydridic positions. The carbonyl groups are indicated by the labels of their oxygen atoms.

The stereochemistry of the carbonyl ligands fully supports the indirect location proposed for the hydride ligands (see Experimental Section). The computed positions of Hy(1) and Hy(2), almost coplanar with the Re_3 triangle, show an outward displacement of these hydrides with respect to the intersection point of the transoid (OC) → Re vectors, as found for the hydrides of $Re_3(\mu\text{-}H)_3(CO)_{11}(PPh_3)$ by neutron diffraction study.[23] On the

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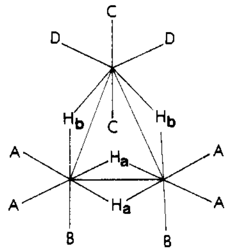
Chart I



contrary, Hy(3) and Hy(4) exhibit a small inward displacement toward the middle point of the Re(2)–Re(3) edge, a situation analogous to that observed in $Os_3(\mu\text{-}H)_2(CO)_{10}$[3] and in the other $M(\mu\text{-}H)_2M$ systems.[6a] The computed Hy(3)···Hy(4) contact, 2.43 Å, compares well with the corresponding contact in the Os_3 species, 2.376 (3) Å.[3]

The structures of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ and of $Os_3(\mu\text{-}H)_2(CO)_{10}$, with analogous carbonyl geometries, show differences (apart from those due to the covalent radii of the metals) related to the presence of the two additional hydrides in the rhenium compound. These hydrides cause a lengthening of the subtended Re–Re edges, while the two lateral Os–Os bonds are normal single bonds. The coordination within the $M(CO)_4$ moieties is different with regard to the equatorial carbonyl ligands, the M–M–C(cis) angles being on average larger and the C–M–C angle smaller in the Re than in the Os compound (Re–Re–C mean = 108.2°, Os–Os–C mean = 102.8°, C–Re–C = 91.6 (5)°, C–Os–C = 97.52 (6)°). A major difference consists of the fact that Re(2) and Re(3) attain a more regular octahedral coordination than the corresponding osmium atoms, for the presence of the hydrides Hy(1) and Hy(2). This strongly influences the folding in the $(CO)_2M(\mu\text{-}H)_2M(CO)_2$ moiety along the H···H axis, which is quite larger in the osmium than in the rhenium compound (dihedral angles between the $(CO)_2MH_2$ planes 137.6 vs. 163.8°).

The carbonyl groups belong to four classes with the following mean bond lengths: Re(1)–C(axial) = 2.000 Å, Re(1)–C(equatorial) = 1.946 Å (C–O for these groups bound to Re(1) 1.135 Å), Re(2,3)–C(equatorial) = 1.916 Å, and Re(2,3)–C(diagonal) = 1.909 Å (C–O for the groups bound to Re(2) and Re(3) 1.148 Å). The trend resembles that found in $Os_3(\mu\text{-}H)_2(CO)_{10}$, except for the inversion between the M–C interactions of the second and of the third class, involving the CO groups transoid to the two additional hydrides in the rhenium species.

NMR Analysis. ^1H and ^{13}C NMR spectroscopy confirm in solution the solid-state structure determined for the title compound.

Proton NMR spectra of the anion exhibit two high-field singlets at δ −8.54 and −13.36 (Me_4Si internal standard, room temperature, THF-d_8). The hydride resonances remain essentially unchanged throughout the temperature range −90 to +50 °C; even at 120 °C (Me_2SO-d_6) we could not see any significant change apart from some decomposition. The integration of these signals with respect to the hydrogen atoms in the cation indicates that both are due to two equivalent hydridic atoms. Comparison with the spectrum of $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$[24] allows the unambiguous assignment of the lower field signal to the two hydrides bridging the short Re–Re bond (H_a in Chart I). Similar low-field resonances are found in all analogous unsaturated species.[2a,6a]

$^{13}C\{^1H\}$ NMR spectra (natural abundance), recorded at variable temperature (−90 to +50 °C), always displayed four carbonyl resonances, viz. 196.7 ($\Delta\nu$ = 1.1 Hz), 187.4 ($\Delta\nu$ = 1.0 Hz), 184.9 ($\Delta\nu$ = 1.4 Hz), and 184.5 ($\Delta\nu$ = 1.5 Hz) ppm (−90 °C) of intensity ratios 2:1:1:1 (see Figure 2a). As the temperature is increased, a downfield shift up to 0.5 ppm is observed for the resonance at 187.4 ppm along with a considerable line broadening of all the signals.

