Journal of Organometallic Chemistry, 282 (1985) 191–200
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STUDIES ON THE INTERACTION OF ISOCYANIDES WITH TRANSITION METAL COMPLEXES

XXVII *. PREPARATION OF ZEROVALENT ISOCYANIDE COMPLEXES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN. THE CRYSTAL STRUCTURE OF HEXAKIS(2,6-XYLYL ISOCYANIDE)MOLYBDENUM CONTAINING BENZENE AS A SOLVATED MOLECULE

YASUHIRO YAMAMOTO* and HIROSHI YAMAZAKI
Riken (The Institute of Physical and Chemical Research), Wako, Saitama 351-01 (Japan)

(Received August 27th, 1984)

Summary

Hexakis(isocyanide)metals, $M(RNC)_6$ (M = Cr, Mo, W; R = $2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, $2,4\text{-t-}Bu_2\text{-}6\text{-}MeC_6H_2$, $2,4,6\text{-t-}Bu_3C_6H_2$ and t-Bu), were prepared by the reduction of a halide of chromium(III), molybdenum(IV), molybdenum(V) or tungsten(VI) with sodium amalgam in the presence of an isocyanide. An X-ray crystallographic study of $Mo(2,6\text{-}Me_2C_6H_3NC)_6 \cdot C_6H_6$ revealed that the molybdenum atom is approximately octahedrally coordinated by six isocyanide ligands.

Introduction

There have been reports of zerovalent homoleptic isocyanide complexes of the chromium triad which are isoelectronic congeners of hexacarbonyl metals, $M(CO)_6$ (M = Cr, Mo, W) [1]. A variety of preparative methods of these complexes are known [1–6]. However, they have several disadvantages: (1) the syntheses of the starting metal compounds are tedious; and (2) relatively low yields of the products are obtained [4].

We report herein a convenient preparation of the title compounds by the reduction of commercially available metal halides with sodium amalgam in the presence of an isocyanide and an X-ray crystallographic analysis of hexakis(2,6-xylyl isocyanide)molybdenum.

---

* For part XXVI see: Y. Yamamoto and H. Yamazaki, Bull. Chem. Soc. Jpn., 57 (1984) 297. Presented at the 46th Annual Meeting of the Chemical Society of Japan, Kyoto, Japan, April 1983 (see Preprint 4B14).

0022-328X/85/$03.30

Preparation

Hexakis(isocyanide)metals such as $Cr(RNC)_6$, $Mo(RNC)_6$, and $W(RNC)_6$ (R = $2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, $2,4\text{-t-}Bu_2\text{-}6\text{-}MeC_6H_2$, $2,4,6\text{-t-}Bu_3C_6H_2$, and t-Bu) were prepared simply by the reduction of $CrCl_3(THF)_3$, $MoCl_4(C_2H_5CN)_2$, $MoCl_5$, or WCl_6 with Na-Hg in the presence of an appropriate isocyanide.

The isocyanide complexes are mostly air-sensitive, but complexes containing bulky 2,4,6-tri-t-butylphenyl isocyanide as ligands are exceptionally so stable that they can be kept, unchanged, for 2 years. The proton NMR spectra of these zerovalent isocyanide complexes showed the presence of one kind of isocyanide group. The variable-temperature NMR spectra of the $M(2,6\text{-}Me_2C_6H_3NC)_6$ (M = Cr, Mo, W)/$2,6\text{-}Me_2C_6H_3NC$ systems did not indicate the existence of ligand exchange,

