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THE SYNTHESIS AND MOLECULAR STRUCTURE OF A SEVEN-COORDINATE RHENIUM ISOCYANIDE COMPLEX

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Summary

Oxidative additions of Br_2 to $Re(CO)L_4Br$ (L = CNMe, *p*-CNC_6H_4Me) produce the rhenium(III) isocyanide complexes ReL_4Br_3. The structure of the *p*-tolyl isocyanide complex was determined using single crystal X-ray diffraction techniques. In this complex rhenium is seven coordinate; there is a capped octahedral geometry about the metal with three isocyanide and three bromide ligands in *fac*-octahedral arrangement and the fourth isocyanide ligand situated on the face bounded by the three isocyanides. The presence of the unique isocyanide causes the three isocyanides to move apart distorting the octahedral arrangement so that the average C—Re—C angle is 115°, and the average C—Re—Br angle is 158° instead of 180°.

Introduction

Isocyanide complexes of manganese and rhenium in oxidation states greater than one are known although they are less common than well studied oxidation state one (18 electron) complexes. Electrochemical studies have indicated that electron loss in the manganese complexes is a favorable process [1,2,3], however, the only manganese(II) isocyanide complexes isolated are several $[MnL_6]^{2+}$ complexes [4] and $[Mn(CO)(CNMe)_5]^{2+}$ [1]. Attempts to oxidize MnL_5X complexes with various oxidizing agents gave only $[MnL_6]^+$ [5]. The complexes $[ReL_6]^+$ are more difficult to oxidize according to electrochemical measurements [6]; interestingly, no $[ReL_6]^{2+}$ complexes have as yet been isolated. There are a number of known isocyanide complexes of rhenium(II) and rhenium(III); none, however, correspond to simple oxidation products of $[ReL_6]^+$. Mononuclear rhenium(III) complexes having formulas $Re(CNtol)_3X_3$ and $Re(CNtol)_4X_3$ (X = Br, I) are formed from K_2ReX_6 and CNtol [7]. Compounds of similar stoichiometries, $Re(PPh_3)_2(CNMe)Cl_3$, $Re(dpe)(CNMe)Cl_3$, and $Re(PPh_3)(CNMe)_3Cl_3$ are also reported as is the compound $[Re(PPh_3)(CNMe)_4Cl_2]PF_6$ [8]. A trinuclear compound $Re_3L_3I_9$ is a product of the ReI_3/CNC_6H_{11} reaction [9]. Rhenium(II) compounds include $Re(CNtol)_4(CO)I_2$ [7] and $Re(CNC_6H_{11})_4Br_2$ [9]. Rhenium offers a more varied pattern of behavior than manganese in its coordination chemistry using these ligands. While the most striking difference is the ability of rhenium to achieve coordination numbers greater than six, there are other significant differences; polynuclear complex formation, a wider range of oxidation states, and enhanced kinetic stability are all identified in rhenium isocyanide chemistry.

As noted earlier we have looked at the oxidative chemistry of manganese isocyanide complexes. It was a logical step to proceed next to the oxidative chemistry of rhenium complexes, particularly because of the anticipated variations between these metals. Here we report initial work on reactions of several rhenium(I) complexes with halogens. These reactions occur not with simple electron transfer as seen for manganese but by oxidative addition to give seven-coordinate rhenium complexes. A structural study on one of the products was undertaken to define the coordination geometry for this seven-coordinate species.

Experimental

The starting materials $Re(CO)(L)_4Br$ (L = CNMe, CNtol) [4], CNMe [10], and CNtol [11] were prepared by the cited procedures. Reactions were carried out routinely in a nitrogen atmosphere. Infrared data were recorded on a Beckman IR-10 using CH_2Cl_2 solutions (±5 cm^{-1}). Analyses were carried out by the Galbraith Laboratories, Knoxville, Tenn.

Preparation of $Re(CNtol)_4Br_3$. A sample of $Re(CO)(CNtol)_4Br$ (0.80 g, 1.05 mmol) was dissolved in 50 ml CH_2Cl_2 and treated with bromine (0.22 g, 1.37 mmol). The mixture was stirred at room temperature, the progress of the reaction being monitored by sampling periodically and recording an infrared spectrum (ν(CN) of starting material, 2080 cm^{-1}; ν(CN) of product, at 2150 cm^{-1}). There was evidence at short reaction times for an intermediate having ν(CN) at 2190 cm^{-1} and ν(CO) at 2040 cm^{-1}. After 50 h the solution was filtered and solvent evaporated. The residue was crystallized from a CH_2Cl_2/Et_2O mixture giving the yellow crystalline product, 0.75 g, 80% yield; m.p. 225—227°C.