The observed pattern of resonances suggests that the solid-state structure, of C_{2v} idealized symmetry, is retained in solution. The most intense peak is due to the four carbonyls A (Chart I), trans to the hydrides H_a bridging the short Re–Re bond, while the other resonances (each corresponding to two carbonyls) are not attributable on this simple basis.

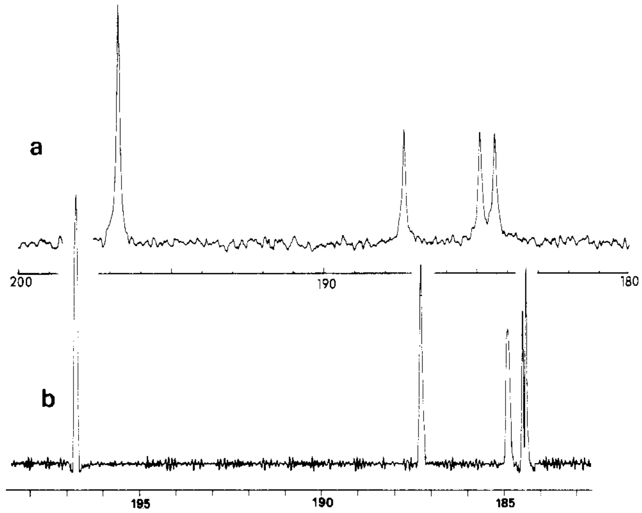


Figure 2. Carbonyl region of the NMR spectrum of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (natural-abundance sample, ca. 0.1 M in THF-d_8, 183 K): (a) $^{13}C\{^1H\}$ decoupled spectrum at 20.15 MHz; (b) ^{13}C–^1H-coupled spectrum at 50.31 MHz, with resolution enhancement.

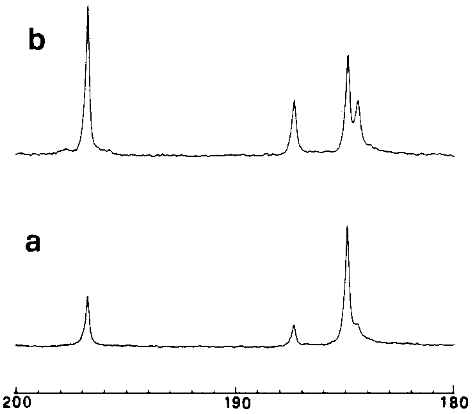


Figure 3. Carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of a sample of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (0.05 M in THF-d_8) stirred under CO atmosphere (90% ^{13}CO) for (a) 2.5 h and (b) 8 h (20.15 MHz, 183 K). After 48 h the $^{13}C\{^1H\}$ NMR spectrum appears nearly like that in Figure 2a.

A moderately ^{13}CO-enriched sample (ca. 30%) was prepared by stirring a solution of $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ in acetone under a ^{13}CO atmosphere. The ^{13}C NMR spectrum revealed that all carbonyls were effectively enriched, but the peak at 184.9 ppm was anomalously enhanced. To clarify this effect, the enrichment process was monitored by ^{13}C NMR, with spectra recorded at successive times within 2 days. Figure 3 shows that, with an increase in the time of contact, the relative enhancement of the peak at 184.9 ppm decreases as the statistical equilibrium between the free and coordinated ^{13}CO is approached. This behavior indicates that (i) carbon monoxide exchange occurs with a higher rate for the carbonyls at 184.9 ppm but their selective enrichement can be detected only after short times of contact with ^{13}CO and (ii) any fluxional process of the carbonyls involved can be ruled out. Selective enrichment has been reported in only one previous occasion[25] due to the fact that fluxionality of ligands is more rapid than external CO exchange.

Selective irradiations at the resonances of the hydrides, performed on the 30% ^{13}C-enriched sample, allowed us to assign the signal occurring at 187.4 ppm to the carbonyls B, cis to the H_a

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(24) This species shows two hydridic signals, at δ −8.4 and −11.1 (intensity ratio 2:1); see ref 7.