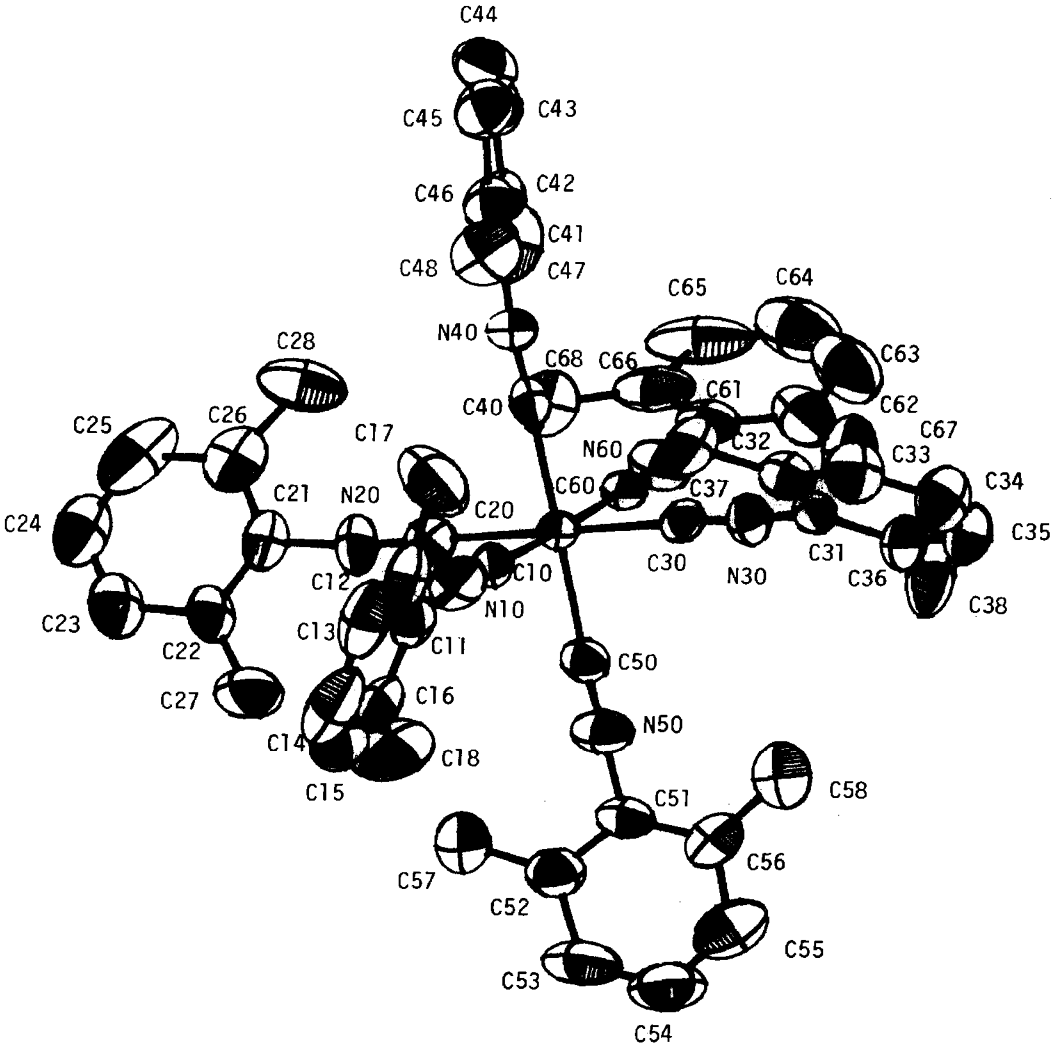

Fig. 1. The complex $Mo(2,6\text{-}Me_2C_6H_3NC)_6$ with atom designations. The thermal ellipsoids are shown at the 50% probability level.

even at 95°C, suggesting great metal–ligand bond strength. A ligand exchange reaction between hexakis(phenyl isocyanide)chromium and phenyl isocyanide is known to occur [7]. Sterically bulky isocyanide ligands prevented the ligand exchange.

Description of the structure of $Mo(2,6\text{-}Me_2C_6H_3NC)_6 \cdot C_6H_6$

The structure consists of hexakis(2,6-xylyl isocyanide)molybdenum and benzene in a 1/1 ratio. The molecular geometry of $Mo(2,6\text{-}Me_2C_6H_3NC)_6$ and the crystal structure of its benzene-solvated molecule are shown in Figs. 1 and 2, respectively. The geometry of the solvated benzene is normal.

The bond lengths and angles are given in Table 1. The molybdenum atom is approximately octahedrally coordinated by six isocyanide ligands, the deviation from the ideal 90° C–Mo–C angles being ca. 3.3°. The phenyl groups in each MoC_4 plane are somewhat torsional to minimize the steric repulsion between the *o*-methyl groups of the neighboring ligands. The sums of the dihedral angles between the

