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Synthesis and Structural Characterization of *cis* and *trans* [$MoCl_4(H_2NBu^t)_2$]

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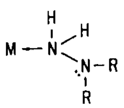
Abstract

The reaction of [$MoCl_4(PPh_3)_2$] with NH_2Bu^t in CH_2Cl_2 yields yellow crystals of [$MoCl_4(NH_2Bu^t)_2$]·$2NH_2Bu^t$. The structure is shown to consist of both *cis* and *trans* isomers of [$MoCl_4(NH_2Bu^t)_2$] and uncoordinated NH_2Bu^t molecules. Crystal data: triclinic space group, $P\bar{1}$, $a = 11.767(4)$, $b = 12.428(4)$, $c = 19.338(5)$ Å, $\alpha = 90.40(2)$, $\beta = 93.19(2)$, $\gamma = 102.20(2)°$, $V = 2759.3(14)$ Å^3, $D_{calc} = 1.28$ g cm^{-3}, $Z = 4$. Structure solution and refinement based on 2651 reflections (Mo Kα, $\lambda = 0.71073$ Å, $F_o \geqslant 6\sigma(F_o)$) converged at $R = 0.058$.

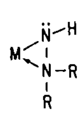
Introduction

Complexes of molybdenum with simple monodentate nitrogen donor ligands, formally related to organoamines and organohydrazines in various stages of protonation, are of fundamental chemical interest in defining the structural characteristics and the chemical interrelationships of the various members of the series (1–8). Furthermore, such moieties are plausible intermediates in the enzymatic nitrogen fixation process [1]. The molybdenum–nitrogen multiply bonded types (3, 4, 6–8) have been extensively studied in recent years [2, 3], and the amido species [$Mo(NR_2)_4$] and [$Mo_2(NMe_2)_6$] have proved particularly useful synthetic precursors [4]. In contrast, structurally characterized examples of molybdenum–amine complexes, where the amine is not part of a polydentate ligand framework, are relatively unusual and largely limited to species with alkoxy or siloxy coligands, such as [Mo(adamantoxy)$_4$($NHMe_2$)] [5], [$Mo(CH_3C_6H_4O)_4(NHMe_2)_2$] [6], [$Mo(OSiMe_3)_4(NHMe_2)_2$] [7] and [$Mo_2(OSiMe_3)_6(NHMe_2)_2$] [8]. In this paper, we report the synthesis of [$MoCl_4(NH_2Bu^t)_2$] and the structures of the *cis* and *trans* isomers which are both present in the asymmetric unit of crystals of the title complex.



1

Hydrazino



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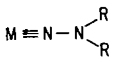
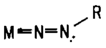
Hydrazido (1-)



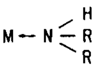
3

Hydrazido (2-)



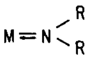
4

Diazenido



5

Amine



6

Amido

$M{\equiv}N{-}R$

7

Imido

$M{\equiv}N$

8

Nitrido

Experimental

Materials and Methods

All reactions were performed in freshly dried and distilled solvents under an atmosphere of argon. Dichloromethane was technical grade and was distilled from $CaCl_2$ and P_4O_{10}. All reagents were obtained from standard commercial sources. [$MoCl_4(PPh_3)_2$] was prepared by the literature method [9].

The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Siemens R3m/V diffractometer.

Preparation of Compounds

[$MoCl_4(NH_2Bu^t)_2$]·$2NH_2Bu^t$

An excess of NH_2Bu^t (1 g, 13.7 mmol) was added to a solution of [$MoCl_4(PPh_3)_2$] (1 g, 1.32 mmol) in CH_2Cl_2 (20 cm^3) under argon. After stirring at room temperature for 1 h and concentration of the solution to 15 cm^3, the dark brown solution was carefully layered with 15 cm^3 of heptane. After standing for 3 weeks at 4 °C, yellow crystals of [$MoCl_4(NH_2Bu^t)_2$]·$2NH_2Bu^t$ were obtained in *c.* 15% yield. *Anal.* Calc. for $C_{16}H_{44}N_4Cl_4Mo$: C, 36.2; H, 8.31; N, 10.6. Found: C, 35.8; H, 7.99; N, 10.4%. IR (KBr pellet, cm^{-1}): 3185(m), 2960(s), 1375(m), 1269(s), 1209(m), 1140(br), 1070(br), 1030(s), 801(s), 742(w), 649(w), 623(w), 320(m).

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Reactions with alcohols and silanols

Attempts to displace the Cl donors of $[MoCl_4(NH_2Bu^t)_2]$ with alkoxy or siloxy groups resulted in displacement of the NH_2Bu^t ligand and partial substitution of Cl donors. No analytically pure materials were isolated.