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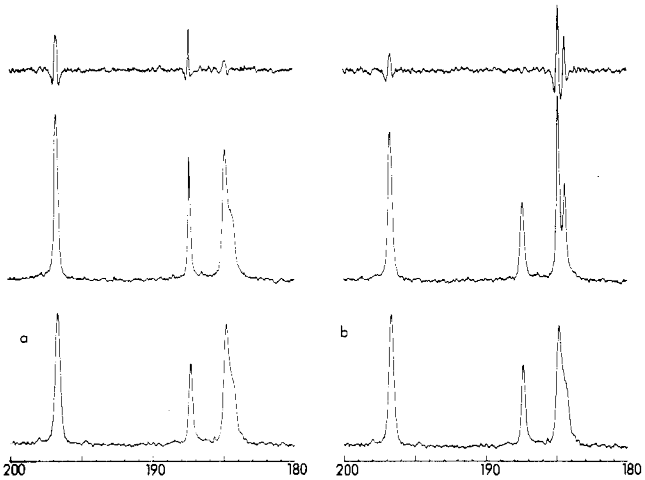

Figure 4. ^{13}C NMR selectively decoupled spectra of a ^{13}CO-enriched sample of the title compound (20.15 MHz, 183 K): (a) irradiation of H_a; (b) irradiation of H_b; (lower) off-resonance spectra; (middle) on-resonance spectra; (upper) difference spectra (64 scans with saturation field on resonance minus 64 scans with saturation field off resonance, followed by Fourier transformation).

hydrides (Chart I); in Figure 4a it is shown that, when H_a's are irradiated, the major effect is on the two downfield peaks. Saturation of H_b hydrides (Figure 4b) sharpens all the resonances, except the one occurring at 187.4 ppm, thus indicating absence of coupling between H_b and carbonyls B.

The assignment of carbonyls C and D was done on the basis of a ^{13}C–^{1}H-coupled spectrum (natural abundance, 50.31 MHz), where the only fine structure observed is a doublet occurring at 184.5 ppm whose inner separation is 4.8 Hz (Figure 2b). We assign this resonance to carbonyls D, since carbonyls C should give rise to a triplet because of their coupling with two equivalent hydrides (H_b).

These assignments allow the identification of carbonyls C as those selectively enriched. This feature can be related to the mutual trans labilization of these ligands.

In the $^{13}C\{^{1}H\}$ spectrum of the enriched compound $^{2}J_{C-C} = 3.7$ Hz is observable for the two downfield resonances; the spectrum results from the presence of different isotopomers, but due to the moderate enrichment, only strong singlets overlapping with weak doublets are visible. This ^{2}J value is in agreement with those observed[26] in the analogous hydridoosmium cluster $Os_3(\mu\text{-H})_2(CO)_{10}$ ($^{2}J_{C-C(cis)} = 3.2$ Hz).

The ^{17}O spectrum (natural abundance, 27.12 MHz) recorded at room temperature shows four resonances at 348.6, 339.9, 335.0, and 331.0 ppm (in CH_2Cl_2, relative to an external H_2O sample).

Scrambling of carbonyls at the apical position has been already ruled out. In order to check if an exchange process (on a time scale of the order of relaxation time) could occur between carbonyls A and B, a selective population transfer experiment, achieved with use of a DANTE sequence with cumulative flip angle of 180° on the resonance at 196.7 ppm, was performed at 30 °C. The longitudinal magnetization of the carbonyls B, monitored at variable delays after selective inversion of the aforementioned resonance, remained unchanged, thus indicating the absence of any detectable scrambling at these sites. A proton SPT experiment showed as well that there is not fluxionality between the hydrides.[27]

The reported results indicate an unusual rigidity of this system, different from other related species, e.g. $Os_3(\mu\text{-H})_2(CO)_{10}$, which shows a slow exchange process at 21 °C.[28] The ligand overcrowding in our rhenium species is responsible for this behavior. As a consequence, the generalized broadening of signals, observed on raising the temperature, cannot be ascribed to exchange processes, but rather to scalar coupling of the carbon atoms with ^{185}Re, ^{187}Re having $I = {}^{5}/_{2}$. Indeed, at lower temperatures the more effective quadrupole-induced Re spin relaxation decouples rhenium from carbon ("thermal decoupling"), decreasing the line width of signals.[29]