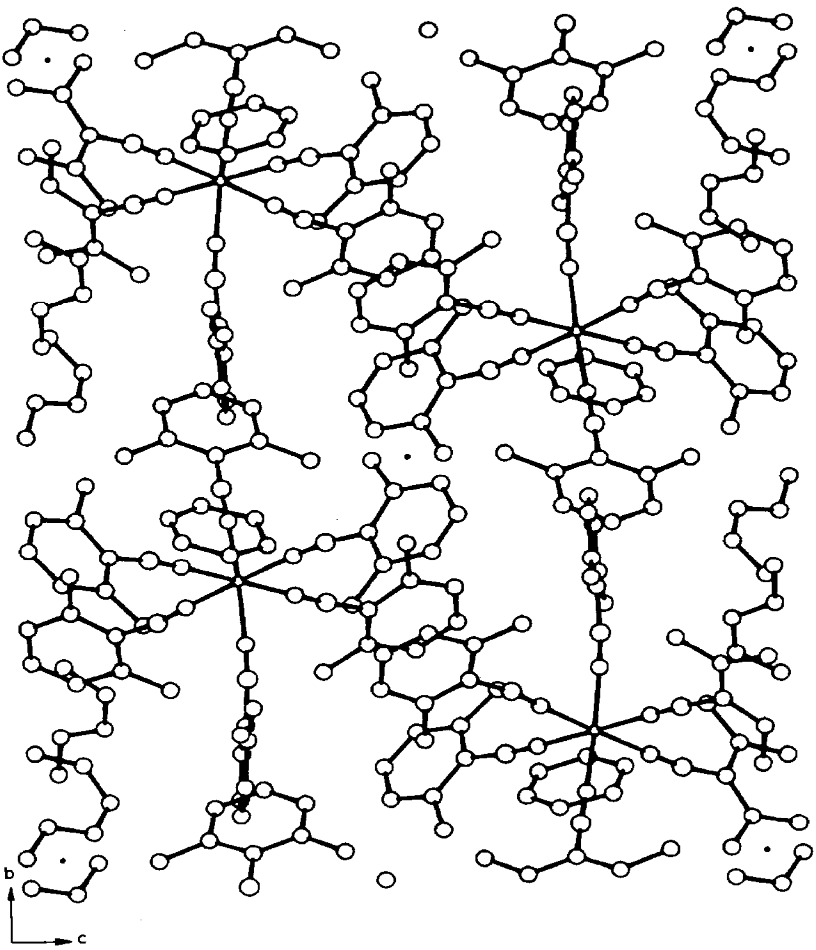

Fig. 2. Crystal structure of $Mo(2,6\text{-}Me_2C_6H_3NC)_6 \cdot C_6H_6$ projected along crystallographic axis *a*.

planes containing the molybdenum atom [MoC(10)C(20)C(30)C(60), MoC(10)-C(40)C(50)C(60), or MoC(20)C(30)C(40)C(50)] and their related phenyl rings are 235°, 214° and 246°, respectively (Table 2). These results show that the molecular geometry keeps a steric balance around the MoC_4 planes. The shortest distance between *o*-methyl groups in the *cis*-positioned ligands is 3.83 Å (C(38)...C(58)), shorter than that of the Van der Waals radii, 4.0 Å. The average Mo–C distance of 2.078 Å is longer than that (1.938 Å) of $Cr(PhNC)_6$ [8]. This result reveals the expected 0.12 Å difference between the radius of chromium and that of molybdenum in a similar environment. A similar M–C bond difference has been observed between seven-coordinate complexes of chromium and molybdenum, [Cr(t-

TABLE 1

SELECTED BOND LENGTHS, ANGLES AND NON-BONDED CONTACTS

(a) Bond lengths (Å)

Mo–C(10)	2.077(9)	C(10)–N(10)	1.16(1)
Mo–C(20)	2.078(9)	C(20)–N(20)	1.15(1)
Mo–C(30)	2.071(9)	C(30)–N(30)	1.17(1)
Mo–C(40)	2.086(9)	C(40)–N(40)	1.15(1)
Mo–C(50)	2.079(9)	C(50)–N(50)	1.16(1)
Mo–C(60)	2.075(9)	C(60)–N(60)	1.17(1)

(b) Bond angles (Deg)

C(10)–Mo–C(20)	88.6(4)	C(50)–Mo–C(60)	93.8(4)
C(10)–Mo–C(30)	90.7(4)	Mo–C(10)–N(10)	177.7(8)
C(10)–Mo–C(40)	88.9(4)	Mo–C(20)–N(20)	178.0(8)
C(10)–Mo–C(50)	86.6(4)	Mo–C(30)–N(30)	178.4(8)
C(10)–Mo–C(60)	178.0(4)	Mo–C(40)–N(40)	177.3(8)
C(20)–Mo–C(30)	179.2(4)	Mo–C(50)–N(50)	175.2(8)
C(20)–Mo–C(40)	89.0(4)	Mo–C(60)–N(60)	178.1(8)
C(20)–Mo–C(50)	91.9(4)	C(10)–N(10)–C(11)	166.4(10)
C(20)–Mo–C(60)	93.4(4)	C(20)–N(20)–C(21)	173.6(10)
C(30)–Mo–C(40)	91.2(3)	C(30)–N(30)–C(31)	170.8(10)
C(30)–Mo–C(50)	87.8(4)	C(40)–N(40)–C(41)	164.4(9)
C(30)–Mo–C(60)	175.4(3)	C(50)–N(50)–C(51)	170.3(9)
C(40)–Mo–C(50)	90.7(4)	C(60)–N(60)–C(61)	169.4(10)
C(40)–Mo–C(60)			