Crystal Data

$C_{16}H_{44}N_4Cl_4Mo$: formula weight = 530.1; triclinic, $P\bar{1}$, $a = 11.767(4)$, $b = 12.428(4)$, $c = 19.338(5)$ Å; $\alpha = 90.40(2)°$, $\beta = 93.19(2)°$, $\gamma = 102.20(2)°$; $V = 2759.3(14)$ Å^3, $D_{calc} = 1.28$ g cm^{-3}, $Z = 4$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), $\mu = 8.13$ cm^{-1}, $T = 296$ K, crystal dimensions: 0.21 × 0.23 × 0.26 mm.

X-ray Structure Determination

Full details of the crystallographic methodologies may be found in ref. 10. For full details of the crystal data, data collection and refinement procedures see 'Supplementary Material'.

In no instance was an extinction correction applied to the data. Idealized hydrogen atom positions were used throughout the analysis, with the C–H and N–H distances set at 0.96 and 0.94 Å, respectively. All non-hydrogen atoms of the $[MoCl_4(NH_2Bu^t)_2]$ molecules were refined anisotropically, as were the N atoms of the NH_2Bu^t molecules of crystallization. All other atoms were treated isotropically. The final discrepancy factor was 0.058 for 2651 reflections with $F_o \geqslant 6\sigma(F_o)$ (4622 collected).

Results and Discussion

Synthesis and Spectroscopic Properties

The reaction of $[MoCl_4(PPh_3)_2]$ with excess NH_2Bu^t yields the paramagnetic yellow compound $[MoCl_4(NH_2Bu^t)_2]\cdot 2NH_2Bu^t$ as a crystalline product. The major product is a brown insoluble powder which gave no analytically consistent composition. The infrared of $[MoCl_4(NH_2Bu^t)_2]\cdot 2NH_2Bu^t$ exhibited bands in the 1000–3200 cm^{-1} region which confirmed the presence of the NH_2Bu^t moiety. The broad band at 700–900 cm^{-1} associated with liquid amines (N–H bending) and arising from extensive hydrogen bonding in the neat liquid is absent in spectrum of the complex, which exhibits in contrast a sharp strong band at 801 cm^{-1}. The only other noteworthy feature of the infrared spectrum is the appearance of a medium intensity band at 320 cm^{-1}, assigned to ν(Mo–Cl).

TABLE 1. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3)

	x	y	z	U_{eq} [a]
Mo(1)	340(1)	4694(1)	2625(1)	46(1)
Mo(2)	2568(1)	−334(1)	2264(1)	45(1)
Cl(1)	−1479(4)	3337(4)	2528(3)	73(2)
Cl(2)	−423(4)	5892(4)	3369(2)	72(2)
Cl(3)	2267(4)	5940(3)	2704(2)	66(2)
Cl(4)	1127(4)	3590(3)	1768(2)	62(2)
Cl(5)	4604(4)	588(3)	2356(2)	66(2)
Cl(6)	2172(4)	495(3)	1158(2)	71(2)
Cl(7)	1989(4)	1187(3)	2846(2)	65(2)
Cl(8)	589(4)	−1421(3)	2208(3)	71(2)
N(1)	978(12)	3581(10)	3396(7)	59(6)
N(2)	71(11)	5799(10)	1745(7)	63(6)
N(3)	2942(14)	−1326(11)	3159(6)	85(8)
N(4)	2782(11)	−1789(10)	1627(6)	56(6)
C(1)	876(18)	3547(18)	4195(11)	63(10)
C(2)	1353(17)	2639(15)	4480(9)	62(10)
C(3)	−380(19)	3383(15)	4339(9)	99(12)
C(4)	1489(17)	4651(16)	4470(10)	60(10)
C(5)	−912(16)	5772(14)	1224(9)	58(8)
C(6)	−592(17)	6648(14)	722(10)	58(9)
C(7)	−1932(16)	6005(16)	1611(11)	107(11)
C(8)	−1298(16)	4640(13)	866(9)	85(9)
C(9)	2988(15)	−1115(15)	3905(11)	67(9)
C(10)	1747(21)	−1126(18)	4092(12)	101(14)
C(11)	3591(17)	1(15)	4147(8)	89(10)
C(12)	3251(23)	−1967(18)	4312(11)	196(17)
C(13)	3792(16)	−2006(13)	1275(9)	59(8)
C(14)	4740(15)	−2201(15)	1781(9)	83(9)
C(15)	4298(15)	−1074(15)	794(9)	86(10)
C(16)	3386(16)	−3058(14)	791(10)	93(10)
N(5)	9471(11)	985(10)	1772(6)	56(6)
N(6)	3713(10)	2932(9)	1815(6)	49(5)
N(7)	6052(28)	5163(20)	3347(15)	128(16)
N(8)	9031(22)	157(20)	3116(14)	156(14)
C(17)	8695(13)	733(12)	1113(8)	50(5)
C(18)	7538(14)	1042(14)	1233(9)	83(6)
C(19)	8494(16)	−472(14)	928(9)	89(6)
C(20)	9322(15)	1351(14)	536(9)	90(6)
C(21)	4300(15)	3403(14)	1198(9)	65(5)
C(22)	4766(18)	4619(15)	1358(11)	117(8)
C(23)	5328(17)	2908(16)	1077(11)	114(8)
C(24)	3478(16)	3279(16)	565(10)	110(7)
C(25)	5550(22)	4105(21)	3535(13)	118(8)
C(26)	4343(24)	3894(24)	3666(16)	141(13)
C(27)	6085(26)	3630(25)	4087(16)	153(14)
C(28)	5478(15)	3267(14)	2973(9)	87(6)
C(29)	7961(20)	−427(19)	3446(12)	95(7)
C(30)	7572(28)	−1296(25)	3092(17)	203(17)
C(31)	7293(26)	306(24)	3513(17)	151(14)
C(32)	8565(30)	−624(29)	3982(17)	158(16)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Attempts to react $[MoCl_4(NH_2Bu^t)_2]$ with alcohols and silanols yielded intractable mixtures in which the NH_2Bu^t ligand as well as the Cl donors had been partially or totally displaced. This behavior contrasts with that of $[Mo(OSiMe_3)_4(NHMe_2)_2]$ [7] which undergoes ligand substitution reactions of the siloxy ligands, retaining the $[Mo(NHMe_2)_2]$ core, but is similar to that of $[Mo_2(OSiMe_3)_6(NHMe_2)_2]$

