



Reduction of Ammonium Pertechetate and Ammonium Perrhenate with CO: Synthesis of $M_2(CO)_{10}$ (M: Tc, Re) and Crystal and Molecular Structure of the Trinuclear Cyano-Bridged Derivative $Re_3(CN)_3(CO)_{12}$

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**REDUCTION OF AMMONIUM PERTECHNETATE AND
AMMONIUM PERRHENATE WITH CO: SYNTHESIS OF
 $M_2(CO)_{10}$ (M = Tc, Re) AND CRYSTAL AND MOLECULAR
STRUCTURE OF THE TRINUCLEAR CYANO-BRIDGED
DERIVATIVE $Re_3(CN)_3(CO)_{12}$ (*) (**)**

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(**) Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic
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Summary - The reaction of the tetra-oxo MO_4^- anions with CO under pressure and at temperatures around 290 °C (Re) or 200 °C (Tc) leads to the corresponding decacarbonyls $\text{Re}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$, in yields as high as 69% (Re) or almost quantitative (Tc). The ammonium counteranion (NH_4^+) is an essential pre-requisite for the carbonylation of the tetra-oxo anions, although the $[\text{N-}n\text{-Bu}_4]^+$ or the $[\text{N-}(n\text{-C}_8\text{H}_{17})_4]^+$ cations led to satisfactory results in the case of ReO_4^- . The trimeric cyano-complex $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$ forms as a by-product in the reaction of ReO_4^- ; its crystal and molecular structure was solved by X-ray diffraction methods. *Crystal data* for $\text{C}_{15}\text{N}_3\text{O}_{12}\text{Re}_3$, MW 972.9: orthorhombic; space group $Pna2_1$; $a = 20.639(3)$, $b = 6.705(3)$, $c = 16.657(3)$ Å, $V = 2305(1)$ Å³; $Z = 4$; $D_c = 2.802$ g cm⁻³; μ (Mo- K_α) = 159.7 cm⁻¹; $R_w = 0.036$. The molecular structure consists of a cyano-bridged trimer, the rhenium atom being in a pseudo-octahedral coordination of four carbonyl groups, the other two coordination sites being occupied by atoms from bridging cyano groups.

When a metal derivative is to be converted to the corresponding metal-carbonyl complex in the zero-valent state or lower, usually the crucial point is the choice of the reducing system. Molecular hydrogen, as the CO/H₂ mixture¹, an alkali metal in an ethereal solvent², an alkylating agent³ or the Zn/Mg mixture in pyridine⁴ have been used. In some cases, CO functions as both the reducing agent and the ligand: this is generally limited to metal oxides or metal chlorides, the corresponding oxidation products being CO₂ or COCl₂, respectively. The use of CO in combination with metal oxides is exemplified by osmium^{1c}, rhenium⁵, rhodium⁶ and, more recently⁷, by molybdenum, tungsten, cobalt and iron. The preparation of AuCOCl from anhydrous gold(III) chloride and CO in thionyl chloride has been reported⁸. In this connection, also the preparations of K[Co(CO)₄] and Ni(CO)₄ from Co(II) and Ni(II) salts, respectively, in strong alkaline solution⁹ are to be mentioned.

Concerning the metal carbonyls of Group 7¹⁰ Hieber and Fuchs⁵ reported that $\text{Re}_2(\text{CO})_{10}$ can also be obtained by carbonylating KReO_4 with CO under drastic conditions (270 °C, 500 atm of CO). The use of the co-reductant copper has been introduced subsequently^{11a,b}.

We now report that NH_4ReO_4 and NH_4TcO_4 can be reduced by CO giving the corresponding decacarbonyls $\text{Re}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$ without any additional reducing agent. In the case of rhenium, the carbonylation yields a cyano-bridged by-product whose crystal and molecular structure has been solved by single crystal X-ray diffraction methods. The carbonylation of NH_4ReO_4 to $\text{Re}_2(\text{CO})_{10}$ has been reported in a preliminary communication¹².

EXPERIMENTAL

Unless otherwise stated, all operations were carried out in an atmosphere of prepurified nitrogen. Solvents were dried by conventional methods.

Infrared spectra were recorded with Perkin-Elmer mod. 283 and 580B instruments equipped with grating on solutions or Nujol mulls of the compounds prepared under exclusion of moisture and oxygen. UV-VIS spectra were recorded using a Cary 17D spectrophotometer.

Crystalline NH_4TcO_4 was obtained from 0.1 M ammonia solutions (Radiochemical Centre, Amersham, UK) after evaporation of the solvent at atmospheric pressure; after drying *in vacuo* at room temperature, it was stored over CaCl_2^a .