(c) Non-bonded contacts (Å) (< 3.70 Å)

	sym. [a]			sym. [a]	
			C(16)...C(32)	2	3.66(2)
C(21)...C(4)	1	3.60(2)	C(18)...C(33)	3	3.66(2)
C(25)...C(3)	1	3.69(2)	C(45)...N(50)	4	3.62(1)
N(10)...C(2)	1	3.68(2)	N(50)...C(1)	5	3.57(2)
C(13)...C(38)	2	3.67(2)	N(50)...C(2)	5	3.68(2)
C(13)...C(66)	2	3.69(2)	N(50)...C(45)	6	3.62(1)
C(14)...C(30)	2	3.54(2)	C(51)...C(1)	7	3.65(2)
C(14)...N(30)	2	3.49(2)	C(51)...C(2)	7	3.55(2)
C(15)...N(30)	2	3.50(2)	C(62)...C(64)	8	3.68(2)
C(15)...C(31)	2	3.54(2)	C(63)...C(63)	9	3.45(2)
C(16)...C(31)	2	3.69(2)	C(64)...C(64)	9	3.69(2)

[a] 1: x, y, z. 2: $-x+0.5, y+0.5, -Z+1$. 3: $-x+0.5, y+0.5, -z$. 4: $x+0.5, -y+0.5, z$. 5: $x, y, z-1$. 6: $x+0.5, -y+0.5, z$. 7: $x+1, y, z$. 8: $-x, -y, -z+1$. 9: $-x, -y+1, -z+1$.

TABLE 2

LEAST-SQUARES PLANES AND DIHEDRAL ANGLES BETWEEN THE MoC_4 PLANES AND PHENYL RINGS

A. Plane	
(1) $0.9006X - 0.1015Y + 0.4141Z = 3.547$	
Mo	−0.000
C(10)	0.008
C(20)	−0.005
C(30)	−0.005
C(60)	0.009
(2) $-0.2579X + 0.7091Y + 0.6587Z = 3.452$	
Mo	0.001
C(10)	−0.034
C(40)	−0.016
C(50)	−0.021
C(60)	−0.037
(3) $0.3914X + 0.6736Y - 0.6307Z = 3.420$	
Mo	−0.001
C(20)	0.013
C(30)	0.011
C(40)	0.071
C(50)	0.090
(4) $0.6579X + 0.1972Y + 0.7205Z = 4.264$	
C(11)	0.006
C(12)	−0.004
C(13)	−0.008
C(14)	0.021
C(15)	−0.012
C(16)	−0.003
(5) $0.5727X + 0.5400Y - 0.6222Z = 3.072$	
C(21)	0.016
C(22)	−0.013
C(23)	0.004
C(24)	0.000
C(25)	0.008
C(26)	−0.016
(6) $0.6342X - 0.2989Y + 0.7070Z = 1.733$	
C(31)	0.011
C(32)	−0.015
C(33)	0.004
C(34)	0.021
C(35)	−0.017
C(36)	−0.003
(7) $-0.676X + 0.9964Y + 0.0519Z = 4.072$	
C(41)	−0.001
C(42)	−0.003
C(43)	0.004
C(44)	0.002
C(45)	−0.009
C(46)	0.006
(8) $0.7126X + 0.1579Y - 0.6904Z = 1.295$	
C(51)	0.001
C(52)	0.000
C(53)	−0.001
C(54)	0.001
C(55)	0.000
C(56)	−0.001

(continued)

TABLE 2 (continued)

(9) $-0.5279X+0.4793Y+0.7062Z=2.438$	
C(61)	-0.016
C(62)	0.012
C(63)	0.005
C(64)	-0.025
C(65)	0.010
C(66)	0.016

B. Dihedral Angle

MoC_4 plane	Phenyl ring	Dihedral angle
1	4	28.4(4)
1	5	78.4(4)
1	6	25.5(4)
1	9	103.2(4)
2	4	63.4(4)
2	7	40.7(3)
2	8	121.4(4)
2	9	20.6(4)
3	5	12.9(4)
3	6	113.6(4)
3	7	52.2(3)
3	8	35.5(4)

[a] The equation for each plane is defined by $AX+BY+CZ=D$, where X, Y, and Z are measured in Å along the crystallographic a, b and c axes, respectively.

$BuNC)_7]^{2+}$ (1.993 Å) [9] and $[Mo(t\text{-}BuNC)_7]^{2+}$ (2.122 Å) [10]. The C≡N distances are reasonable values and the Mo–C–N angles are nearly linear, within the experimental errors. The close contacts in the $Mo(2,6\text{-}Me_2C_6H_3NC)_6$ molecule are 3.82 (C(38)...C(58)), 3.85 (C(17)...C(48)) and 3.86 Å (C(28)...C(42)). The close contacts in the crystals are 3.45 Å between C(63) and C(63) ($-x$, $1-y$, $1-z$), and 3.49 Å between C(14) and N(30) ($0.5-x$, $0.5+y$, $1-z$), all shorter than the sum of the Van der Waals radii.