The "Amphoteric" Behavior of $[Re_3(\mu\text{-H})_4(CO)_{10}]^-$. It is well-known that hydridic ligands in transition-metal complexes can display either an acidic (H^+) or a basic (H^-) behavior. Our previous studies[9–15] on the reactivity of the anion $[Re_3(\mu\text{-H})_4(CO)_{10}]^-$ pointed out the hydridic nature of the H ligands of the $Re(\mu\text{-H})_2Re$ system, which are abstracted as H^- by reaction with acids. This suggests that the anionic charge should be mainly localized on the unsaturated moiety as supported also by a local electron count. The hydrides bridging the longer triangular edges of the anion, on the contrary, seem to have a different polarization and to show some acidic character: indeed, we have now found that they can be selectively abstracted upon treatment with $(NBu_4)OH$,[30] in a reaction inverse to that previously described for the synthesis of the compound (see Experimental Section):

$$[Re_3(\mu\text{-H})_4(CO)_{10}]^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Re_3(\mu\text{-H})_3(CO)_{10}]^{2-} + H_2O$$

The presence of two types of hydrides, the first one able to react with H^+ (giving H_2) and the second one with OH^- (giving H_2O), makes the anion $[Re_3(\mu\text{-H})_4(CO)_{10}]^-$ uncommon if not unique.

Experimental Section

The reactions were performed in deoxygenated solvents anhydrified by standard methods. The title compound is air stable, and its manipulation was accomplished without undue cautions.

Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer, in 0.1 mm CaF_2 cells, and were calibrated against polystyrene absorptions.

NMR Measurements. NMR spectra were recorded on a Bruker WP 80 SY spectrometer operating at 80.13 MHz for ^{1}H and 20.15 MHz for ^{13}C. Accumulations of 64–400 transients were performed at each temperature at a spectral width of 1000 Hz. Sample temperatures were controlled by using the temperature control unit B-VT 1000 of the spectrometer with an accuracy of approximately ±1 °C.

The 90° pulse width was 4.3 μs for ^{1}H and 11.5 μs for ^{13}C. All chemical shifts are reported downfield positive with respect to internal Me_4Si. The solutions, in deuterated THF (unless otherwise indicated), were typically 0.1 M.

Selective population transfer experiments, in the case of ^{1}H, were performed with use of the Forsên–Hoffman method.[31] In the case of ^{13}C a DANTE[32] pulse sequence of 20 on-resonance pulses of 1.17 μs duration, spaced by 0.2 ms, produced the best inversion.

Coupled NMR spectra were obtained on a Varian XL 200 spectrometer operating at 50.31 MHz. The 90° pulse width was 16.5 μs.

^{17}O spectra (natural abundance) were obtained on a Varian XL 200 spectrometer operating at 27.12 MHz. The sample, dissolved in CH_2Cl_2, was contained in a 10-mm tube; the 90° pulse width was 16 μs. Chemical shifts reported are relative to a H_2O external sample.

Synthesis of $[Re_3(\mu\text{-H})_4(CO)_{10}](NEt_4)$ (1). (a) Synthesis from $[ReH_2(CO)_4](NEt_4)$. The reaction and all the manipulations until the isolation of $[Re_3(\mu\text{-H})_3(CO)_{10}](NEt_4)_2$ were performed under N_2. A 2.4-g amount of $[ReH_2(CO)_4](NEt_4)$ (5.6 mmol), obtained as previously described,[33] was treated with 5 mL of anhydrous ethanol and refluxed in a two-necked vessel. The color of the solution turned rapidly from cream to red, and a precipitate of $[Re_3(\mu\text{-H})_3(CO)_{10}](NEt_4)_2$ began to separate in a few hours. After 24 h the hot solution was tranferred into another vessel and the precipitate was washed five times with 5 mL of boiling ethanol and then dried under vacuum (yield 754 mg). The

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(27) This has been confirmed by the preparation of $[Re_3(\mu\text{-H})_3(\mu\text{-D})(CO)_{10}]^-$, obtained by treatment of $[Re_3(\mu\text{-H})_3(CO)_{10}]^{2-}$ with a stoichiometric amount of CF_3COOD in CD_2Cl_2. ^{1}H NMR spectra showed an intensity ratio $H_b/H_a = 0.6$, unchanged in successive spectra. This rules out the possibility of a scrambling which would equalize the integrals of the two signals. The difference from the theoretical ratio (0.5) was due to traces of water: it is well-known that protonation reactions have a very high isotopic effect.

