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The Reaction of the Octachlorodirhenate(III) Ion with Methyl Isocyanide giving the Pentachloro(methylisocyano)rhenium(IV) Ion*

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Methyl isocyanide reacts rapidly with $(NBu^n_4)_2Re_2Cl_8$ *in ethanol at 25 °C to give a green product, shown by X-ray crystallographic study to be* $(NBu^n_4)[ReCl_5(CNCH_3)]$. *The* $[ReCl_5(CNCH_3)]^-$ *ion is essentially octahedral, with all cis Re–Cl distances in the range 2.316(7) Å to 2.336(7) Å and the* trans *Re–Cl distance equal to 2.343(6), thus indicating little or no structural* trans *effect by the isocyanide ligand. The failure to find any simple substitution product, such as* $Re_2Cl_6(CNCH_3)_2$, *is consistent with other observations where strongly π-acid ligands cause degradation of M–M multiple bonds, although we cannot entirely rule out the formation of a small amount of such a product, nor is the identity of the oxidizing agent that converts* Re^{III} *to* Re^{IV} *known. The compound crystallizes in space group* $P2_1/c$ *with* a = *11.255(3)* Å, b = *14.651(6)* Å, c = *16.274(6)* Å, *β = 93.82(6)°, V = 2677(3)* Å³, *and Z = 4. The structure was refined to* $R_1 = 0.065$ *and* $R_2 = 0.076$ *using 1558 reflections with* $I > 3\sigma(I)$ *and corrected for absorption.*

Introduction

The reactivity of quadruply bonded dimetal species towards various kinds of ligands, though still not well explored, has already revealed great diversity. Simple substitution, with full retention of the M–M bond order, was the first type of reaction discovered, and is illustrated by reactions (1)–(4). Oxidation and reduction reactions necessarily change the M–M bond order.

$$Re_2Cl_8^{2-} + 2PEt_3 \rightarrow Re_2Cl_6(PEt_3)_2 + 2\,Cl^- \quad (1)[1]$$

$$Re_2Cl_8^{2-} + 4CH_3CO_2^- \rightarrow Re_2(O_2CCH_3)_4Cl_2 + 6Cl^- \quad (2)\,[2]$$

$$Mo_2(O_2CCH_3)_4 + 8\,Cl^- \rightarrow Mo_2Cl_8^{4-} + 4CH_3CO_2^- \quad (3)\,[3]$$

$$Mo_2Cl_8^{4-} + 4PR_3 \rightarrow Mo_2Cl_4(PR_3)_4 + 4\,Cl^- \quad (4)\,[4]$$

They may merely lower the order of the bond, as illustrated in (5)–(8), without rupturing it entirely (that is, a bond order of at least unity is preserved), or they may, as illustrated in (9), cause the M–M bond to vanish entirely. There are also reactions such

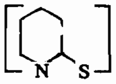
$$Re_2Cl_8^{2-} + Cl_2 \rightarrow Re_2Cl_9^- \quad (5)\,[5]$$

$$Re_2Cl_8^{2-} + PEt_3 \rightarrow Re_2Cl_4(PEt_3)_4 \quad (6)\,[6]$$

$$Mo_2Cl_8^{4-} + H_3PO_4 + O_2 \rightarrow Mo_2(HPO_4)_4^{2-} \quad (7)\,[7]$$

$$Mo_2(O_2CCH_3)_4 + HCl \rightarrow [Mo_2Cl_8H]^{3-} \quad (8)\,[8]$$

$$Mo_2(O_2CCH_3)_4 + NS + O_2 \rightarrow (\overset{\frown}{NS})_2Mo(O)OMo(O)(\overset{\frown}{NS})_2 \quad (9)\,[9]$$

(N S) =


$$Re_2Br_8^{2-} + tu \rightarrow ReBr_3tu_3 \quad (tu = SC(NH_2)_2) \quad (10)\,[10]$$

$$Mo_2(O_2CCH_3)_4 + CH_3NC \rightarrow [Mo(CNCH_3)_7]^{2+} \quad (11)\,[11]$$

as (10) and (11) in which the M–M bond is severed without a change in oxidation number.

In this report we describe the reaction of $Re_2Cl_8^{2-}$ with methylisocyanide. Contrary to our expectation this reaction did not afford a simple substitution product, such as $Re_2Cl_6(CNCH_3)_2$, nor a reduction product, but instead, the only isolated product is a mononuclear rhenium(IV) species, $[ReCl_5(CH_3NC)]^-$.