SYNTHESIS of $\text{Re}_2(\text{CO})_{10}$

Ammonium perrhenate, NH_4ReO_4 , (9.92 g, 37.0 mmol) was introduced in a 700 ml stainless-steel autoclave; after evacuation, dry toluene (200 ml) was introduced by suction and commercially available CO (containing 3% of dihydrogen) was compressed up to about 90 atm at room temperature. The autoclave was shaken and heated at 290 °C for 40 h. The gas was vented [CO_2 was detected by precipitation with aqueous $\text{Ba}(\text{OH})_2$] and the content of the autoclave, consisting of a yellow solution and some grey solid (*vide infra*) was filtered, no special precaution being used for avoiding the admission of air^b. The solution was evaporated to small volume *in vacuo* and then cooled to about -30 °C. The solid $\text{Re}_2(\text{CO})_{10}$ which crystallized out was filtered and dried *in vacuo* (7.4 g, 61.3% yield). The carbonyl was found to be spectroscopically pure in comparison with an authentic sample (ν_{CO} , toluene: 2069 ms , 2008 vs and 1971 s cm^{-1}).

No carbonylation of rhenium was observed when the reaction temperature was decreased to 250 °C, other conditions being essentially the same as described above. Also, no carbonylation of rhenium was observed when NH_4ReO_4 (1.55 g; 5.8 mmol) suspended in dry toluene (50 ml) was treated in a 110 ml stainless-steel autoclave with a 1:1 CO/H_2 mixture (80 atm pressure at room temperature) at 290 °C for 10 h. No IR carbonyl absorption bands were present in the solution after

^a CAUTION. Technetium-99 emits low-energy (292 keV) β -particles with a half-life of 2.12×10^5 years. When this material is handled in milligram amounts, it does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the relatively low energy of the β -particle emission; however, normal radiation safety procedures must be used at all times to prevent contamination.

^b Similar results were obtained if the autoclave content was handled under exclusion of air.

this treatment.

ATTEMPTED CARBONYLATION OF KReO_4

Potassium perrhenate, KReO_4 , (0.99 g, 3.4 mmol) was introduced in a 110 ml stainless-steel autoclave; after evacuation, dry toluene (25 ml) was introduced by suction and commercially available CO (containing 3% of dihydrogen) was compressed up to about 90 atm. The autoclave was shaken and heated at 290 °C for 24 h. The gas was vented and an IR spectrum of the solution revealed no carbonyl absorptions in the carbonyl stretching region.

CARBONYLATION OF $[\text{NOct}_3\text{H}]\text{ReO}_4$, (Oct = *n*-octyl)

A mixture of tri-*n*-octylamine (2 ml, 4.6 mmol) and water (50 ml) was treated with 37% hydrochloric acid (6 ml). KReO_4 (1.3 g, 4.5 mmol) was then added to the suspension and, after 2 h stirring at room temperature, the mixture was extracted with toluene (5 x 10 ml) and the combined toluene extracts were washed with water to neutrality and dried over CaCl_2 . The solution was evaporated to 25 ml *in vacuo*, transferred by suction in a 110 ml stainless-steel autoclave and pressurized with 100 atm (at room temperature) of CO freed from dihydrogen. After 15 h at 100 °C, the gas was vented and an infrared spectrum in the carbonyl stretching region showed no carbonyl absorptions in the 2100-1900 cm^{-1} region. The autoclave was pressurized once again with 100 atm of H_2 -free carbon monoxide and heated at 270 °C for 30 h. The gas was discharged and found to contain significant amounts of dihydrogen (by gas-chromatography). An IR spectrum of the solution in the carbonyl stretching region revealed absorptions due to $\text{Re}_2(\text{CO})_{10}$ and to unidentified carbonyl derivatives with bands at 2110w, 2040ms, 1930ms and 1885m cm^{-1} which could not be isolated. The solvent was partially removed *in vacuo*, pentane was added and the solution cooled at -30 °C. The colourless crystals which separated were filtered and dried *in vacuo* affording 0.34 g (23% yield with respect to KReO_4) of pure (IR) $\text{Re}_2(\text{CO})_{10}$.

CARBONYLATION OF $[\text{NBu}_4][\text{ReO}_4]$ (Bu = *n*-butyl)

Tetra-*n*-butylammonium perrhenate (2.27 g, 4.6 mmol), prepared from NH_4ReO_4 and NBu_4I in aqueous solution, was introduced in a 110 ml stainless-steel autoclave; after evacuation, dry toluene

(50 ml) was introduced by suction and commercially available CO (containing 3% of dihydrogen) was compressed up to about 90 atm at room temperature. After 48 h at 290 °C, the gas was vented and the IR spectrum of the solution revealed the presence of $\text{Re}_2(\text{CO})_{10}$. The autoclave content was filtered from traces of grey insoluble material (*vide infra*). On cooling at dry-ice temperature, the filtrate gave colourless crystals (1.12 g; 72% yield) of spectroscopically (IR) pure $\text{Re}_2(\text{CO})_{10}$.