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Table II. Final Positional Parameters within the Salt $[Re_3(\mu\text{-}H)_4(CO)_{10}](PPN)$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Re(1)	0.13491 (5)	0.24191 (4)	−0.01512 (2)	C(122)	0.952 (1)	0.367 (1)	0.1626 (4)
Re(2)	0.38385 (5)	0.17114 (4)	0.03040 (2)	C(123)	0.915 (1)	0.448 (1)	0.1354 (5)
Re(3)	0.39390 (5)	0.30917 (4)	−0.03670 (2)	C(124)	0.860 (1)	0.427 (1)	0.0972 (5)
C(11)	0.007 (1)	0.160 (1)	0.0066 (5)	C(125)	0.836 (1)	0.327 (1)	0.0847 (5)
O(11)	−0.0694 (9)	0.114 (1)	0.0179 (4)	C(126)	0.872 (1)	0.243 (1)	0.1108 (4)
C(12)	0.024 (1)	0.316 (1)	−0.0537 (6)	C(131)	1.092 (1)	0.2044 (9)	0.2203 (4)
O(12)	−0.045 (1)	0.359 (1)	−0.0756 (5)	C(132)	1.081 (1)	0.213 (1)	0.2625 (5)
C(13)	0.158 (1)	0.131 (1)	−0.0573 (4)	C(133)	1.174 (1)	0.251 (1)	0.2889 (5)
O(13)	0.1759 (9)	0.0663 (9)	−0.0802 (3)	C(134)	1.280 (1)	0.278 (1)	0.2737 (4)
C(14)	0.136 (1)	0.351 (1)	0.0304 (5)	C(135)	1.292 (1)	0.267 (1)	0.2320 (5)
O(14)	0.141 (2)	0.413 (1)	0.0559 (5)	C(136)	1.198 (1)	0.229 (1)	0.2045 (5)
C(21)	0.552 (1)	0.157 (1)	0.0439 (4)	C(211)	0.695 (1)	0.278 (1)	0.2103 (4)
O(21)	0.6497 (9)	0.144 (1)	0.0536 (4)	C(212)	0.616 (1)	0.303 (1)	0.1775 (5)
C(22)	0.366 (1)	0.021 (1)	0.0360 (4)	C(213)	0.590 (2)	0.410 (1)	0.1679 (6)
O(22)	0.356 (1)	−0.0680 (8)	0.0402 (4)	C(214)	0.645 (1)	0.486 (1)	0.1927 (5)
C(23)	0.359 (1)	0.195 (1)	0.0875 (4)	C(215)	0.724 (1)	0.464 (1)	0.2251 (5)
O(23)	0.3529 (9)	0.215 (1)	0.1215 (3)	C(216)	0.749 (1)	0.357 (1)	0.2341 (4)
C(31)	0.562 (1)	0.308 (1)	−0.0384 (5)	C(221)	0.631 (1)	0.0596 (9)	0.1916 (4)
O(31)	0.663 (1)	0.3123 (9)	−0.0402 (4)	C(222)	0.657 (1)	0.022 (1)	0.1538 (4)
C(32)	0.369 (2)	0.299 (1)	−0.0959 (4)	C(223)	0.572 (1)	−0.035 (1)	0.1288 (5)
O(32)	0.353 (1)	0.2910 (9)	−0.1312 (3)	C(224)	0.465 (1)	−0.053 (1)	0.1427 (5)
C(33)	0.393 (1)	0.459 (1)	−0.0403 (4)	C(225)	0.440 (1)	−0.017 (1)	0.1804 (5)
O(33)	0.399 (1)	0.5500 (8)	−0.0454 (5)	C(226)	0.523 (1)	0.039 (1)	0.2056 (4)
P(1)	0.9698 (3)	0.1574 (2)	0.1855 (1)	C(231)	0.722 (1)	0.1221 (9)	0.2753 (4)
P(2)	0.7372 (3)	0.1431 (2)	0.2211 (1)	C(232)	0.647 (1)	0.180 (1)	0.2979 (5)
N	0.8686 (8)	0.1158 (8)	0.2120 (3)	C(233)	0.637 (1)	0.160 (1)	0.3392 (5)
C(111)	1.029 (1)	0.0515 (9)	0.1561 (4)	C(234)	0.701 (1)	0.081 (1)	0.3593 (5)
C(112)	1.081 (1)	0.068 (1)	0.1206 (4)	C(235)	0.773 (1)	0.021 (1)	0.3377 (5)
C(113)	1.131 (1)	−0.015 (1)	0.0997 (5)	C(236)	0.786 (1)	0.041 (1)	0.2957 (5)
C(114)	1.129 (1)	−0.115 (1)	0.1162 (5)	HY(1)[a]	0.2212	0.1663	0.0244
C(115)	1.078 (1)	−0.133 (1)	0.1522 (5)	HY(2)	0.2348	0.3304	−0.0390
C(116)	1.023 (1)	−0.051 (1)	0.1728 (4)	HY(3)	0.4079	0.3109	0.0208
C(121)	0.932 (1)	0.2624 (9)	0.1497 (4)	HY(4)	0.4005	0.1624	−0.0270