Analysis. Found: C, 43.10; H, 3.02; N, 6.36. $C_{32}H_{28}N_4Br_3Re$ calcd.: C, 42.97; H, 3.15; N, 6.26%.

Preparation of $Re(CNMe)_4Br_3$. Bromine (0.087 g, 0.54 mmol) was added to a solution of $Re(CO)(CNMe)_4Br$ (0.25 g, 0.54 mmol) in 50 ml CH_2Cl_2. Within minutes the starting material peaks at 2130 and 1858 cm^{-1} in the infrared spectral region had disappeared, being replaced initially by new absorptions at 2240 and 2040 cm^{-1}: these in turn were eventually replaced by the product peak at 2190 cm^{-1}. After 24 h of stirring, solvent was removed and the residue recrystallized as yellow crystals from CH_3CN (0.10 g, 30% yield) decomp. 190°C.

Analysis. Found: C, 16.17; H, 1.97; N, 9.48. $C_8H_{12}Br_3N_4Re$ calcd.: C, 16.28; H, 2.05; N, 9.49%.

Determination of the structure of $Re(CNtol)_4Br_3$. Preliminary precession photographs showed orthorhombic symmetry and the systematic absences $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd. The space group $P2_12_12_1$ was thus indi-

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY

(A) Crystal parameters (at 21°C) [a]

a 10.4915(23) Å	Space group $P2_12_12_1$ [D_2^4; No. 19]
b 23.3046(76) Å	$Z = 4$
c 13.3278(40) Å	Mol. wt. 894.53 [b]
V 3258.65 Å^3	density (calcd.) 1.823 g/cm^3
	density (obs.) [b] 1.82(2) g/cm^3

(B) Measurement of intensity data
Radiation Mo-K_α
Filters: Nb foil at counter aperture (~47% transmission of Mo-K_α)
Attenuators: Cu (inserted when $I > 10^4$ counts/sec)
Takeoff angle: 3.0°
Detector aperture: 5 x 5 mm
Crystal-detector distance: 330 mm
Crystal orientation: mounted on [100]
Reflections measured: $+h, +k, +l$
Maximum 2θ: 50.0°
Scan type: coupled θ(crystal) — 2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (1.30 + 0.692 \tan \theta)$°, starting 0.65° below the Mo-K_α peak.

Background measurement: stationary crystal, stationary counter, 40 seconds each at beginning and end of 2θ scan.

Standard reflection: three remeasured after every 48 reflections; rms deviations (after application of anisotropic linear decay correction) were 1.90% for 310, 2.41% for 040, 1.74% for 002.

Reflections collected: 3396 independent measurements, of these 108 were duplicate, or equivalent measurements (averaged into primary data set), 27 were systematic absences.

(C) Treatment of intensity data
Conversion to $|F_0|$ and $(\sigma|F_0|)$: as in ref. 12 using an "ignorance factor" of $p = 0.04$
Absorption coefficient: μ 74.36 cm^{-1}; maximum and minimum transmission factors were 0.487 and 0.240 [c].

(D) Details of refinement
Unique data used: 3261
Function minimized: $\Sigma w(|F_0| - |F_0|)^2$ where $w = 1/\sigma^2(|F_0|)$
Final number of variables: 361 independent, 84 dependent (for "riding" hydrogen atoms)
Final error in observation of unit wt.: 1.121
Final $R(F)$ $R(wF)$ 0.0359

[a] Based on λ(Mo-K_α) 0.709300 Å [24]. [b] By neutral buoyancy in CCl_4/C_2H_5Br. [c] Absorption connections were carried out using the FORTRAN IV program DRABZ by B.G. DeBoer, see ref. 12.

cated. A prismatic crystal of approximate dimensions 0.24 × 0.14 × 0.73 mm was used for intensity data collection. It was mounted on a Picker FACS-1 computer-controlled four-circle diffractometer. The crystal was accurately centered and aligned with [100] coincident with the ϕ axis of the diffractometer. Accurate cell dimensions were determined by least-squares procedures based on the angular positions of 12 high 2θ reflections widely separated in reciprocal space. This and other aspects of the data collection and processing are described elsewhere [12]. Details specific to the present analysis are summarized in Table 1.

