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PREPARATION OF HOMOLEPTIC t-BUTYL ISOCYANIDE COMPLEX OF Mo(0) AND REACTIONS WITH ALKYL HALIDES. MOLECULAR STRUCTURE OF [Mo(t-BuN=CCH$_2$Ph)(t-BuNC)$_5$]Br

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Hexakis(t-butyl isocyanide)molybdenum(0) was prepared and reacted with alkyl halides to give η^2-iminoacyl Mo(II) complexes. An X-ray structural study of the product, [Mo(t-BuN=CCH$_2$Ph)(t-BuNC)$_5$]Br revealed a distorted octahedral molecular structure, regarding the iminoacyl ligand as an unidentate ligand. An intensive bending (137°) of the t-butyl isocyanide trans to the η^2-iminoacyl ligand was salient.

Homoleptic aryl isocyanide complexes of zero-valent VIa metals are well known,[1)] while the corresponding alkyl isocyanide complexes are limited to Cr(RNC)$_6$ (R=t-Bu, cyclo-C$_6$H$_{11}$).[2)] An attempted reduction of Mo(II) complex [MoI(t-BuNC)$_6$]I with Zn/Hg resulted in the formation of [MoI(t-BuNHC≡CNH-t-Bu)(t-BuNC)$_4$]I through reductive coupling of the coordinated isocyanides rather than to give Mo(t-BuNC)$_6$.[3)] A similar reduction of Mo(t-BuS)$_2$(t-BuNC)$_4$ with Na/Hg in the presence of t-BuNC did not afford the zero-valent complex but Mo$_2$(μ-t-BuS)$_2$(t-BuNC)$_8$.[4)] Here we report the preparation of Mo(t-BuNC)$_6$(**1**) and its reactions with alkyl halides together with the molecular structure of the product, [Mo(t-BuN=CCH$_2$Ph)(t-BuNC)$_5$]Br.

The compound **1** [5,6,7)] was prepared by reduction of Mo$_2$(OAc)$_4$ with Na/Hg in the presence of an excess of t-BuNC at room temperature in THF as brown diamagnetic crystals (75 %). The compound **1** is extremely sensitive toward air and readily soluble in saturated hydrocarbons. The IR spectrum (in *n*-hexane) shows ν(NC) at 1885 and 1955 cm^{-1}, which may be compared with those (1880, 1960 cm^{-1}) of Cr(t-BuNC)$_6$.[2)] The cyclic voltammogram of **1** shows a quasi-reversible one electron oxidation with $E_{1/2}$ of -0.55 V vs SCE.[8)]

A reaction of **1** with CH$_3$I took place readily at room temperature in *n*-hexane to give a brown precipitate of [Mo(t-BuN=CCH$_3$)(t-BuNC)$_5$]I (**2**) (55 %),[5,9)] no σ-alkyl complex being detected. A similar reaction with PhCH$_2$I afforded [Mo(t-BuN=CCH$_2$Ph)-(t-BuNC)$_5$]Br (**3**)[5,10)] as brick red crystals (65 %). The ν(C=N) bands of **2** (1758 cm^{-1}) and **3** (1755 cm^{-1}) were observed at a considerably higher region than that expected for η^1-iminoacyl ligand (1580-1660 cm^{-1}).[11)] The iminoacyl carbon observed in the ^{13}C{^{1}H}NMR (δ196-198) was also more deshielded than that found for η^1-iminoacyl group.[12] These spectral features are consistent with η^2-coordination of the iminoacyl ligand[12] which was confirmed by the present X-ray study. It is to be noted that one of the ν(NC) bands[9,10] is observed at an extremely low frequency for Mo(II) isocyanides, e.g. $[Mo(t\text{-}BuNC)_7](I_3)_2$ (2210, 2143, 2055 cm^{-1})[13] and $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_4$ (2120, 2080, 1997 cm^{-1}).[14] In sharp contrast to the facile successive insertion of isocyanide into η^1-iminoacyl-metal bond in group VIII metal compounds,[15] the η^2-iminoacyl compounds **2** and **3** failed to give polyiminoacyl complex on treatment with an excess of t-BuNC or PPh_3 in acetone at 50°.