ISOLATION OF $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$

Ammonium perrhenate, NH_4ReO_4 (10.4 g, 38.8 mmol), suspended in toluene (200 ml) was carbonylated with hydrogen-free CO (100 atm at room temperature) at 250-280 °C for 48 h^c. After carbonylation, a known amount of gas was withdrawn and found (gas-chromatographically) to contain an amount of H_2 corresponding to about 5 mmol in the gas phase totally. The reaction mixture was filtered, the light-yellow solution dried in vacuo at room temperature and the residue sublimed at 70 °C/ 10^{-2} Torr affording 8.78 g (69% yield) of $\text{Re}_2(\text{CO})_{10}$. The grey solid (1.58 g) substantially insoluble in toluene was extracted with tetrahydrofuran (50 ml) under reduced pressure (bath temperature about 40 °C). On cooling at about -30 °C, the colourless solution yielded 0.09 g (0.7% yield) of $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$ as air-stable colourless crystals, slightly soluble in THF and acetone, practically insoluble in hydrocarbons, *Elem. anal.*, found % (calcd. for $\text{C}_{15}\text{N}_3\text{O}_{12}\text{Re}_3$): C, 18.4 (18.5); H, 0.0 (0.0); N, 4.1 (4.3). IR (THF): 2109_w, 2103_w, 2027_{vs}, 1994_{s-br}, 1986_{s-br} and 1969_m cm^{-1} ; (Nujol mull): 2174_w, 2156_w, 2109_m, 2099_m, 2034_m, 2004_s, 1955_{vs} and 580_s cm^{-1} .

X-RAY DATA COLLECTION AND STRUCTURE REFINEMENT OF $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$

A colourless prismatic crystal with dimensions (mm) 0.28 x 0.08 x 0.05, protected in a glass capillary, was mounted on a computer-controlled Philips PW 1100 single-crystal diffractometer, equipped with graphite-monochromatized Mo- K_α , radiation ($\lambda = 0.71069$ Å). The crystals are orthorhombic. The cell dimensions, determined by a least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging between 17 and 20°, are: $a = 20.639(3)$, $b = 6.705(3)$, $c = 16.657(3)$, $V = 2305.1$ Å³. The space group is $Pna2_1$ (from systematic extinctions and intensity

^c The trimeric compound was formed also when reagent-grade CO (containing about 3% of H_2) was used.

statistics). The calculated density for four trimeric $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$ molecules (MW = 972.9) in the unit cell is 2.802 g cm^{-3} . The absorption coefficient for Mo- K_α is $\mu = 159.7 \text{ cm}^{-1}$.

The intensities were collected at room temperature up to $2\theta = 50^\circ$; the $\omega - 2\theta$ scan technique was employed, the scan range being 1.4° and the speed 0.05 deg s^{-1} . A total of 2367 independent reflections were measured, of which 1081, having $I < 3\sigma(I)$ were considered as “unobserved” and excluded from the refinement. Three standard reflections, which were measured periodically, showed no apparent variations in intensity during data collection. The data were corrected for Lorentz and polarization factors. During the refinement, an empirical absorption correction was applied according to the method of Walker and Stuart¹³; the correction factors were in the range 0.83-1.41.

The structure was solved by Patterson and Fourier methods and refined by the full-matrix least-squares method with SHELX 76¹⁴ package of programmes. The quantity minimized was $\sum w(|F_0| - |F_c|)^2$. The refinement converged to $R_{\text{unweighted}} = 0.030$ and $R_{\text{weighted}} = 0.036$ $\{R_w = [\sum w(|F_0| - |F_c|)^2]^{1/2} / (\sum w F_0^2)^{1/2}; w^{1/2} = 1/\sigma(F_0)\}$ for 150 parameters and 1286 observed reflections. Anisotropic thermal parameters were refined for rhenium atoms only.

Due to the presence of the heavy rhenium atoms, the accuracy of the light atom positions is not good, as indicated by the high values of their positional e.s.d.'s. In particular, the distinction between carbon and nitrogen atoms in the bridging CN groups was difficult. Some attempts were made by refining the interchanged C and N positions or by assuming several unsymmetrical arrangements of cyano ligands. The results are substantially identical within the limits of error, with only small variations in the isotropic thermal parameters.

The atomic scattering factors were taken from ref. 14 for O, N and C and from ref. 15 for Re; the correction for anomalous dispersion was included. The atomic coordinates are listed in table 1. Anisotropic thermal parameters for Re, and isotropic thermal parameters for the other atoms and structure factor tables have been deposited as Supplementary Material. Copies can be obtained from Società Chimica Italiana, Viale Liegi 48, I-00198 Roma, Italy, upon full citation of the present article.