To ascertain the severity of the absorption problem the 400 reflection was measured (by repeated $\theta - 2\theta$ scans) at χ 90°, and at 10° intervals from ϕ 0 to 350°. The variation in intensity as a function of ϕ (defined as maximum-minimum/average) was 40.0%. An absorption correction was therefore necessary. Data were corrected using the program DRABZ by De Boer [12]. The corrected

(continued on p. 252)

TABLE 2

FINAL PARAMETERS FOR NON-HYDROGEN ATOMS IN $[Re(CNC_6H_4CH_3)_4Br_3]$ [a,b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	0.20287(3)	0.05856(1)	0.20937(2)	2.81(1)	3.30(1)	2.81(1)	0.15(1)	−0.16(1)	−0.28(1)
Br(1)	0.44902(8)	0.05000(4)	0.23511(7)	2.94(3)	4.98(5)	5.32(5)	0.09(4)	−0.26(3)	−0.56(4)
Br(2)	0.24531(11)	0.15619(5)	0.11900(7)	6.35(6)	4.91(5)	4.60(5)	−0.87(4)	−0.85(4)	1.28(4)
Br(3)	0.22738(10)	0.00653(5)	0.03559(7)	4.67(5)	6.48(5)	3.39(4)	0.95(5)	−0.22(4)	−1.44(4)
N(1)	−0.0191(7)	0.0351(3)	0.3602(5)	3.9(4)	5.0(4)	4.3(3)	−0.2(3)	0.5(3)	−0.1(3)
C(11)	0.0654(8)	0.0431(3)	0.3056(6)	3.6(4)	3.9(4)	3.9(4)	−0.3(3)	−0.8(3)	−0.1(3)
C(12)	−0.1141(8)	0.0396(4)	0.4343(7)	3.1(4)	4.6(4)	3.7(4)	−0.1(3)	0.3(3)	0.2(3)
C(13)	−0.0783(8)	0.0434(4)	0.5331(7)	3.0(4)	5.4(5)	4.5(4)	0.3(3)	−0.0(3)	0.3(4)
C(14)	−0.1696(8)	0.0528(4)	0.6035(7)	3.8(4)	4.8(4)	4.6(4)	0.7(4)	0.1(3)	1.2(4)
C(15)	−0.2958(8)	0.0565(4)	0.5801(6)	3.3(4)	3.6(3)	5.3(4)	0.1(4)	0.6(3)	1.1(4)
C(16)	−0.3305(8)	0.0505(4)	0.4808(7)	2.9(4)	5.9(5)	5.5(5)	−0.1(4)	0.3(3)	0.7(4)
C(17)	−0.2400(9)	0.0420(4)	0.4062(7)	4.1(4)	5.5(5)	4.6(4)	0.2(4)	−0.5(3)	0.3(4)
C(18)	−0.3961(10)	0.0675(5)	0.6612(8)	5.4(6)	6.8(6)	6.6(5)	1.1(5)	2.2(5)	0.8(5)
N(2)	0.2522(7)	−0.0708(3)	0.2673(5)	4.0(3)	4.7(4)	4.1(3)	−0.5(3)	−0.4(3)	−0.0(3)
C(21)	0.2309(8)	−0.1263(3)	0.2479(6)	3.1(4)	3.8(4)	4.2(3)	−0.0(3)	−0.6(3)	−0.1(3)
C(22)	0.3053(8)	−0.1263(3)	0.2665(6)	3.1(3)	3.2(3)	4.3(4)	−0.1(3)	−0.6(3)	0.1(3)
C(23)	0.2811(10)	−0.1631(4)	0.3442(6)	5.4(5)	5.1(5)	3.6(4)	1.7(4)	−0.1(4)	0.4(3)
C(24)	0.3275(9)	−0.2184(4)	0.3356(7)	4.3(5)	5.5(5)	5.4(4)	−0.2(4)	−0.9(4)	2.1(4)
C(25)	0.3965(9)	−0.2374(4)	0.2557(8)	3.9(4)	4.8(5)	7.2(5)	1.1(4)	−1.1(4)	−0.1(4)
C(26)	0.4210(10)	−0.1985(4)	0.1807(8)	4.6(5)	5.1(5)	6.2(5)	1.2(4)	1.0(4)	0.6(4)