[a] Computed positions (see text).

mother liquors and the washing ethanol were collected and concentrated to about 5 mL and then refluxed again. After 24 h the new precipitate was separated in the same way (yield 347 mg). The procedure was repeated once again, leading to an additional 172 mg of precipitate. All the fractions of precipitate were collected and purified through crystallization, by slow diffusion of ethanol in a concentrated acetone solution: 952 mg (0.86 mmol) of $[Re_3(\mu\text{-}H)_3(CO)_{10}](NEt_4)_2$ were obtained as large needle-shaped red crystals (yield of 46%, based on Re atoms). The compound was dissolved in the minimum amount of acetone and treated with the stoichiometric ratio of aqueous $HClO_4$ (1 M). The color turned immediately to yellow and, upon addition of water, a precipitate of $[Re_3(\mu\text{-}H)_4(CO)_{10}](NEt_4)$ was separated (806 mg, 0.83 mmol, after drying under vacuum, yield 96%).

(b) Synthesis from $[Re_3(\mu\text{-}H)_2(CO)_{12}](NEt_4)$. A sample of 100 mg (0.097 mmol) of $[Re_3(\mu\text{-}H)_2(CO)_{12}](NEt_4)$, obtained by deprotonation of $Re_3(\mu\text{-}H)_3(CO)_{12}$,[17] was dissolved in 1 mL of anhydrous tetrahydrofuran and introduced in an autoclave under 100 atm of H_2, at 100 °C, for 24 h. Analysis by ^1H NMR showed that the product of the reaction was mainly compound **1** (ca. 75%), together with unidentified nonhydridic compounds. Crystallization by slow diffusion of diethyl ether into a concentrated dichloromethane solution afforded yellow thin tabular crystals of pure compound **1** (60 mg, isolated yield 64%). The PPN^+ salt of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ was obtained upon addition of water to a methanolic solution containing the NEt_4^+ salt and an excess of (PPN)Br. Crystals suitable for X-ray analysis were grown by slow diffusion of a mixture of ethanol and *n*-heptane into an acetone solution.

Reaction of 1 with CO. (a) Compound **1** (20 mg, 0.02 mmol) in deuterioacetone was kept in a NMR tube, under CO atmosphere, at room temperature for 48 h. ^1H NMR spectra, recorded at different times, did not reveal any significant reaction process. (b) Compound **1** (50 mg, 0.051 mmol) was kept in an autoclave, under 50 atm of CO, at room temperature for 60 h. ^1H NMR analysis showed only the presence of unreacted **1** and of $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$, about 15% and 50%, respectively, by integration vs. the cationic signals. The IR spectrum confirmed the dominant presence of $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ and suggested also the formation of some $Re_2(CO)_{10}$, which was isolated upon extraction with *n*-pentane (yielded ca. 25%).

Reaction of 1 with $(NBu_4)OH$. Compound **1** (18 mg, 0.019 mmol) in tetrahydrofuran (2 mL, distilled directly in the reaction vessel over sodium benzophenone ketyl) was treated with $(NBu_4)OH$ (0.2 mL of a solution 0.1 N in benzene–methanol). The color of the solution turned in a few minutes from yellow to red. Infrared spectra showed transformation of **1** into $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$, complete after about 1 h. No other products were detected by ^1H NMR analysis of the reaction mixture.