TABLE 1. FRACTIONAL ATOMIC COORDINATES OF $\text{Re}_3(\text{CN})_3(\text{CO})_{12}^a$

Atom	X/a	Y/b	Z/c	Ueq
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Re1	1216(2)	173(5)	10000(-)	362(11)
Re2	-797(1)	-2816(1)	8424(3)	342(3)
Re3	1125(1)	149(4)	6855(1)	308(10)
O1	2029(17)	-3599(59)	9512(24)	769(114)
O2	512(23)	3994(70)	10473(23)	721(117)
O3	2474(16)	2059(43)	10607(16)	543(84)
O4	1069(14)	-1376(44)	11721(16)	508(76)
O5	-79(9)	-7003(26)	8339(21)	566(63)
O6	-1784(16)	-4340(51)	8678(21)	784(95)
O7	-1529(11)	1253(33)	8395(42)	756(74)
O8	-1659(14)	-4050(44)	6970(18)	609(73)
O9	465(21)	4342(66)	6619(21)	812(112)
O10	1907(15)	-3883(49)	7253(20)	550(85)
O11	2457(16)	2534(45)	6435(16)	540(78)
O12	890(15)	-1741(46)	5189(18)	608(82)
N1	296(15)	-1253(45)	9580(20)	269(79)
N2	-102(21)	-1750(60)	7549(25)	569(124)
N3	1342(40)	828(103)	8078(44)	641(177)
C1	1764(20)	-2257(67)	9641(27)	509(118)
C2	741(17)	2749(59)	10260(22)	262(74)
C3	2027(23)	1673(67)	10251(29)	537(125)
C4	1073(19)	-1002(55)	11074(22)	216(79)
C5	-355(12)	-5455(36)	8339(26)	451(78)
C6	-1418(18)	-3765(54)	9211(22)	411(86)
C7	-1248(10)	-122(34)	8527(38)	361(69)
C8	-1298(26)	-3589(79)	7518(34)	715(144)
C9	723(42)	2446(131)	6654(52)	1033(219)
C10	1640(12)	-2404(43)	7116(16)	189(61)
C11	2036(14)	1297(44)	6490(18)	188(69)
C12	1063(34)	-646(93)	5791(38)	650(168)
C13	-65(14)	-1849(45)	9217(20)	166(68)
C14	417(22)	-1055(71)	7282(30)	457(131)
C15	1339(18)	1047(48)	8772(23)	238(67)

(^a) Estimated standard deviations in parentheses refer to the least significant digits.

SYNTHESIS OF Tc₂(CO)₁₀

Ammonium pertechnetate, NH₄TcO₄ (0.11 g, 0.61 mmol), was introduced in a 100 ml stainless-steel autoclave; after evacuation, dry toluene (20 ml) was introduced by suction and CO (containing 50-100 ppm of dihydrogen) was compressed up to about 90 atm at room temperature. The autoclave was stirred and heated at 200 °C for 4 h. The gas was vented and an infrared spectrum of the solution revealed absorptions typical¹⁶ of Tc₂(CO)₁₀. The content of the autoclave, consisting of a colourless solution and of some grey solid, was filtered. The solution was evaporated under a nitrogen stream and the resulting pale-yellow powder was dissolved in Et₂O. Slow evaporation of the solvent afforded

$\text{Tc}_2(\text{CO})_{10}$ in the form of colourless crystals (0.07 g, 48% yield with respect to NH_4TcO_4). The carbonyl was found to be spectroscopically pure (ν_{CO} , toluene: 2065 m -s, 2014 vs and 1979 s cm^{-1}) in comparison with an authentic sample¹⁶.

In some experiments, carried out under similar experimental conditions, the carbonyl content of the solution obtained after filtration of the reaction mixture, was measured by UV-VIS spectroscopy [the spectrum in toluene solution consists of a single absorption at 315 nm ($\epsilon = 20,000 \text{ M}^{-1} \text{ cm}^{-1}$)]; carbonylation yields always resulted higher than 90% (with respect to NH_4TcO_4).

By operating under the same conditions of pressure and temperature, the carbonylation yield was found to depend on the reaction time, as indicated below:

Reaction time (h)	Carbonylation yield (% with respect to NH_4TcO_4)
2	45
3	70
4	96
5	90

CARBONYLATION OF NH_4TcO_4 AT 150 °C

Ammonium pertechnetate, NH_4TcO_4 , (0.053 g, 0.29 mmol) suspended in toluene (20 ml) was heated at 150 °C for 4 h under on initial CO (containing 50-100 ppm of dihydrogen) pressure of 90 atm. After filtration of insoluble materials (mainly consisting of unreacted NH_4TcO_4), UV-VIS analysis of the toluene solution revealed the presence of $\text{Tc}_2(\text{CO})_{10}$, corresponding to a carbonylation yield of 1.5% with respect to the starting NH_4TcO_4 .