[8] where the $NHMe_2$ ligand is readily displaced by reaction with alcohols or thermolysis. These differences in reaction behavior appear to reflect the Mo–N bond strength as measured by Mo–N bond distances in the structures. Thus, the Mo–N distance in $[Mo(OSiMe_3)_4(NHMe_2)_2]$ is 2.219(4) Å, while those for $[Mo_2(OSiMe_3)_6(NHMe_2)_2]$ and $[MoCl_4(NH_2Bu^t)_2]$ are 2.282(4) and 2.24(2) Å, respectively (*vide infra*).

Description of the Structure

Atomic coordinates are given in Table 1; Tables 2 and 3 list selected bond lengths and angles, respectively. The crystallographic study shows that both the *cis* and *trans* isomers of $[MoCl_4(H_2NBu^t)_2]$ are present in the asymmetric unit. The structures are illustrated in Figs. 1 and 2.

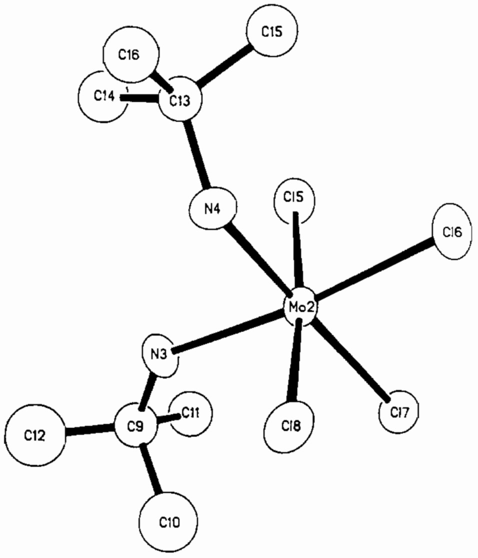

Fig. 1. ORTEP view of the structure of *cis*-$[MoCl_4(H_2NBu^t)_2]$, showing 50% probability thermal ellipsoids.

TABLE 2. Selected bond lengths (Å) for *cis* and *trans*-$[MoCl_4(H_2NBu^t)_2] \cdot 2H_2NBu^t$

trans-$[MoCl_4(H_2NBu^t)_2] \cdot 2H_2NBu^t$		*cis*-$[MoCl_4(H_2NBu^t)_2] \cdot 2H_2NBu^t$	
Mo1–Cl1	2.426(5)	Mo2–Cl5	2.424(4)
Mo1–Cl2	2.401(4)	Mo2–Cl6	2.445(4)
Mo1–Cl3	2.457(5)	Mo2–Cl7	2.430(4)
Mo1–Cl4	2.484(4)	Mo2–Cl8	2.428(5)
Mo1–N1	2.244(11)	Mo2–N3	2.210(13)
Mo1–N2	2.245(12)	Mo2–N4	2.246(12)