Experimental

Nuclear magnetic resonance spectra were recorded on a JEOL C-60HL. A JASCO A-202 spectrometer was used for IR spectra. All operations were performed under nitrogen. Isocyanides were prepared by standard procedures [11]. $CrCl_3(THF)_3$ [12] and $MoCl_4(C_2H_5CN)_2$ [13] were prepared according to published methods. The typical preparation methods are described below.

Hexakis(2,6-xylyl isocyanide)molybdenum. A solution of $MoCl_4(C_2H_5CN)_2$ (0.3 g, 1.02 mmol) and 2,6-xylyl isocyanide (0.83 g, 6.34 mmol) in THF (30 ml) was added to ca. 1.2% sodium amalgam (100 g) and the mixture was stirred at room temperature for 2 h. The reddish-brown solution was filtered and the solvent was removed under vacuum. The residue was chromatographed on alumina containing 10% H_2O (column height ca. 4 cm), using benzene as the eluent. The solvent was removed until ca. 5 ml was left. Orange crystals of the title complex (0.54 g, 60%) were collected and dried under vacuum. ^1H NMR (PhCl): δ 2.44 (s, Me). IR (Nujol):

2005, 1945 cm^{-1} (N≡C). Found: C, 74.47; H, 6.30; N, 8.26. $MoC_{60}H_{60}N_6$ calcd.: C, 74.98; H, 6.29; N, 8.74%.

Hexakis(2,4,6-tri-t-butylphenyl isocyanide)tungsten. A solution of WCl_6 (0.12 g, 0.30 mmol) and 2,4,6-tri-t-butylphenyl isocyanide (0.83 g, 2.33 mmol) in THF (30 ml) was added to ca. 1.2% sodium amalgam (50 g) and the mixture was stirred at room temperature for 3 h. A reddish-brown precipitate was observed. The brown solution was filtered and the residue was washed with THF. The solvent from the combined filtrate was removed until ca. 15 ml was left. Reddish-brown crystals (0.4 g, 86%) of the title compound were collected and dried under reduced pressure. ^1H NMR (PhCl): δ 2.48 (s, Me). IR (Nujol): 1930 cm^{-1} (N≡C). Found: C, 75.77; H, 9.69; N, 4.79. $WC_{54}H_{54}N_6$ calcd.: C, 75.54; H, 9.68; N, 4.64%.

$Mo(2,4,6\text{-}Me_3C_6H_2NC)_6$ (69%) from $MoCl_4(C_2H_5CN)_2$ (0.3 g, 1.02 mmol) and $2,4,6\text{-}Me_3C_6H_2NC$ (0.85 g, 5.9 mmol). IR (Nujol): 2009, 1983 cm^{-1}. Found: C, 74.06; H, 6.84; N, 8.53. $MoC_{60}H_{60}N_6$ calcd.: C, 74.51; H, 6.88; N, 8.69%.

$Mo(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_6$ (83%) from $MoCl_5$ (0.14 g, 0.37 mmol) and $2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC$ (0.52 g, 2.26 mmol). IR (Nujol): 1959 cm^{-1} (N≡C). Found: C, 78.77; H, 9.19; N, 5.82. $MoC_{96}H_{174}N_6$ calcd.: C, 78.33; H, 9.45; N, 5.71%.

$Mo(2,4,6\text{-}t\text{-}Bu_3C_6H_2NC)_6$ (69%) from $MoCl_4(C_2H_5CN)_2$ (0.15 g, 0.51 mmol) and $2,4,6\text{-}t\text{-}Bu_3C_6H_2NC$ (0.84 g, 3.1 mmol). IR (Nujol): 2114, 1933 cm^{-1} (N≡C). Electronic spectrum (CH_2Cl_2): λ 488 (ε 49160), 401(25180), 322(63530), 253(39180) nm. Found: C, 79.40; H, 10.23; N, 4.78. $MoC_{114}H_{174}N_6$ calcd.: C, 79.39; H, 10.17; N, 4.87%.

$Mo(t\text{-}BuNC)_6$ (65%) from $MoCl_4(C_2H_5CN)_2$ (0.3 g, 1.02 mmol) and t-BuNC (0.60 g, 7.2 mmol). ^1H NMR (PhCl): δ 1.45 (s, t-Bu). IR (Nujol): 2100, 1958 cm^{-1} (N≡C). Found: C, 60.63; H, 9.22; N, 14.00. $MoC_{30}H_{54}N_6$ calcd.: C, 60.59; H, 9.15; N, 14.13%.