RESULTS AND DISCUSSION

PREPARATION or DECACARBONYLDIRHENIUM(0)

Decacarbonyldirhenium(0) can be obtained by carbonylation of NH_4ReO_4 at about 100 atm pressure and at temperatures around 290 °C, in yields as high as 69%. The starting rhenium substrate is suspended in toluene, in which the product, $\text{Re}_2(\text{CO})_{10}$, is reasonably well soluble. The infrared spectrum of the crude reaction mixture shows that decacarbonyldirhenium(0) is the only carbonyl species present within the limit of accuracy of this technique. The product can be recovered by filtration of the crude reaction mixture at room temperature, followed by cooling of the resulting solution at dry-ice temperature. The most critical parameter in this synthesis appears to be the temperature. No reaction was observed at temperatures as low as 250 °C with ammonium perrhenate as the starting substrate. However, in certain cases, temperatures as high as 340 °C were used. Under these conditions, formation of rhenium metal was observed. Temperature and p_{CO} are decisive factors for the decomposition equilibrium of $\text{Re}_2(\text{CO})_{10}$ to rhenium metal and CO. The importance of the CO pressure is suggested by the failure to observe formation of $\text{Re}_2(\text{CO})_{10}$ with syngas ($\text{CO}/\text{H}_2 = 1:1$) at a total pressure of 80 atm. It is interesting to note that Hieber and Fuchs⁵ reported the use of temperatures of 270 °C at 500 atm pressure to convert KReO_4 into $\text{Re}_2(\text{CO})_{10}$. Obviously, such a high CO pressure is required to stabilize the metal carbonyl with respect to its decomposition to rhenium metal at the temperature of the experiment. In our hands, however, no carbonylation of KReO_4 could be observed under the conditions used for carbonylating the ammonium salt. Only traces of $\text{Re}_2(\text{CO})_{10}$ were reported independently to be obtained by treating KReO_4 with CO at 535 atm and 270 °C^{11b}. On the other hand, it has been reported^{11b} that NaReO_4 can be converted to $\text{Re}_2(\text{CO})_{10}$ in 90% yield by carbonylation in the presence of copper in methanol, the yield being 70% when copper is absent. Presumably, methanol plays a decisive role in the reduction of rhenium in view of the rather drastic conditions (218 atm working pressure, 230 °C, 48 h) used during the carbonylation.

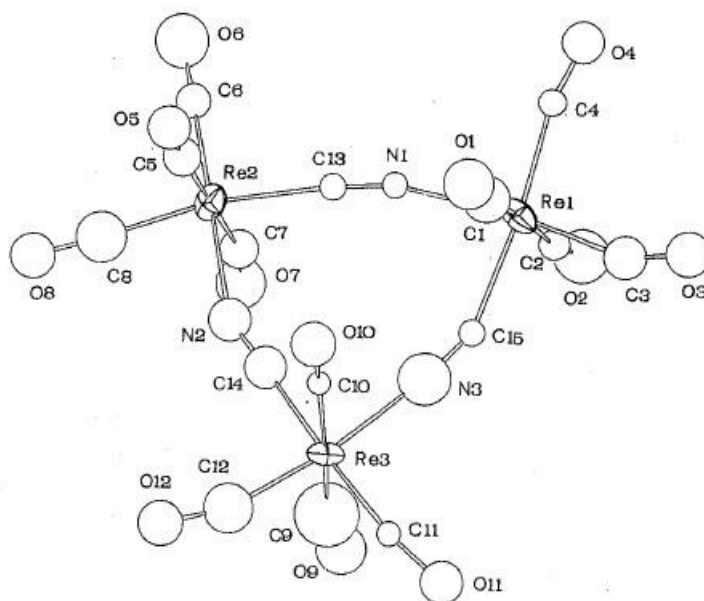
The reaction of NH_4ReO_4 with CO in toluene is assumed to be heterogeneous. On the other hand, both $\text{N}(n\text{-C}_8\text{H}_{17})_3\text{H}[\text{ReO}_4]$ and $\text{N}(n\text{-C}_4\text{H}_9)_4[\text{ReO}_4]$ have also been used as initially toluene-soluble species for the carbonylation to $\text{Re}_2(\text{CO})_{10}$. No specific improvement was observed in either yields or reaction temperature when these soluble salts were used in lieu of NH_4ReO_4 .

The use of commercially available CO (containing about 3% of dihydrogen) is neither detrimental nor beneficial for the carbonylation of NH_4ReO_4 . On the other hand, in an experiment carried out with prepurified, dihydrogen-free carbon monoxide, some H_2 was found at the end of the

reaction. This is probably related to the carbonylation process, in connection with the presence of the ammonium counterion. Although “ $\text{ReO}_3\text{-OH}$ ” is presumably a strong acid, we shall assume that some ammonia will be present in solution upon dissociation of the ammonium perrhenate at the temperature of the carbonylation experiment. The homogeneous metal-catalysed formation of formamides and amines with synthesis gas has been reported¹⁷. Furthermore, the reaction of CO with ammonia has been studied^{18a} and found to yield formamide and HCN, the latter possibly arising by dehydration of the former^{18b}. Hydrogen cyanide is the product of the reaction between ammonia and CO^{18c}. The formation of dihydrogen via the water gas shift reaction cannot be excluded, although rhenium does not appear to be a highly efficient WGS catalyst^{18d}.