C(27)	0.3757(9)	−0.1424(4)	0.1846(7)	5.2(5)	3.6(4)	5.3(5)	0.3(4)	0.9(4)	1.0(3)
C(28)	0.4434(12)	−0.2975(5)	0.2477(10)	6.7(6)	5.8(6)	10.9(8)	2.3(5)	0.4(7)	1.3(6)
N(3)	−0.0548(7)	0.0885(3)	0.0986(6)	3.8(3)	4.7(4)	5.5(4)	0.8(3)	−0.9(3)	0.6(3)
C(31)	0.0391(9)	0.0775(3)	0.1377(6)	4.5(4)	3.4(4)	3.4(3)	0.8(3)	0.4(3)	0.4(3)
C(32)	−0.1501(9)	0.1134(4)	0.0406(7)	3.9(4)	5.0(5)	4.5(4)	0.7(4)	−1.3(4)	0.4(4)
C(33)	−0.2765(9)	0.1002(4)	0.0617(7)	3.6(5)	4.5(4)	5.7(5)	−0.2(4)	−0.5(4)	1.1(4)
C(34)	−0.3682(9)	0.1258(5)	0.0036(8)	3.1(4)	6.4(6)	7.1(6)	−0.4(4)	−0.8(4)	0.2(5)
C(35)	−0.3401(10)	0.1662(5)	−0.0684(8)	5.1(5)	5.4(6)	6.5(6)	0.4(5)	−2.2(5)	0.4(5)
C(36)	−0.2145(11)	0.1787(5)	−0.0855(9)	5.0(5)	8.3(7)	7.4(6)	−0.0(6)	−0.4(5)	3.6(6)
C(37)	−0.1168(11)	0.1532(5)	−0.0316(8)	4.6(5)	7.1(6)	7.0(6)	−0.6(5)	0.0(5)	2.3(5)
C(38)	−0.4417(13)	0.1979(6)	−0.1258(11)	7.9(8)	11.1(1.0)	11.1(9)	3.1(7)	−3.7(7)	3.7(8)
N(4)	0.2596(7)	0.1454(3)	0.3838(5)	3.5(3)	4.7(3)	4.0(3)	0.1(3)	0.2(3)	−1.2(3)
C(41)	0.2379(8)	0.1135(3)	0.3225(6)	3.4(4)	3.5(4)	4.0(3)	0.1(3)	0.2(3)	−0.4(3)
C(42)	0.2985(9)	0.1865(3)	0.4543(6)	3.6(4)	4.3(4)	3.5(3)	−0.2(4)	0.1(3)	−0.8(3)
C(43)	0.3729(10)	0.1712(4)	0.4331(7)	6.8(6)	2.9(4)	5.2(4)	0.8(4)	−1.7(5)	−1.0(3)
C(44)	0.4107(11)	0.2112(5)	0.6016(8)	6.3(6)	5.8(5)	4.7(4)	0.3(5)	−1.9(4)	−0.5(4)
C(45)	0.3713(9)	0.2686(4)	0.5926(7)	4.3(4)	4.5(5)	4.9(5)	−0.1(4)	−0.3(4)	−0.4(4)
C(46)	0.2995(11)	0.2832(4)	0.5134(7)	6.5(6)	2.9(4)	5.8(5)	0.7(4)	−0.7(5)	−0.4(3)
C(47)	0.2590(10)	0.2435(4)	0.4432(7)	6.1(6)	4.2(4)	4.6(4)	0.8(4)	−0.8(4)	−0.2(3)
C(48)	0.4139(12)	0.3116(5)	0.6711(9)	7.2(7)	5.8(6)	8.1(6)	−1.8(5)	−1.2(6)	−2.0(5)

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[a] Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and were derived from the inverse of the final least-squares matrix. [b] Anisotropic thermal parameters are in units of Å^2 and enter the structure factor equation in the form $\exp[0.25(B_{11}h^2a^* + B_{22}k^2b^* + B_{33}l^2c^* + 2B_{12}hka^*b^* + 2B_{13}hla^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE 3

FINAL PARAMETERS FOR "RIDING" HYDROGEN ATOMS[a]