X-ray Analysis. Crystal Data: $C_{46}H_{34}NO_{10}P_2Re_3$, M_r = 1381.3; monoclinic, space group $P2_1/c$ (No. 14), with cell constants a = 11.327 (3) Å, b = 12.672 (2) Å, c = 32.183 (6) Å, β = 95.08 (2)°, V = 4601.3 Å^3, D_{calcd} = 1.99 g cm^{-3} for Z = 4, and $F(000)$ = 2608; Mo Kα radiation (λ = 0.71073 Å), μ(Mo Kα) = 81.05 cm^{-1}.

Intensity Measurements. A yellow crystal of dimensions 0.10 × 0.19 × 0.34 mm was mounted on a glass fiber in the air and transferred to an automated Enraf-Nonius CAD4 diffractometer. The setting angles of 25 random intense reflections ($16 < 2\theta < 25°$) were used to determine by least-squares fit accurate cell constants and orientation matrix. The data collection was performed, with use of graphite-monochromated Mo Kα radiation, by the ω-scan method, within the limits $3 < \theta < 25°$. A variable scan speed (from 2 to 20°/min) and a variable scan range of $(0.8 + 0.35 \tan \theta)°$ were used, with a 25% extension at each end of the scan range for background determination. The total number of collected reflections was 8035. The intensities of three standard reflections were measured every 2 h of X-ray exposure, and no significant decay was observed. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied, on the basis of ψ scans (ψ 0–360° every 10°) of suitable reflections with χ values close to 90°; the maximum, minimum, and average relative transmission values were 1.00, 0.48, and 0.82, respectively. A set of 4622 independent significant reflections, with $I > 3\sigma(I)$, was used in the structure solution and refinement.

Structure Solution and Refinements. All computations were performed on a PDP 11/34 computer, using the Enraf-Nonius structure determination package (SDP) and the physical constants therein tabulated.

The structure solution was based on the deconvolution of a three-dimensional Patterson map, which gave the positions of the metal atoms. After a preliminary refinement of their parameters, a successive difference-Fourier map showed the locations of all the non-hydrogen atoms.

The refinements were carried out by full-matrix least-squares methods. Anisotropic thermal factors were assigned to all atoms, except to the phenyl carbon atoms of the cation. The phenyl hydrogen atoms were located in their idealized positions (C–H = 0.95 Å), with isotropic thermal factors of 5.0 Å^2, after each cycle of refinement, but not refined. Weights were assigned according to the formula $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$

$= \sigma(F_o^2)/2F_o$) and $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{1/2}/Lp$, the fudge factor A being assumed equal to 0.03.

The final values of the conventional R and R_w agreement indices were 0.042 and 0.053, respectively.

The final difference-Fourier map showed some residual peaks of up to ca. 1.5 e Å^{-3}, close to the rhenium atoms, which prevented a direct location of the hydridic atoms. Fourier maps, computed at decreasing values of $(\sin\theta)/\lambda$), did not show peaks suitable for these atoms. They were placed in idealized positions but not included in the structure factor calculations. The locations were calculated by determining the intersection point of the two (CO)–Re vectors trans to each hydride. This led to two different situations: the hydrides bridging the long Re–Re edges and almost lying in the Re_3 plane (Hy(1) and Hy(2)) gave mean Re–H and Re–H–Re bond parameters of 1.70 Å and 140°, while the hydrides bridging the short metal-metal bond (Hy(3) and Hy(4)) gave corresponding mean values of 1.94 Å and 92°. We have then moved the hydrides along the lines defined by these calculated points and the centers of the subtended Re–Re edges, ca. 0.30 Å outward in the first case (up to mean Re–H and Re–H–Re parameters of 1.82 Å and 122°) and slightly inward (ca. 0.12 Å) in the second case (up to mean Re–H and Re–H–Re parameters of 1.86 Å and 97°). The final bond parameters result quite similar to analogous interactions determined by neutron diffraction studies.[3,6a,23]

The final positional parameters are reported in Table II.