X-RAY STRUCTURE OF $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$

In relation with the possible HCN formation, it is interesting to note that our reaction yields, beside $\text{Re}_2(\text{CO})_{10}$, a by-product which was isolated in low yields and identified as the cyano-bridged trimer $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$. In view of its limited solubility, the product can be recovered by filtration of the crude reaction mixture in admixture with some rhenium metal and it can be separated by prolonged extraction with tetrahydrofuran under reduced pressure to minimize thermal decomposition. The IR spectrum shows four main rather broad bands due to carbonyl stretching vibrations, in addition to two weak CN stretching vibrations at 2172 and 2160 cm^{-1} . The low solubility of the product indicated a nuclearity higher than one and the analytical results showed the presence of nitrogen in its composition. This, together with the observation that carbonyl stretching vibrations were present in the infrared spectrum, suggested that we were dealing with a cyano-carbonyl complex of rhenium. In view of the relatively few examples of mixed cyano-carbonyl metal complexes and of the increasing interest for carbonyl complexes of rhenium aggregates¹⁹, it was decided to solve its crystal and molecular structure by X-ray diffraction methods. A view of the molecule is reported in the figure. The structure consists of a cyano-bridged trimer, the rhenium atom being in a pseudo-octahedral coordination of four carbonyl groups, the other two coordination sites being occupied by atoms from the cyano groups. The $\text{Re}_3\text{C}_3\text{N}_3$ system is approximately planar, the atom deviating from the best mean plane by no more than 0.11 Å. Bond distances and angles are listed in table 2.



View of $\text{Re}_3(\text{CN})_3(\text{CO})_{12}$ with the numbering scheme used.

The main problem associated with the solution of the structure was to establish whether the $\text{Re}_3\text{C}_3\text{N}_3$ system has a molecular ternary symmetry corresponding to an equivalent $\text{ReC}_4(\text{Carbonyl})\text{C}(\text{Cyano})\text{N}$ coordination geometry for each rhenium atom; the alternative possibility is that the three rhenium atoms are all not equivalent with coordination geometries $\text{ReC}_4(\text{Carbonyl})\text{C}(\text{Cyano})\text{N}$; $\text{ReC}_4(\text{Carbonyl})\text{C}_2(\text{Cyano})$; $\text{ReC}_4(\text{Carbonyl})\text{N}_2$.

A thorough discussion on the interatomic distances between rhenium atoms and the cyano ligands is hindered by the uncertainty in the carbon and nitrogen assignment and the low accuracy of their localization. It is interesting to note that only a few cases of CN-bridged structurally established compounds are known in the literature, among which the following can be mentioned: a) $(\text{NH}_3)_5\text{Co}(\mu\text{-CN})\text{Co}(\text{CN})_5 \cdot \text{H}_2\text{O}$ ²⁰; b) $[\text{Cu}(\text{L}_4)(\mu\text{-CN})]^+$ ²¹; c) $[\text{Pd}_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_3(\mu\text{-CN})_3]^{3+}$ ^{22a}; d) $[\text{Cp}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Ru}(\mu\text{-CN})\text{RuCp}(\text{PPh}_3)_2]^+$ ²³; e) $\{\text{fac-Mn}(\text{CO})_3(\text{phen})\}(\mu\text{-CN})\}^-$ ²⁴; f) $[\text{Ru}_6(\mu\text{-CN})_2(\text{CO})_{20}]^{2-}$ ²⁵.

Particularly relevant from the point of view of the present structural problem is the palladium(II) complex^{22a}, for which a structure without ternary symmetry was suggested on the basis of the ³¹P NMR spectrum, although the crystallographic experiment could not distinguish between the two possible arrangements. A similar case of positional uncertainty was reported for an *ortho*-metallated pyridine moiety bridging two iridium atom^{22b}.