Experimental

Methyl isocyanide and tetra-n-butylammonium octachlorodirhenate were prepared by standard methods. All solvents were distilled under nitrogen and transferred using syringe serum cap techniques. In a typical reaction 0.2 g of $(NBu^n_4)_2Re_2Cl_8$ was treated with 15 ml of methanol and then 2 ml of CH_3NC. The blue suspension immediately began to

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*Reprints not available.

TABLE I. Positional and Thermal Parameters and Their Estimated Standard Deviations.

Atom	*X*	*Y*	*Z*	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
Re(1)	0.20560(9)	0.00607(8)	0.28992(8)	4.02(4)	2.12(3)	4.90(4)	−0.26(6)	0.64(3)	−0.01(8)
Cl(1)	0.0355(6)	0.0197(4)	0.3631(5)	4.5(3)	3.4(4)	8.9(5)	0.2(3)	2.4(3)	−0.3(4)
Cl(2)	0.3701(6)	−0.0254(6)	0.2147(5)	5.1(3)	7.4(5)	7.4(5)	−0.3(3)	2.0(3)	−1.0(4)
Cl(3)	0.2638(7)	0.1560(5)	0.3227(6)	5.9(4)	3.0(3)	8.6(5)	−0.8(3)	1.5(4)	−0.3(4)
Cl(4)	0.3088(7)	−0.0497(5)	0.4088(6)	6.3(4)	5.4(4)	5.5(5)	0.6(3)	−0.6(4)	0.4(4)
Cl(5)	0.0996(8)	0.0485(6)	0.1691(6)	8.3(5)	5.5(4)	5.7(5)	2.1(4)	−1.3(4)	0.6(4)
N(1)	0.114(2)	−0.199(1)	0.248(1)	8(1)	4(1)	3(1)	−1(1)	−0(1)	−1(1)
N(10)	0.293(2)	0.373(1)	0.141(1)	3.8(5)					
C(1)	0.144(3)	−0.129(2)	0.260(2)	6(2)	3(1)	9(2)	1(1)	1(2)	2(1)
C(2)	0.066(2)	−0.290(2)	0.229(2)	5(1)	4(1)	11(2)	−3(1)	2(2)	−2(2)
C(11)	0.372(3)	0.286(2)	0.154(2)	5.9(8)					
C(12)	0.433(3)	0.261(2)	0.073(2)	6.2(8)					
C(13)	0.511(3)	0.171(2)	0.094(2)	7.7(9)					
C(14)	0.616(3)	0.194(3)	0.149(3)	9.3(11)					
C(21)	0.371(2)	0.451(2)	0.122(2)	5.0(7)					
C(22)	0.311(3)	0.545(2)	0.127(2)	5.8(8)					
C(23)	0.415(2)	0.616(2)	0.117(2)	5.6(7)					
C(24)	0.364(3)	0.716(2)	0.113(2)	6.0(8)					
C(31)	0.200(3)	0.364(2)	0.064(2)	5.6(7)					
C(32)	0.122(2)	0.281(2)	0.077(2)	5.1(7)					
C(33)	0.029(3)	0.278(3)	−0.001(3)	8.8(11)					
C(34)	−0.054(3)	0.190(2)	0.003(2)	7.6(9)					
C(41)	0.224(3)	0.385(2)	0.217(2)	6.5(8)					
C(42)	0.308(3)	0.411(2)	0.294(2)	5.4(7)					
C(43)	0.225(3)	0.424(2)	0.361(2)	8.1(10)					
C(44)	0.286(4)	0.441(3)	0.442(3)	12.9(16)					

[a] The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

dissolve to give a brown solution. After 4 h at 25 °C the solvent was evaporated, the residue dissolved in methylene chloride, filtered, concentrated, treated with 0.5 ml of methanol and placed in a cold chest (−20 °C) for 24 h. Crystals suitable for X-ray diffraction were harvested from the cooled solution. Yield: 46 mg (20%). These green crystals can be exposed to air for several hours without any evidence of decomposition.