TABLE 3

CRYSTALLOGRAPHIC DATA AND DATA COLLECTION OF $Mo(2,6\text{-}Me_2C_6H_3NC)_6 \cdot C_6H_6$ [a]

space group	$P2_1/a$
mol. wt.	961.1
a, Å	23.903(7)
b, Å	18.871(5)
c, Å	11.787(3)
β, deg	90.56(2)
V, Å^3	5316.4
Z	4
abs. coeff., Mo-K_α, cm^{-1}	0.54
method	$\omega + 2\theta$ ($2 \leq 40°$), ω ($2\theta > 40°$)
scan speed, deg/s	4
2θ limits, deg	< 45°
no. of total data	4728
no. of data used	
$F_0 > 3\sigma(F_0)$	4319
final no. of variables	605
R	0.0623 [b]
R_w	0.0736 [c]

[a] Data collection was carried out in a sealed capillary filled with nitrogen. [b] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [c] $R_w = [\Sigma\omega(|F_0| - |F_0|)^2/\Sigma\omega|F_0|^2]^{1/2}$ ($\omega = 1$).

TABLE 4

POSITIONAL[a] AND THERMAL PARAMETERS OF $Mo(2,6\text{-}Me_2C_6H_3NC)_6 \cdot C_6H_6$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	1529(0)	2428(0)	1477(1)	42(0)	42(0)	42(0)	3(0)	−2(0)	−2(0)
C(10)	1849(4)	3185(5)	331(8)	52(6)	56(6)	47(6)	7(5)	−9(5)	−3(5)
N(10)	2036(4)	3591(4)	−254(7)	85(6)	64(6)	61(6)	−22(5)	5(5)	8(4)
C(11)	2138(4)	4186(5)	−857(9)	80(7)	50(6)	66(7)	−23(5)	−22(6)	7(5)
C(12)	2626(4)	4110(6)	−1648(8)	69(7)	107(9)	47(7)	−22(7)	−4(5)	16(6)
C(13)	2779(5)	4754(8)	−2218(10)	98(10)	137(12)	67(9)	−56(9)	−18(7)	26(8)
C(14)	2522(7)	5394(8)	−1938(11)	177(15)	127(12)	72(10)	−48(11)	−39(10)	3(9)
C(15)	2087(7)	5440(7)	−1242(12)	183(15)	66(8)	110(11)	−5(9)	−66(11)	−15(8)
C(16)	1905(5)	4824(6)	−624(10)	99(9)	82(8)	77(9)	−14(7)	−33(7)	−19(7)
C(17)	2880(6)	3422(8)	−1914(13)	132(13)	136(13)	112(12)	67(11)	35(10)	27(10)
C(18)	1440(6)	4830(9)	270(13)	96(11)	172(16)	113(12)	24(10)	30(9)	−55(11)
C(20)	1343(4)	3237(5)	2607(8)	59(6)	49(6)	54(6)	2(5)	5(5)	3(5)
N(20)	1255(4)	3691(4)	3234(7)	86(7)	57(5)	69(6)	2(5)	23(5)	−10(4)
C(21)	1211(4)	4267(5)	3978(9)	82(8)	46(6)	63(7)	1(5)	24(6)	−4(5)
C(22)	745(5)	4730(6)	3791(10)	94(9)	65(7)	73(8)	6(6)	20(7)	−4(6)
C(23)	716(6)	5326(6)	4543(12)	135(12)	55(7)	131(12)	10(8)	44(10)	−15(8)
C(24)	1114(6)	5412(7)	5411(13)	139(13)	84(10)	117(12)	−5(9)	19(10)	−34(9)
C(25)	1547(6)	4941(7)	5552(11)	113(11)	104(10)	80(9)	−37(8)	13(8)	−29(8)
C(26)	1619(5)	4325(6)	4665(10)	75(8)	90(8)	68(8)	−18(7)	−3(6)	−9(6)
C(27)	311(6)	4586(8)	2867(11)	99(10)	142(13)	85(10)	30(9)	−29(8)	−10(9)
C(28)	2081(5)	3791(7)	5010(12)	74(8)	111(10)	107(11)	22(8)	−8(7)	5(8)
C(30)	1715(4)	1631(5)	332(8)	44(6)	61(6)	46(6)	7(5)	−5(5)	10(5)
N(30)	1812(4)	1189(4)	−333(7)	78(6)	55(5)	66(5)	12(4)	−7(5)	−13(4)
C(31)	1908(4)	594(5)	−975(8)	76(7)	56(6)	46(6)	21(5)	−8(5)	−10(5)
C(32)	2341(5)	613(6)	−1781(9)	85(8)	98(9)	49(7)	28(7)	−6(6)	−18(6)
C(33)	2426(6)	−66(8)	−2373(10)	112(11)	141(12)	61(8)	52(9)	3(7)	−19(8)
C(34)	2081(7)	−659(7)	−2127(12)	185(16)	78(9)	104(12)	26(10)	−33(11)	−8(6)
C(35)	1647(6)	−630(7)	−1364(12)	149(13)	92(10)	97(11)	8(9)	−40(10)	0(8)
C(36)	1555(5)	−3(6)	−734(10)	105(10)	58(7)	96(9)	8(7)	−50(8)	−9(6)
C(37)	2681(6)	1248(7)	−1936(12)	97(10)	107(11)	117(12)	−17(8)	25(9)	15(9)
C(38)	1091(6)	37(9)	131(12)	82(9)	173(15)	96(11)	−24(10)	18(8)	29(10)
C(40)	2320(4)	2343(5)	2229(7)	58(6)	54(6)	41(5)	−1(5)	0(4)	−1(5)
N(40)	2757(3)	2323(4)	2632(6)	50(4)	73(6)	61(5)	4(4)	−15(4)	2(4)
C(41)	3334(4)	2359(5)	2830(8)	55(6)	45(6)	65(6)	10(5)	−17(5)	−5(5)
C(42)	3525(4)	2338(6)	3969(8)	58(6)	81(8)	70(7)	11(6)	−24(5)	−10(6)
C(43)	4105(4)	2385(7)	4141(9)	66(7)	87(8)	87(8)	9(7)	−29(6)	−2(7)
C(44)	4470(4)	2445(8)	3226(10)	58(6)	118(10)	100(9)	−6(8)	−22(6)	2(9)
C(45)	4261(4)	2457(7)	2141(9)	64(6)	100(9)	87(8)	1(7)	3(6)	−3(8)
C(46)	3689(4)	2424(6)	1835(8)	62(6)	61(6)	68(6)	3(6)	1(5)	4(6)
C(47)	3123(5)	2250(9)	4950(10)	77(8)	205(17)	55(7)	27(10)	2(6)	5(9)
C(48)	3451(5)	2436(7)	711(9)	98(8)	98(9)	56(7)	−3(8)	−13(6)	−3(7)
C(50)	771(3)	2558(5)	623(7)	51(5)	60(6)	52(6)	−1(5)	7(4)	2(5)
N(50)	370(3)	2648(5)	33(7)	49(5)	98(7)	70(6)	7(5)	−9(4)	7(5)
C(51)	−55(4)	2713(6)	−713(8)	36(5)	95(8)	53(6)	−8(5)	0(4)	5(6)
C(52)	−269(4)	3398(6)	−911(9)	45(6)	79(8)	84(8)	8(5)	−12(5)	6(6)
C(53)	−681(5)	3464(7)	−1748(10)	77(8)	104(10)	84(9)	20(7)	−10(7)	7(7)
C(54)	−860(5)	2877(9)	−2340(10)	54(7)	197(16)	72(9)	12(8)	−6(6)	−16(9)
C(55)	−640(5)	2185(8)	−2131(10)	63(8)	170(14)	82(9)	−22(8)	10(6)	−46(9)
C(56)	−223(4)	2093(7)	−1291(10)	58(7)	104(9)	78(8)	−6(6)	16(6)	−13(7)
C(57)	−59(6)	4017(7)	−246(14)	111(11)	67(8)	171(15)	3(8)	−36(10)	−30(9)
C(58)	28(6)	1377(7)	−1026(14)	111(11)	60(8)	172(15)	1(8)	23(10)	−8(9)
C(60)	1223(4)	1643(5)	2537(8)	58(6)	51(6)	54(6)	15(5)	−9(5)	−4(5)
N(60)	1059(4)	1188(4)	3115(7)	92(7)	54(5)	71(6)	2(5)	25(5)	12(5)