TABLE 2 - BOND DISTANCES (Å) AND ANGLES (deg) IN Re₃(CN)₃(CO)₁₂^a

Re(1)-C(1)	2.07(4)	C(2)-Re(1)-N(1)	173(2)
Re(1)-C(2)	2.03(4)	C(4)-Re(1)-C(15)	172(1)
Re(1)-C(3)	2.00(5)	C(4)-Re(1)-N(1)	89(1)
Re(1)-C(4)	1.98(4)	C(15)-Re(1)-N(1)	85(1)
Re(1)-C(15)	2.14(4)	C(5)-Re(2)-C(6)	93(1)
Re(1)-N(1)	2.24(3)	C(5)-Re(2)-C(7)	179.2(9)
Re(2)-C(5)	2.00(2)	C(5)-Re(2)-C(8)	87(2)
Re(2)-C(6)	1.94(4)	C(5)-Re(2)-C(13)	89(1)
Re(2)-C(7)	2.04(2)	C(5)-Re(2)-N(2)	87(1)
Re(2)-C(8)	1.90(6)	C(6)-Re(2)-C(7)	86(1)
Re(2)-C(13)	2.11(3)	C(6)-Re(2)-C(8)	95(2)
Re(2)-N(2)	2.16(4)	C(6)-Re(2)-C(13)	99(1)
Re(3)-C(9)	1.89(9)	C(6)-Re(2)-N(2)	180(2)
Re(3)-C(10)	1.96(3)	C(7)-Re(2)-C(8)	93(2)
Re(3)-C(11)	1.94(3)	C(7)-Re(2)-C(13)	90(1)
Re(3)-C(12)	1.88(6)	C(7)-Re(2)-N(2)	94(1)
Re(3)-C(14)	1.98(5)	C(8)-Re(2)-C(13)	166(2)
Re(3)-N(3)	2.10(7)	C(8)-Re(2)-N(2)	85(2)
C(1)-O(1)	1.07(6)	C(13)-Re(2)-N(2)	81(1)
C(2)-O(2)	1.02(6)	C(9)-Re(3)-C(10)	172(3)
C(3)-O(3)	1.13(6)	C(9)-Re(3)-C(11)	95(3)
C(4)-O(4)	1.11(4)	C(9)-Re(3)-C(12)	88(3)
C(5)-O(5)	1.18(3)	C(9)-Re(3)-C(14)	86(3)
C(6)-O(6)	1.15(5)	C(9)-Re(3)-N(3)	93(3)
C(7)-O(7)	1.11(4)	C(10)-Re(3)-C(11)	92(1)
C(8)-O(8)	1.22(6)	C(10)-Re(3)-C(12)	92(2)
C(9)-O(9)	1.38(10)	C(10)-Re(3)-C(14)	86(1)
C(10)-O(10)	1.16(4)	C(10)-Re(3)-N(3)	86(2)
C(11)-O(11)	1.20(4)	C(11)-Re(3)-C(12)	88(2)
C(12)-O(12)	1.29(7)	C(11)-Re(3)-C(14)	177(2)
C(13)-N(1)	1.04(4)	C(11)-Re(3)-N(3)	97(2)
C(14)-N(2)	1.25(6)	C(12)-Re(3)-C(14)	94(2)
C(15)-N(3)	1.16(8)	C(12)-Re(3)-N(3)	174(3)
		C(14)-Re(3)-N(3)	81(3)
Re(1)···Re(2)	5.307(4)	Re(1)-C(1)-O(1)	174(4)
Re(1)···Re(3)	5.239(2)	Re(1)-C(2)-O(2)	172(4)
Re(2)···Re(3)	5.310(3)	Re(1)-C(3)-O(3)	156(4)
		Re(1)-C(4)-O(4)	167(3)
C(1)-Re(1)-C(2)	173(1)	Re(2)-C(5)-O(5)	176(2)
C(1)-Re(1)-C(3)	90(2)	Re(2)-C(6)-O(6)	179(3)
C(1)-Re(1)-C(4)	92(2)	Re(2)-C(7)-O(7)	163(2)
C(1)-Re(1)-C(15)	83(1)	Re(2)-C(8)-O(8)	175(4)
C(1)-Re(1)-N(1)	92(1)	Re(3)-C(9)-O(9)	166(6)
C(2)-Re(1)-C(3)	86(2)	Re(3)-C(10)-O(10)	177(2)

C(2)-Re(1)-C(4)	94(1)	Re(3)-C(11)-O(11)	157(3)
C(2)-Re(1)-C(15)	92(1)	Re(3)-C(12)-O(12)	160(5)
C(2)-Re(1)-N(1)	91(1)	Re(2)-C(13)-N(1)	175(3)
C(3)-Re(1)-C(4)	98(2)	Re(3)-C(14)-N(2)	178(4)
C(3)-Re(1)-C(15)	88(2)	Re(1)-C(15)-N(3)	156(5)
		Re(1)-N(1)-C(13)	163(3)
		Re(2)-N(2)-C(14)	158(4)
		Re(3)-N(3)-C(15)	171(7)

(a) Estimated standard deviations in parentheses referring to the last significant digit.

As mentioned earlier, in our rhenium derivative, the lack of ternary symmetry corresponds to not equivalent rhenium atoms, formally of different oxidation states, Re(I), Re(0) and Re(II). In such a case, the three $\text{Re}(\text{CO})_4$ fragments should be in principle spectroscopically discernible: however, by applying the local symmetry approximation to each of them, the three $\text{Re}(\text{CO})_4$ groups may differ little from one another and the corresponding carbonyl stretching vibrations may not be distinguishable in the solvent of relatively low resolution (tetrahydrofuran) which necessarily was used for measuring the infrared spectra.

A further complication arises from the fact that a comparison of the Nujol and THF spectra of the trimer suggests a possible structure change from the solid state to solution. The IR and the solid state data can be reconciled under either of the following two hypotheses: a) the solid state structure has approximately C_s symmetry. The three rhenium centres become substantially equivalent in solution due to either an efficient electronic delocalisation within the $\text{Re}_3\text{C}_3\text{N}_3$ system or cleavage of the solid state structure by the solvent; b) the solid state structure has effective ternary symmetry and the three rhenium atoms are substantially equivalent. We tend to believe that situation b) is the more likely one in our system. This is also substantiated on the basis of the interatomic distances within the $\text{Re}_3\text{C}_3\text{N}_3$ fragment; the significantly longer Re-N bond distances with respect to the Re-C ones for any given rhenium atom, are in better agreement with the corresponding metal-donor atom distances encountered in other CN-bridged complexes^{20,24,25}.