Atom	x	y	z
H(13)	0.0090	0.0404	0.5512
H(14)	−0.1464	0.0568	0.6721
H(16)	−0.4182	0.0526	0.4634
H(17)	−0.2631	0.0381	0.3376
H(18)	−0.4774	0.0689	0.6300
H(18')	−0.3801	0.1028	0.6945
H(18")	−0.3945	0.0370	0.7086
H(23)	0.2324	−0.1509	0.4003
H(24)	0.3118	−0.2446	0.3886
H(26)	0.4699	−0.2106	0.1248
H(27)	0.3920	−0.1157	0.1323
H(28)	0.4990	−0.3062	0.3020
H(28')	0.3731	−0.3232	0.2487
H(28")	0.4882	−0.3015	0.1862
H(33)	−0.2974	0.0732	0.1126
H(34)	−0.4549	0.1161	0.0153
H(36)	−0.1942	0.2060	−0.1361
H(37)	−0.0301	0.1626	−0.0438
H(38)	−0.4034	0.2239	−0.1718
H(38')	−0.4911	0.1706	−0.1616
H(38")	−0.4950	0.2185	−0.0809
H(43)	0.3988	0.1323	0.5403
H(44)	0.4637	0.1998	0.6558
H(46)	0.2743	0.3222	0.5068
H(47)	0.2063	0.2545	0.3885
H(48)	0.3804	0.3485	0.6562
H(48')	0.5044	0.3134	0.6723
H(48")	0.3835	0.2994	0.7348

[a] Numbering of atoms corresponds to that of attached carbons, see Table 1 and Fig. 1.

data were first used in a rather late stage of refinement. Their use caused the conventional R factor for a model including all the non-hydrogen atoms to drop from 0.0593 to 0.0397. When the ϕ-scan data were corrected for the effects of absorption, the variation in intensity was reduced to 24.0%. Maximum and minimum transmission coefficients were 0.487 and 0.240.

Other computer programs used during the structural analysis include FORDAP (Fourier syntheses, by A. Zalkin), LSHF (structure factor calculations * and least-squares refinement , by DeBoer), PLOD (least-squares planes and lines, by DeBoer), and ORTEP (thermal ellipsoid drawings, by Johnson). All calculations were performed on an IBM 370/158 computer.

The structure was solved by the heavy-atom method. Atomic scattering factors for neutral non-hydrogen atoms were taken from Cromer and Waber [13] and for hydrogen from Stewart, Davidson and Simpson [14]. Refinement included the use of anisotropic thermal parameters for all non-hydrogen atoms

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* The table of structure factors has been deposited as NAPS Document No. 03392 (13 p.) with ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy can be secured by citing the document number and remitting $3.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 4

BOND LENGTHS AND SELECTED BOND ANGLES[a]

A. Bond Lengths (Å)

Re—Br(1)	2.6129(11)	C(12)—N(1)	1.406(11)
Re—Br(2)	2.6123(12)	C(22)—N(2)	1.409(10)
Re—Br(3)	2.6263(11)	C(32)—N(3)	1.392(12)
		C(42)—N(4)	1.402(10)
Re—C(11)	1.964(8)		
Re—C(21)	1.985(8)	N(1)—C(11)	1.162(11)
Re—C(31)	2.014(7)	N(2)—C(21)	1.170(11)
Re—C(41)	2.012(8)	N(3)—C(31)	1.144(12)
		N(4)—C(41)	1.128(10)
C(15)—C(18)	1.530(14)		
C(25)—C(28)	1.488(15)	C(14)—C(15)	1.363(12)
C(35)—C(38)	1.506(18)	C(24)—C(25)	1.362(14)
C(45)—C(48)	1.516(15)	C(34)—C(35)	1.378(15)
		C(44)—C(45)	1.406(14)
C(15)—C(16)	1.380(12)		
C(25)—C(26)	1.375(15)	C(13)—C(14)	1.359(12)
C(35)—C(36)	1.368(16)	C(23)—C(24)	1.380(13)
C(45)—C(46)	1.341(18)	C(33)—C(34)	1.377(14)
		C(43)—C(44)	1.363(18)
C(16)—C(17)	1.389(13)		
C(26)—C(27)	1.393(13)	C(12)—C(13)	1.372(12)
C(36)—C(37)	1.387(16)	C(22)—C(23)	1.368(11)
C(46)—C(47)	1.382(13)	C(32)—C(33)	1.390(13)
C(12)—C(17)	1.374(13)	C(42)—C(43)	1.356(12)
C(22)—C(27)	1.369(12)		
C(32)—C(37)	1.380(14)		
C(42)—C(47)	1.401(12)		