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Registry No. **1**, 64478-51-9; $[ReH_2(CO)_4](NEt_4)$, 67047-76-1; $[Re_3(\mu\text{-}H)_3(CO)_{13}](NEt_4)_2$, 60544-31-2; $[Re_3(\mu\text{-}H)_2(CO)_{12}](NEt_4)$, 96791-00-3; $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$, 51779-06-7; $[Re_3(\mu\text{-}H)_4(CO)_{10}](PPN)$, 96760-23-5; $Re_3(\mu\text{-}H)_3(CO)_{12}$, 73463-62-4.

Supplementary Material Available: Tables of thermal parameters, calculated positions for the hydrogen atoms, and observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Energy Transfer vs. Electron Transfer in the Excited-State Quenching of Tris(2,2′-bipyridine-*N*,*N*′)ruthenium(II) Complexes by Cobalt(III) Cage Complexes: Applications to the Photoreduction of Water

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A variety of cobalt cage complexes act as electron-transfer agents (ETA) in the $[Ru(bpy)_3]^{2+}$/ETA/Pt(PVA)/edta-mediated photoreduction of water (bpy = 2,2′-bipyridine; Pt(PVA) = colloidal platinum dispersion on polyvinyl alcohol; edta = 1,2-ethanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid). At pH 5.0 a very narrow potential range of the Co(III)/Co(II) couple (~−0.25 to −0.42 V vs. NHE) is suitable for acceptably efficient ($0.05 \lesssim \Phi(^1/_2H_2) \lesssim 0.10$) photoreduction of water. The most effective cage complex is $[Co(CLsar)]^{3+}$ (CLsar = 1-chlorosar = 1-chloro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane). At 4×10^{-3} M, methylviologen (mv^{2+}) and $[Co(CLsar)]^{3+}$ are comparable in their abilities to produce hydrogen, while at 2×10^{-3} M, mv^{2+} is about 3 times as efficient. The narrow bell-shaped potential vs. rate of H_2 production curve obtained is due to the lack of thermodynamic driving force for water reduction at more positive potentials and an increased competition of energy-transfer over electron-transfer quenching of $[Ru^*(bpy)_3]^{2+}$ at more negative potentials. With $[Ru(4,4'\text{-}Me_2bpy)_3]^{2+}$ as sensitizer, the curve is displaced to more negative potentials in concert with the greater reducing power of its excited state compared with that of $[Ru^*(bpy)_3]^{2+}$. The quenching constants observed for the cage complexes reacting with the Ru(II) excited states are generally lower than those of viologen molecules of the same electrochemical potential. This partially explains the increased concentrations of cage complexes required to obtain maximum rates of H_2 production. The sulfur-containing capten cobalt cage complexes (capten = 1-methyl-6,13,19-triaza-3,10,16-trithiabicyclo[6.6.6]eicosane) and sar cage complexes with potentials $\gtrsim -0.2$ V vs. NHE are very efficient oxidative quenching agents for $[Ru^*(bpy)_3]^{2+}$ with quenching rate constants approaching those of mv^{2+} and quantum yields approaching unity. Thus solvent-cage escape before back electron transfer is not considered a limiting factor to oxidative quenching by cage complexes in contrast to the case for viologens. Although the reduction potentials of these complexes are too high (~0 V vs. NHE) at pH 5.0 for reduction of water, at pH ~0 quantum yields for H_2 production approach unity. Cage complexes based on sar with neutral substituents become more effective quenching agents of the excited states of the ruthenium sensitizers as the Co(III)/Co(II) redox potential is made more positive. Those with potentials more positive than −0.34 V vs. NHE quench $[Ru^*(bpy)_3]^{2+}$ exclusively ($\gtrsim 95\%$) by electron transfer; however, their ability to produce hydrogen at pH 5.0 is limited by zero to unfavorable free energy changes. By contrast, electron transfer contributes less than 50% to the quenching of $[Ru^*(4,4'\text{-}Me_2bpy)_3]^{2+}$ by cage complexes. The major advantage of the cage complexes is their long-term stability in the photochemical cycles compared to that of viologens.

Introduction

There are now available a large variety of encapsulated cage complexes of Co(III),[2-14] which are substitution inert in both the Co(III) and Co(II) oxidation states.[2,4-8,10-15] The kinetic inertness of the Co(II) states is unusual, and it allows the Co(II)/Co(III) oxidation states to be cycled without loss of complex integrity.

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