TABLE 3. Selected bond angles (°) for *cis* and *trans*-$[MoCl_4(H_2NBu^t)_2] \cdot 2H_2NBu^t$

trans-$[MoCl_4(H_2NBu^t)_2] \cdot 2H_2NBu^t$		*cis*-$[MoCl_4(H_2NBu^t)_2] \cdot 2H_2NBu^t$	
Cl1–Mo1–Cl2	93.2(2)	Cl5–Mo2–Cl6	94.1(2)
Cl1–Mo1–Cl3	175.1(2)	Cl5–Mo2–Cl7	92.1(2)
Cl1–Mo1–Cl4	88.6(2)	Cl5–Mo2–Cl8	174.4(2)
Cl1–Mo1–N1	86.9(4)	Cl5–Mo2–N3	87.6(4)
Cl1–Mo1–N2	100.9(3)	Cl5–Mo2–N4	97.0(3)
Cl2–Mo1–Cl3	91.2(2)	Cl6–Mo2–Cl7	88.4(2)
Cl2–Mo1–Cl4	174.4(2)	Cl6–Mo2–Cl8	90.0(2)
Cl2–Mo1–N1	101.5(3)	Cl6–Mo2–N3	170.5(4)
Cl2–Mo1–N2	88.1(4)	Cl6–Mo2–N4	85.8(3)
Cl3–Mo1–Cl4	87.2(2)	Cl7–Mo2–Cl8	91.9(2)
Cl3–Mo1–N1	90.1(4)	Cl7–Mo2–N3	100.8(4)
Cl3–Mo1–N2	81.3(3)	Cl7–Mo2–N4	169.6(3)
Cl4–Mo1–N1	83.8(3)	Cl8–Mo2–N3	87.7(4)
Cl4–Mo1–N2	86.4(4)	Cl8–Mo2–N4	79.4(3)
N1–Mo1–N2	167.3(5)	N3–Mo2–N4	84.7(5)

The metrical parameters associated with the isomers of $[MoCl_4(H_2NBu^t)_2]$ are unexceptional. The average Mo–Cl bond distances of 2.432(8) and 2.442(9) Å for the *cis* and *trans* isomers, respectively, are essentially identical, as are the average Mo–N

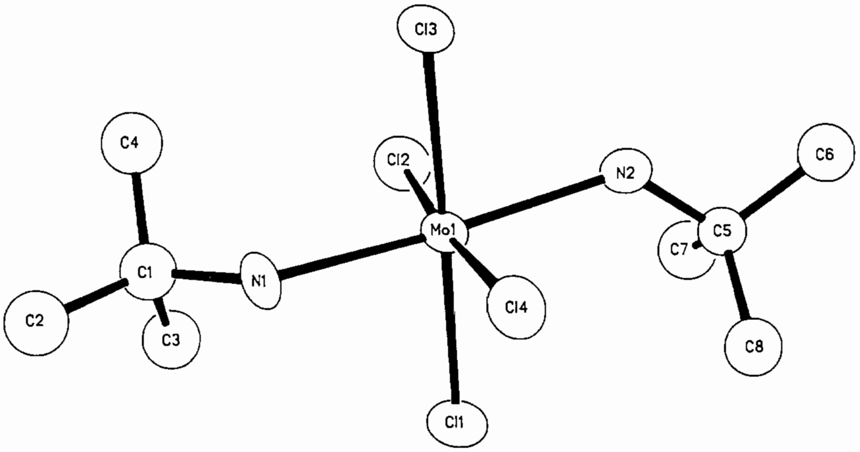

Fig. 2. ORTEP view of the structure of *trans*-$[MoCl_4(H_2NBu^t)_2]$.

distances of 2.23(2) and 2.24(2) Å. The Mo–N distances of this study are intermediate between the values of 2.219(4) Å for [$Mo(OSiMe_3)_4(HNMe_2)_2$] [7] and 2.282(4) Å for [$Mo_2(OSiMe_3)_6(HNMe_2)_2$] [8], a feature consistent with the relative ease of displacement of the H_2NBu^t group in ligand substitution reactions.

The most significant angular distortions from idealized octahedral angles result from steric interactions between the tert-butyl groups and Cl ligands. Thus, the Cl1–Mo1–N2 and Cl2–Mo1–N1 angles of 100.9(3) and 101.5(3)°, respectively, for *trans*-[$MoCl_4(H_2NBu^t)_2$] are consequences of the eclipsed orientations of the Mo1–Cl1 and N2–C5 bond vectors and of the Mo1–Cl2 and N1–C1 bond vectors, which require the Mo valence angles to adjust in order to minimize the steric interactions between the bulky tert-butyl groups and the chloride donors. Similarly, the Cl5–Mo2–N4 angle of 97.0(3)° and the Cl7–Mo2–N3 angle of 100.8(4)° for the *cis* isomer reflect steric constraints imposed by eclipsing the Mo2–Cl5 and N4–C13 bond vectors and the Mo2–Cl7 and N3–C9 bond axes, respectively.

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