B. Bond Angles (°)

Br(1)—Re—Br(2)	87.64(3)		
Br(1)—Re—Br(3)	89.08(3)		
Br(2)—Re—Br(3)	88.81(4)		
Br(1)—Re—C(11)	128.75(25)	C(11)—Re—C(21)	76.39(34)
Br(2)—Re—C(11)	125.85(24)	C(11)—Re—C(31)	73.93(34)
Br(3)—Re—C(11)	124.30(24)	C(11)—Re—C(41)	76.13(33)
Br(2)—Re—C(21)	157.75(24)		
Br(1)—Re—C(31)	157.24(24)		
Br(3)—Re—C(41)	159.53(23)		
Br(1)—Re—C(21)	75.32(24)		
Br(1)—Re—C(41)	76.69(23)	C(21)—Re—C(31)	117.25(23)
		C(21)—Re—C(41)	112.67(33)
Br(2)—Re—C(31)	74.72(24)	C(31)—Re—C(41)	111.83(33)
Br(2)—Re—C(41)	76.15(23)		
Br(3)—Re—C(21)	76.91(24)		
Br(3)—Re—C(31)	76.51(23)		

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[a] See Fig. 1 for labelling of the atoms.

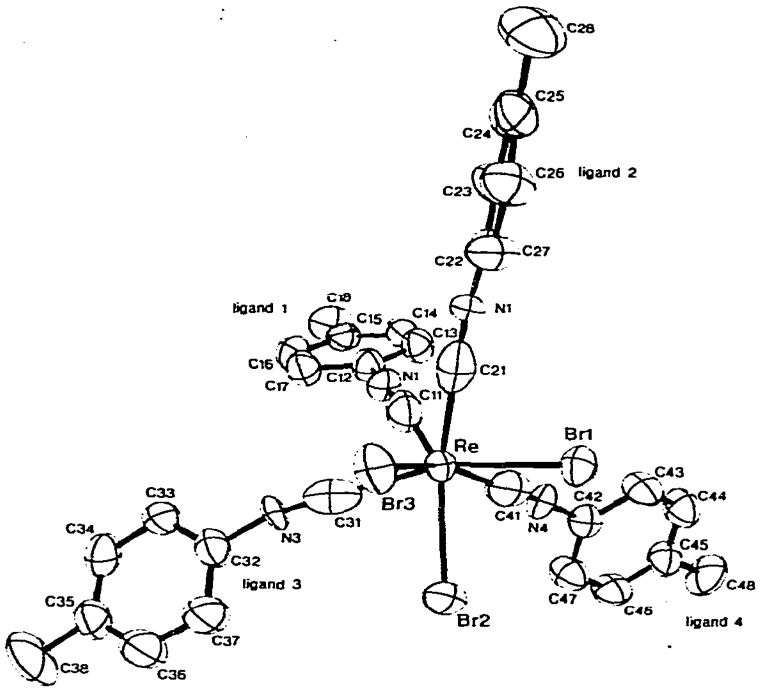

Fig. 1. A general perspective view of the molecular structure of Re(CNtol)$_4$Br$_3$ showing the labelling of the atoms. Hydrogen atoms are omitted for clarity. Ligand 1 is the unique ligand that "caps the octahedron".

and the insertion of twenty-eight "riding" hydrogens in idealized positions (based on d(C—H) 0.95, d(N—H) 0.87 Å) [15]. The methyl carbons' hydrogens were inserted so as to have positions staggered with respect to the phenyl ring. All hydrogens had shifts in positional parameters held equal to the shifts of their attached atoms. Isotropic thermal parameters for each hydrogen were not varied; they were held at 1 + the isotropic equivalent value of the attached carbon atom.

The final cycles of refinement treated 361 variable parameters. Alternate-cycle block-diagonal least squares fitting was used. All parameters for the Re atom and the Br atoms were varied in each cycle; positional parameters and anisotropic temperature factors for the atoms of a different pair of the four organic ligands were held constant in alternate cycles. Discrepancy indices used in Table 1 are as defined previously [16].

The largest shift during the last cycle of refinement was 0.064 σ for a nonhydrogen parameter. The highest peak on a final difference Fourier map was 0.44 $e/Å^3$ at (0.21, 0.03, 0.131). Both the real and imaginary components of anomalous dispersion were included throughout the refinement for all non-hydrogen atoms. Final positional and thermal parameters are given in Tables 2 and 3.

During the final stages of refinement a reversal of handedness to the enantiomeric coordinates gave significantly higher discrepancy indices. The absolute configuration of the molecule was thus determined to be that given in Fig. 1 and Table 2. The final conventional $R(F)$ was 3.44%

Significant bond lengths and angles are given in Table 4.