TABLE 4 (continued)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(61)	941(5)	572(5)	3714(9)	107(9)	59(7)	55(7)	20(6)	37(6)	2(5)
C(62)	430(5)	206(6)	3371(10)	121(10)	61(7)	92(9)	−14(7)	54(8)	−14(7)
C(63)	339(7)	−458(7)	3946(14)	170(15)	68(9)	154(15)	−22(9)	88(12)	−14(9)
C(64)	731(8)	−688(8)	4754(14)	232(20)	105(12)	118(13)	56(12)	84(13)	39(10)
C(65)	1194(8)	−220(9)	5098(12)	239(20)	146(14)	80(11)	105(14)	52(12)	39(10)
C(66)	1349(7)	372(8)	4587(10)	171(14)	130(12)	57(8)	76(11)	51(9)	20(8)
C(67)	37(6)	507(8)	2495(12)	104(11)	125(12)	93(11)	3(9)	−13(8)	−9(9)
C(68)	1849(6)	822(10)	4851(14)	108(12)	194(18)	128(14)	28(12)	−31(10)	−40(12)
C(1)	1207(6)	2537(10)	7592(11)	100(10)	183(15)	89(9)	31(12)	11(7)	22(11)
C(2)	1032(6)	3227(8)	7430(12)	94(10)	147(13)	92(10)	−18(9)	5(8)	−13(9)
C(3)	730(5)	3402(8)	6522(11)	79(9)	131(12)	95(10)	−3(8)	−1(7)	4(9)
C(4)	577(5)	2939(9)	5741(12)	73(9)	176(15)	96(10)	−18(9)	−2(8)	7(10)
C(5)	747(6)	2176(10)	5864(13)	121(12)	200(19)	108(12)	−44(12)	30(9)	−56(12)
C(6)	1083(7)	2006(9)	6850(14)	136(13)	125(13)	135(14)	16(10)	53(11)	7(10)

[a] The positional parameters are multiplied by 10^4. The anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*]$ and are multiplied by 10^3.