Crystals of **3** suitable for X-ray study were obtained by recrystallization from acetone-toluene. Crystal data:[16] monoclinic, space group $P2_1$, a=1.5743(6), b=2.6023(9), c=1.0943(3) nm, β=92.77(2)°, Z=4, D_c=1.135 Mg m^{-3}, R=0.059 for 2399 refelctions ($I>3\sigma(I)$ and $2\theta<43°$). Two independent molecules with very similar molecular parameters are contained in the asymmetric unit. The molecular structure and the mean molecular parameters are shown in Figure 1 and Table 1, respectively. Regarding the iminoacyl group as an unidentate ligand, the Mo atom assumes a distorted octahedral configuration; the C1-Mo-C2 angle is almost linear, while the inter-ligand angles in the equatorial plane, e.g. C3-Mo-C4, C3-Mo-M, and C5-Mo-M[17] where M represents the center of the C6-N6 bond, are in the range of 80-106°. The deviation of the Mo atom from the equatorial plane C3-C4-C5-M is only 2 pm. The C=N coordination of the iminoacyl ligand is nearly parallel to the equatorial plane, the dihedral angle between the C6-N6-Mo and C3-C4-C5-M planes being 9.2°.

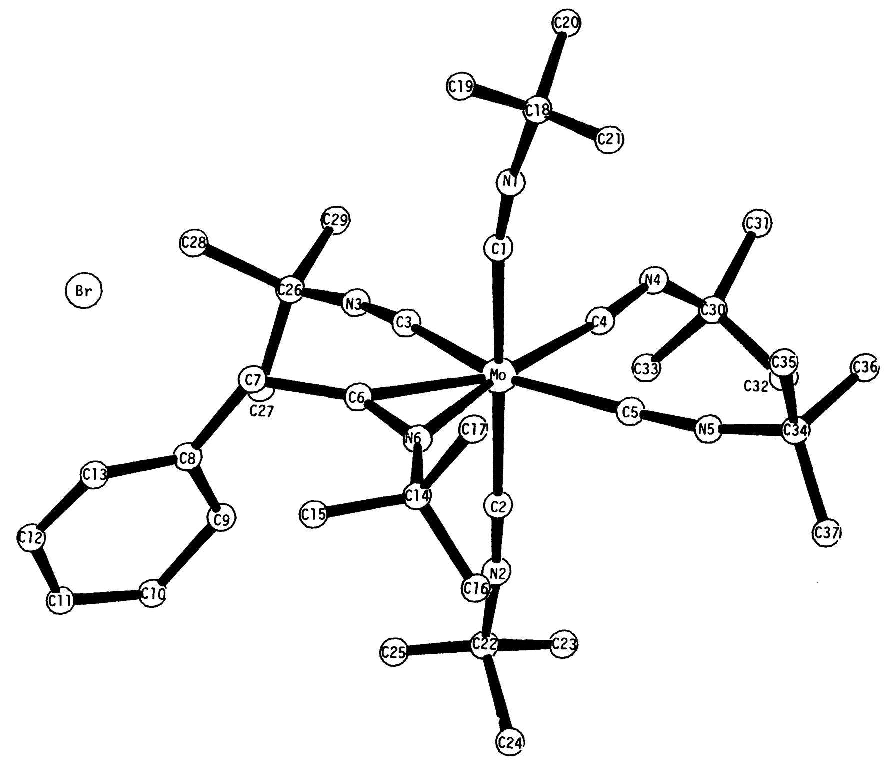

Figure 1. Molecular structure of $[Mo(t\text{-}BuN{=}CCH_2Ph)(t\text{-}BuNC)_5]Br$

Table 1. Selected Bond Distances(pm) and Angles(°)[a]

Mo-C1	212	Mo-C2	211	Mo-C3	208	Mo-C4	203
Mo-C5	217	Mo-C6	214	Mo-N6	217	C1-N1	114
C2-N2	115	C3-N3	115	C4-N4	120	C5-N5	114
C6-N6	125	N1-C18	137	N2-C22	144	N3-C26	146
N4-C30	141	N5-C34	142	N6-C14	151	C6-C7	150
C1-Mo-C2	176.4	C1-Mo-C3	97.1	C1-Mo-C4	91.5	C1-Mo-C5	86.7
C1-Mo-C6	84.7	C1-Mo-N6	86.8	C2-Mo-C3	85.9	C2-Mo-C4	90.8
C2-Mo-C5	91.2	C2-Mo-C6	94.2	C2-Mo-N6	90.6	C3-Mo-C4	79.8
C3-Mo-C5	158.7	C3-Mo-C6	78.1	C3-Mo-N6	111.4	C4-Mo-C5	79.3
C4-Mo-C6	156.9	C4-Mo-N6	168.9	C5-Mo-C6	123.1	C5-Mo-N6	89.7
C6-Mo-N6	33.8	Mo-C1-N1	174	Mo-C2-N2	175	Mo-C3-N3	177
Mo-C4-N4	175	Mo-C5-N5	174	Mo-C6-C7	148	Mo-N6-C14	149
Mo-C6-N6	75	Mo-N6-C6	72	N6-C6-C7	137	C6-N6-C14	139

[a] The corresponding bond distances and angles of two independent molecules are averaged. E.s.d.'s are 1-2 pm for Mo-C and Mo-N distances, 2-3 pm for C-N and C-C distances, 1° for C-Mo-C and C-Mo-N angles, and 1-2° for Mo-C-N, Mo-N-C, Mo-C-C, and N-C-C angles.