Discussion

This project was undertaken with two goals in mind. The first was to further clarify the oxidation—reduction chemistry of rhenium isocyanide complexes which was expected to contrast with chemistry of complexes of the congener element manganese. The second goal was to determine the structure of rhenium complexes of isocyanides which have coordination numbers greater than six.

The oxidative chemistry of manganese(I) isocyanide complexes is known to involve simple electron transfer. With a variety of oxidizing agents, including halogens, $[Mn(CNR)_6]^+$ complexes can be oxidized to isolable low-spin species, $[Mn(CNR)_6]^{2+}$ [5]. There is electrochemical evidence for a second one electron oxidation to give $[Mn(CNR)_6]^{3+}$ complexes [1]; these complexes are not stable and have not been isolated. In addition $Mn(CNR)_5X$ complexes have been subjected to various oxidative reactions; however the only products in these experiments are $[Mn(CNR)_6]^+$ complexes. Although electrochemical data suggested that $Mn(CNR)_5X$ compounds should be easily oxidized [5], the process of halide loss appears to take preference in these systems. This reaction is interesting when contrasted to the results described here for $Re(L)_5X$ species.

No information is currently available on oxidations for $[Re(CNR)_6]^+$. There are, however, several monomeric rhenium(III) complexes ReL_nX_3 ($n = 3, 4$) reported [7]. It seemed reasonable that known rhenium(I) and rhenium(III) complexes might be related by a simple oxidative addition reaction. This proved to be the case, and in this work we determined that the reactions defined by equation 1 occurred readily giving bright yellow crystalline products. (It is noted in passing that the literature [7] reports $Re(CNtol)_4I_3$ as brown crystals.)

$$Re(CNR)_4(CO)Br + Br_2 \rightarrow Re(CNR)_4Br_3 + CO \qquad (1)$$

Re^I (d^6, 18e) $\qquad$ Re^{III} (d^4, 18e)
($R = Me$, p-tol)

The reaction occurred at a moderate rate in CH_2Cl_2. The progress of the reaction can be monitored using infrared data, watching the disappearance of $\nu(CO)$ and $\nu(CN)$ at about 1860 and 2130 cm^{-1} (for CNMe) or 2080 cm^{-1} (for CNtol), and the appearance of $\nu(CN)$ peaks in the product at higher frequencies (2190 cm^{-1} for CNMe, 2150 cm^{-1} for CNtol). In monitoring the infrared spectra of these solutions, there was evidence for an intermediate in these reactions which still contained coordinated CO ($\nu(CO)$ at 2040 cm^{-1}); also a higher frequency $\nu(CN)$ peak was observed at either 2204 cm^{-1} (CNMe) or 2190 cm^{-1} (CNtol). A reasonable two step reaction pathway to accommodate these data should be:

Step (1) $Re(CNR)_4(CO)Br + Br_2 \rightarrow [Re(CNR)_4(CO)Br_2]^+ Br^-$

Step (2) $[Re(CNR)_4(CO)Br_2]^+ Br^- \xrightarrow{slow} Re(CNR)_4Br_3 + CO$

Here the starting complex, which is electron rich owing to the strong donor capability of the ligands, reacts initially to add the strongly electrophilic Br^+ to give an ionic intermediate which then slowly loses CO and coordinates bromide ion in a second step. It is noted that a compound similar to this intermediate, $[Re(PPh_3)(CNMe)_4Cl_2]PF_6$, has been reported [8].

In contrast to the reactions reported here is the reaction of $Re(CO)(phos)_4Cl$

(phos = $PPhMe_2$, 1/2 dppe) and Cl_2 [17], in which a 17*e* compound $[Re(CO)(phos)_4Cl]^+$ was isolated. Using an excess of chlorine the reactions gave either $[Re(CO)(PPhMe_2)_3Cl_3]$ or $Re(dpe)Cl_4$.

It seemed worthwhile to determine the structure of one of the rhenium complexes prepared in this study. Few structural studies have been carried out previously on mononuclear rhenium complexes having coordination numbers for the metal greater than six; and indeed, as far as we can tell there is no structural information on any rhenium isocyanide complex. The compound $Re(CNtol)_4Br_3$, which gave nicely formed yellow crystals, was selected for a single crystal X-ray diffraction study.