$W(2,6\text{-}Me_2C_6H_3NC)_6$ (73%) from WCl_6 (0.28 g, 0.71 mmol) and $2,6\text{-}Me_2C_6H_3NC$ (0.55 g, 4.2 mmol). ^1H NMR (PhCl): δ 2.48 (s, Me). IR (Nujol): 1927 cm^{-1} (N≡C). Found: C, 66.70; H, 5.73; N, 8.70. $WC_{54}H_{54}N_6$ calcd.: C, 66.80; H, 5.61; N, 8.66%.

$Cr(2,6\text{-}Me_2C_6H_3NC)_6$ (64%) from $CrCl_3(THF)_3$ (0.2 g, 0.53 mmol) and $2,6\text{-}Me_2C_6H_3NC$ (0.43 g, 3.3 mmol). ^1H NMR (PhCl): δ 2.45 (s, Me). IR (Nujol): 2115, 1945 cm^{-1} (N≡C). Found: C, 77.40; H, 6.55; N, 9.99. $CrC_{54}H_{54}N_6$ calcd.: C, 77.30; H, 6.49; N, 10.02%.

X-Ray data and structure determination [14]

Orange crystals of $Mo(2,6\text{-}Me_2C_6H_3NC)_6C_6H_6$ were obtained by crystallization from benzene. The crystals were monoclinic with the systematic absence of $h0l$, $h = 2n + 1$ and $0k0$, $k = 2n + 1$, consistent with space group $P2_1/a$. The crystallographic data are given in Table 3. Intensity data were collected with a crystal mounted in a nitrogen-filled capillary. Three standard reflections were monitored at intervals of 150 reflections throughout the data collection. The crystal became somewhat dark during the measurement. The position of the molybdenum atom was determined from a Patterson map. Subsequent difference Fourier maps and cycles of block-diagonal least-squares refinement revealed the positions of the remaining non-hydrogen atoms. The atomic scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were obtained from ref. 15. All non-hydrogen atoms were refined anisotropically. The final difference synthesis showed no peaks higher than 0.36 e Å^{-3}. No attempt was made to locate the hydrogen atoms. No correction was made for absorption. A list of the observed and calculated structure amplitudes is available from the authors. The final atomic coordinates and thermal parameters are listed in Table 4.

References

1 L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, John Wiley & Sons Ltd. London, 1969.

2 P.M. Treichel, Adv. Organomet. Chem., 11 (1973) 21.

3 F. Bonati and G. Minghetti, Inorg. Chim. Acta, 9 (1974) 95.

4 Y. Yamamoto, Coord. Chem. Rev., 32 (1980) 193.

5 T. Yoshida, K. Hirotsu, T. Higuchi and S. Otsuka, Chem. Lett., (1982) 1017.

6 K.W. Chiu, C.G. Howard, G. Wilkinson, A.M.R. Galas and M.B. Hursthouse, Polyhedron, 1 (1982) 803.

7 G. Cetini and O. Gambino, Ann. Chim. (Italy), 53 (1963) 236.

8 (a) E. Ljungstrom, Acta. Chem. Scand. Ser. A, 32 (1978) 47; (b) K.R. Mann, Ph.D. Thesis, California Institute of Technology, 1976.

9 J.C. Dewan, W.S. Mialki, R.A. Walton and S.J. Lippard, J. Am. Chem. Soc., 104 (1982) 133.

10 D.L. Lewis and S.J. Lippard, J. Am. Chem. Soc., 97 (1975) 2697.

11 (a) M. Walborsky and G.E. Niznik, J. Org. Chem., 37 (1972) 187; (b) Y. Yamamoto, K. Aoki and H. Yamazaki, Inorg. Chem., 18 (1979) 1681.

12 H. Herwig and H.H. Zeiss, J. Am. Chem. Soc., 81 (1959) 4800.

13 E.A. Allen, B.J. Brisdon and G.W.A. Fowles, J. Chem. Soc. Dalton Trans., (1964) 4531.

14 The following program was used; UNICS III (1978) by T. Sakurai and K. Kobayashi.

15 International Table for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974.