The C6-N6 distance is intermediate of free C≡N (116 pm)[18] and C=N (129-131 pm) bond lengths.[19] The C6-Mo distance is in the range of Mo-C(≡C) bond length found for alkyne complexes (197-214 pm).[20] The bent back angles, C6-N6-C14 and N6-C6-C7 are also comparable to the corresponding angle of alkyne complexes (135-150°).[20] Thus, **3** can be described both by η^2-iminoacyl Mo(II) complex [Mo(η^2-t-BuN=CCH_2Ph)-(t-BuNC)$_5$]Br and nitrilium Mo(0) complex [Mo(t-Bu$\overset{+}{N}$≡CCH_2Ph)(t-BuNC)$_5$]Br. The η^2-iminoacyl Mo(II) complex has a precedent Mo(η^2-CH_3N=CCH_3)(η^5-C_5H_5)(CO)$_2$.[12]

As expected from the low ν(NC) band, an intensive bending was found for the t-BuNC ligand trans to the t-BuN=CCH_2Ph ligand. Thus, the C4-N4-C30 angles is only 137°, while the corresponding angles of the remaining t-BuNC are normal (168-176°). A simialr bending of isocyanide is known for Fe(t-BuNC)$_5$.[21] The enhanced sp^2 character of the N4 atom reflects in the short Mo-C4 and long C4-N4 distances compared to the corresponding distances of the other isocyanides. No unusually short intra- and intermolecular contacts were found for the methyl groups of t-BuN4C4. The intensive bending, thus, may arise from the electronic origin, rather than steric one, manifesting an efficient electron donation from the η^2-iminoacyl ligand.

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References

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5) Elemental analysis agrees well with the required values.

6) ^{1}H NMR (δ, in benzene-d_6); 1.43(s).

7) Recently Drs. Y. Tamamoto and H. Yamazaki have also prepared $Mo(t\text{-}BuNC)_6$ by reduction of $MoCl_5$; private communication.

8) Measured in CH_2Cl_2 using Et_4NClO_4 as an electrolyte.

9) IR (cm^{-1}, nujol mull): ν(NC), 1884, 2040, 2075, 2110; ν(C=N), 1758. ^{1}H NMR(δ, in acetone-d_6): t-Bu, 1.48(9H), 1.50(45H); CH_3, 3.04(3H). $^{13}C\{^{1}H\}$ NMR (δ, in acetone-d_6): C(=N), 196.3; CH_3, 19.5; C(≡N), 166.5; $(CH_3)_3CN$=, 60.1; $(CH_3)_3CN$=, 31.6; $(CH_3)_3CN$≡, 57.4; $(CH_3)_3CN$≡, 29.9, 31.1. All signals were singlet.

10) IR (cm^{-1}, nujol mull): ν(NC), 1865, 2038, 2070, 2115; ν(C=N), 1755. ^{1}H NMR (δ, in acetone-d_6): t-Bu, 1.43(45H), 1.50(9H); CH_2, 4.82(2H). $^{13}C\{^{1}H\}$NMR (δ, in acetone-d_6): C(=N), 198.6; CH_2, 38.4; C(≡N), 167.9; $(CH_3)_3CN$=, 60.2; $(CH_3)_3CN$=, 31.6; $(CH_3)CN$≡, 57.4; $(CH_3)_3CN$≡, 30.0, 31.1. All signals were singlet.

11) For example, (a) Y. Yamamoto, H. Yamazaki, and N. Hagihara, Bull. Chem. Soc. Jpn., 41, 532(1968). (b) S. Otsuka, A. Nakamura, and T. Yoshida, J. Am. Chem. Soc., 91, 7196(1969), (c) Y. Yamamoto and H. Yamazaki, Inorg. Chem., 13, 2145(1974).

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16) Tables of fractional coordinates, thermal parameters, and observed and calculated structure factors are available from K. H. and T. H.

17) The mean C3-Mo-M and C5-Mo-M angles of two independent molecules are 94.9 and 106.3°, respectively.

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