Beck and coworkers described the preparation of $\text{ReCN}(\text{CO})_5$ from $\text{Re}(\text{CO})_5\text{FBF}_3$ and $\text{K}_2[\text{Ni}(\text{CN})_4]$ in water²⁶. The compound was reported to melt at 188-94 °C with gas evolution; melting was then followed by solidification. It has been found²⁷ that the pentacarbonyl-cyano derivative of rhenium(I), by thermal treatment at ca. 200 °C, undergoes decarbonylation to the corresponding

tetracarbonyl. The infrared spectrum (Nujol mull and THF solution) of the decarbonylation product²⁷ is similar to ours and we can conclude that a single product is obtained by carbonylation of NH_4ReO_4 or by decarbonylation of $\text{ReCN}(\text{CO})_5$. Usually, decarbonylation of pentacarbonyl-halo complexes of rhenium(I) leads²⁸ to the corresponding tetracarbonyl dimers, $\text{Re}_2\text{X}_2(\text{CO})_8$. Failure to form $\text{Re}_2(\text{CN})_2(\text{CO})_8$ dimer is probably due to the stringent geometric requirements of the CN groups engaged with both atoms in a bridge to two metal atoms. Only the formation of a larger ring, as in the trimeric complex reported in this paper, makes such a bridging arrangement for CN possible, although considerable distortions from the ideal linear geometry for the M-C-N-M grouping may be observed, see table 2.

PREPARATION of $\text{Tc}_2(\text{CO})_{10}$

Technetium is the final product of thermal neutron capture by molybdenum²⁹. Since this nuclear reaction is normally carried out on ammonium molybdate(VI), ammonium pertechnetate(VII) is a primary commercially available product. Thus, the possibility of using it as a starting material for preparing $\text{Tc}_3(\text{CO})_{10}$ appeared particularly interesting. Earlier preparations¹⁶ of $\text{Tc}_2(\text{CO})_{10}$ involved carbonylation of Tc_2O_7 alone^{16a-c} or in admixture with Re_2O_7 ^{16c} with CO at 220-275 °C and 215-250 atm pressure.

It has now been found that NH_4TcO_4 is directly converted to $\text{Tc}_2(\text{CO})_{10}$, under conditions similar to those used for the corresponding carbonylation of NH_4ReO_4 , in toluene as reaction medium. The yields of carbonylated product, as determined by the UV spectra of the carbonyl present in the crude reaction solution, are as high as 96%. Radiometric counting of the crude solution agrees quite well with the spectrophotometric determination. The temperature used for the carbonylation reactions and the reaction time are important, the best combination being 200 °C/4 h. The temperature is somewhat lower and the reaction time is considerably shorter than in the case of rhenium (290 °C, 48 h), which is in agreement with the usually observed higher reactivity of 4d complexes with respect to their 5d congeners³⁰. Also with technetium, similar to what mentioned above for rhenium, the reaction appears to be almost completely suppressed by an about 50 °C decrease of the temperature with respect to the optimum value.

We believe that the preparation of $\text{Tc}_2(\text{CO})_{10}$ by this route represents a considerable improvement with respect to the earlier routes. This should make the low-valent technetium complexes, some of them used for radio-pharmaceutical purposes³¹, more easily accessible. It should be observed that, similar to what already noted in the case of rhenium, this preparation method is highly chemo-selective and $\text{Tc}_2(\text{CO})_{10}$ is the only carbonyl product which can be detected spectroscopically in the crude reaction solutions.

CONCLUSIONS

This study has established that oxo-metallates as the ammonium derivatives can be carbonylated by CO, the latter acting both as the reducing agent and the ligand, as exemplified by the carbonylation of the ammonium salts of the oxo-metallates of Group 7 in their VII oxidation state to the corresponding decacarbonyls $\text{Re}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$. This fact can be particularly relevant when oxide-supported rhenium-carbonyl species are required for specific catalytic purposes. Although this has not been verified experimentally, carbonyl species of this type could be obtained by carbonylation of ammonium perrhenate adsorbed on metal oxides³².

An important factor in the carbonylation of ReO_4^- and TcO_4^- is believed to be the interaction of CO with the metal-coordinated oxide ligands, presumably leading to CO_2 with simultaneous reduction of the metal. This mechanism is also probably operating in the case of the covalent neutral metal oxides of osmium(VIII) and rhenium(VII), OsO_4 and Re_2O_7 , respectively. The relatively bulky ammonium, or trialkyl- or tetraalkyl-ammonium cations, in addition to provide a sufficiently low lattice energy for these ionic metal oxides, are probably involved in some stage of the carbonylation process. This is suggested by the isolation of the cyano-bridged trimer reported in this paper.

The successful formation of metal carbonyls from the ammonium derivatives of the MO_4^- tetraoxo species suggests that other high-valent ammonium oxometallates may undergo the carbonylation. Attempts will be made to explore this possibility.

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