The structural study was carried out using a crystal approximately 0.3 × 0.2 × 0.2 mm which was first coated with epoxy cement and mounted on the end of a glass fiber. A Syntex P$\bar{1}$ four-circle automated diffractometer with monochromated MoKα radiation was employed to examine the crystal and collect data. Procedures and methods were those frequently described in previous papers [12]. Using the settings for fifteen reflections in the range $20° \leqslant 2\theta \leqslant 35°$ the following crystallographic parameters were established: Crystal class: monoclinic. Unit cell dimensions: a = 11.255(3) Å, b = 14.651(6) Å, c = 16.274(6) Å, β = 93.82(6)°, V = 2677(3) Å^3. The calculated density is 1.597 g cm^{-3} for $Z = 4$. Systematic absences found later in the intensity data were indicative of the space group $P2_1/c$.

A total of 3815 independent reflections were measured in the range $0° < 2\theta \leqslant 45°$. Variable scan rates from 4° to 24° min^{-1} were used and the scan width extended from 1.2° below Mo Kα_1 to 1.2° above MoKα_2. The wide scan range was used because the peaks were exceptionally broad. Three standard reflections were measured after every 97 reflections and displayed only small random variations in intensity.

An absorption correction was made since the linear absorption coefficient is 52.95 cm^{-1}. This correction was made empirically using nine sets of ψ-scans in each of which counts were recorded at $\chi \approx 90°$ for ψ = 0, 10, 20, ... 360°. The minimum transmission was 63.41%, the maximum 99.89% with an average of 87.20%. The structure was determined using heavy atom techniques. The final values for discrepancy indices were

$$R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.065$$

$$R_2 = [\Sigma w(\| F_o | - | F_c \|)^2 / \Sigma w | F_o |^2]^{1/2} = 0.076$$

and the error in an observation of unit weight was 1.424. The weighting scheme using was as previously

TABLE II. Bond Distances (A) and Angles (Deg).

(a) *Bond Distances* (A)	
Re(1)–Cl(1)	2.330(6)
Re(1)–Cl(2)	2.332(7)
Re(1)–Cl(3)	2.343(6)
Re(1)–Cl(4)	2.336(7)
Re(1)–Cl(5)	2.316(7)
Re(1)–C(1)	2.14(3)
C(1)–N(1)	1.10(3)
N(1)–C(2)	1.47(3)
N(10)–C(11)	1.56(3)
N(10)–C(21)	1.49(3)
N(10)–C(31)	1.59(3)
N(10)–C(41)	1.52(3)
C(11)–C(12)	1.57(4)
C(12)–C(13)	1.61(4)
C(13)–C(14)	1.48(4)
C(21)–C(22)	1.54(3)
C(22)–C(23)	1.58(3)
C(23)–C(24)	1.57(4)
C(31)–C(32)	1.52(3)
C(32)–C(33)	1.59(4)
C(33)–C(34)	1.59(4)
C(41)–C(42)	1.56(4)
C(42)–C(43)	1.50(4)
C(43)–C(44)	1.46(5)
(b) *Bond Angles* (deg)	
Cl(1)–Re(1)–Cl(2)	173.3(2)
Cl(3)	91.7(2)
Cl(4)	89.3(3)
Cl(5)	91.0(3)
C(1)	86.2(8)
Cl(2)–Re(1)–Cl(3)	94.9(3)
Cl(4)	89.8(3)
Cl(5)	89.4(3)
Cl(1)	87.3(8)
Cl(3)–Re(1)–Cl(4)	91.3(3)
Cl(5)	93.6(3)
C(1)	177.5(8)
Cl(4)–Re(1)–Cl(5)	175.1(3)
C(1)	90.0(9)
Cl(5)–Re(1)–C(1)	85.1(9)
C(1)–N(1)–C(2)	176(3)
C(11)–N(10)–C(21)	108(2)
C(31)	112(2)
C(41)	108(2)
C(21)–N(10)–C(31)	106(2)
C(41)	115(2)
C(31)–N(10)–C(41)	108(2)
N(10)–C(11)–C(12)	111(2)
C(11)–C(12)–C(13)	106(2)
C(12)–C(13)–C(14)	110(3)
N(10)–C(21)–C(22)	114(2)
C(21)–C(22)–C(23)	104(2)
C(22)–C(23)–C(24)	110(2)
N(10)–C(31)–C(32)	108(2)
C(31)–C(32)–C(33)	106(2)
C(32)–C(33)–C(34)	111(3)
N(10)–C(41)–C(42)	111(2)
C(41)–C(42)–C(43)	104(2)
C(42)–C(43)–C(44)	113(3)

reported [12] and only the 1558 reflections with $I \geqslant 3\sigma(I)$ were used. The final difference Fourier map had no peaks larger than 0.8 e/Å^3.