The general structural features for this molecular compound can be seen in Fig. 1. The metal has approximate C_{3v} symmetry; its geometry is essentially that of a monocapped octahedron (Fig. 2). Three bromides and three isocyanide carbons occupy octahedral positions with the fourth isocyanide bonding to the metal through the face defined by the three other isocyanides. The presence of this unique isocyanide on one face distorts the octahedron, causing the three isocyanide ligands to be displaced away from the unique ligand and toward the bromides. The extent of this displacement is easiest to visualize from the bond angle data (Table 4). Although the three Br—Re—Br angles are close to 88°, the (*cis*) C—Re—Br angles are compressed from the 90° to about 75°, and the *trans* C—Re—Br angles are reduced to about 158° from the idealized octahedral values of 180°.

We have calculated the δ' angles [18] associated with this structure. They have values of 0.37, 7.75 and 6.23°, differing from idealized values of 24.2° for a regu-

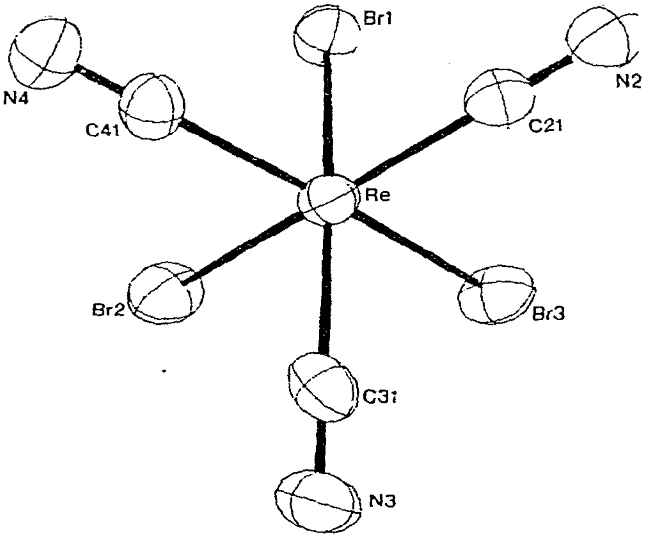

Fig. 2. An ORTEP drawing of the structure of $Re(CNtol)_4Br_3$ that emphasizes the approximate C_{3v} symmetry about the seven-coordinate Re. The view looks down the linear (N(1)—C(11)—Re) grouping, that is the isocyanide of ligand 1. (See Fig. 1 for labelling of atoms.) Both the N and C, which would eclipse the Re, are omitted for clarity. All *p*-tolyl C's and H's are likewise omitted. The plane of the phenyl ring of each of the four tolyl groups is approximately (within 8°) perpendicular to the plane of the paper in this projection; the plane of the phenyl ring of ligand 1 is parallel to the Re—Br(1) bond vector.

lar ML_7 capped octahedral structure. The deviations from this "idealized" value are presumed to be a consequence of the long Re—Br distance (relative to the Re—C distances) and the larger Br—Re—Br angles. A similar result is found with the species $[W(CO)_4Br_3]^-$ for which δ' angles of 5.1, 4.0, and 4.0 were measured [19].

The only other mononuclear seven-coordinate rhenium complex whose structure has been determined, that we are aware of, is $Re(CO)(S_2CNEt_2)_3$ [20]. Its general structure is rather different than that of our compound, being described as a distorted pentagonal bipyramid. Possible comparisons with other seven coordinate isocyanide complexes, $[Mo(CNBu\text{-}t)_6I]I$ [21] and $[Mo(CNBu\text{-}t)_7](PF_6)_2$ [22] are also not possible because these molybdenum complexes have monocapped trigonal prismatic structures. Greatest similarity seems to be with the species $[W(CO)_4Br_3]^-$ which has the same overall geometry. The point has been made that this geometry seems to be the best one to accommodate three large halogen atoms in the metal coordination sphere [23].

There are, of course, no significant comparisons to be made between bond lengths in this molecule and bond lengths in other complexes since no previous structural data on rhenium isocyanide complexes have been generated. There is internal comparison of rhenium—carbon distances: the bond to the unique isocyanide is found to be 1.964(8) Å, very slightly shorter than the bond lengths of the three other rhenium—carbon bonds, which average about 2.00 Å. These rhenium—carbon distances are all shorter than the molybdenum—carbon distances in $[Mo(CNBu\text{-}t)_6I]^+$ which average 2.06—2.12 Å and in $[Mo(CNBu\text{-}t)_7]^{2+}$ which run 2.05—2.17 Å. This is a reasonable difference considering the oxidation state differences in these compounds.

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