The presence of methyl isocyanide rather than methyl cyanide was confirmed by reversing the assignments of N(1) and C(1) and attempting to refine. The temperature factors of both atoms behaved unrealistically, that for 'C' becoming suspiciously small and that for 'N' increasing markedly, and the discrepancy indices rose several percent.

A table of observed and calculated structure factors is available from F.A.C. on request.

Results and Discussion

The only isolated product of the reaction is $[N(Bu^n{}_4)_4][ReCl_5(CNCH_3)]$, a green, crystalline solid. The anion is a straightforward octahedral complex of rhenium(IV); its structure is shown in Fig. 1. The atomic positional and thermal parameters are listed in Table I and the interatomic distances and angles are listed in Table II.

The following features of the $[ReCl_5(CNCH_3)]^-$ ion merit comment. (1) The methyl isocyanide ligand does not appear to be strongly coordinated considering the rather long Re–C distance of 2.14(3) Å and the fact that the *trans* Re–Cl bond, at 2.343(6) Å, is not significantly longer than the average of the four *cis* Re–Cl bonds, 2.328(6) Å. (2) The average of all five Re–Cl distances, 2.331(7) Å, is not significantly

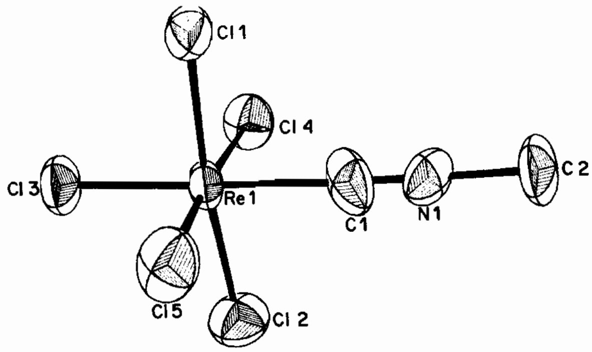

Fig. 1. The $[ReCl_5(CNCH_3)]^-$ ion. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of its electron density.

different from the Re–Cl distance reported [13] for the $ReCl_6^{2-}$ ion in K_2ReCl_6, *viz.*, 2.35(1) Å.

The detailed course of the reaction leading from the $[Re_2Cl_8]^{2-}$ ion to the $[ReCl_5(CNCH_3)]^-$ ion is not known. Since isocyanides are ordinarily reducing agents, the oxidation of Re^{III} to Re^{IV} must be considered surprising. Although the reaction was carried in an atmosphere of nitrogen, using solvent and reagents purged of O_2 and serum cap techniques, it is possible that adventitious air may be responsible. On the other hand, this reaction may be similar to one reported by Walton [14] in which the $Re_2Cl_8^{2-}$ ion reacted with another nominal reducing agent, $Ph_2PCH_2CH_2PPh_2$, to give an oxidized product. In this case it was proposed that following intial rupture of the quadruple bond (which is surely a factor tending to stabilize the otherwise uncommon oxidation state III), oxidation of a chloride-bridged Re^{III} dimer in the presence of (or by the agency of) the chlorinated solvent could occur.

Whether the low yield is attributable to incomplete oxidation or incomplete crystallization is also uncertain. The UV–visible spectrum of the supernatant solution after the crystals were separated was very similar to that of a solution prepared by redissolving some of the crystals, suggesting that reaction may have been fairly complete but that the product is rather soluble. No effort was made to increase the harvest of product since we do not find the product to be of particular interest.

It should be noted that one of the products we had considered likely from the reaction of $Re_2Cl_8^{2-}$ with CH_3NC was $Re_2Cl_6(CNCH_3)_2$. Some years ago it was reported [15] that the analogous $Re_2Cl_6(CNC_6H_4Me)_2$ was obtained by reaction of *p*-totylisocyanide with Re^{III} chloride, which was not, in 1960, known to be Re_3Cl_9 (a fact not generally known until 1964 [16]). We have repeated the latter preparation and confirm that a product of composition $[ReCl_3(CNC_6H_4CH_3)]_x$ is obtained. However, the UV–visible spectrum shows unambiguously that x is 3. This, of course, is not unexpected since reaction of Re_3Cl_9 with neutral ligands leads quite routinely to $Re_3Cl_9L_3$ products. In any event, no substance of the class $Re_2Cl_6L_2$ with L an isocyanide is yet known to exist, although compounds of this sort with L a phosphine have long been known [1].

Acknowledgement

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