Reaction of a Molybdenum(0) Dinitrogen Complex containing a Crown Thioether with Isocyanides. Formation of the Extensively Bent PhNC Complex *trans*-$\mathrm{Mo(PhNC)_2(Me_8[16]aneS_4)}$ and Facile Dealkylation of Bu^{t}NC to give *trans*-$\mathrm{Mo(CN)_2(Me_8[16]aneS_4)}$ ($\mathrm{Me_8[16]aneS_4}$ = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane)

Tomohiro Adachi, Nobuyoshi Sasaki, Tatsuo Ueda, Manabu Kaminaka, and Toshikatsu Yoshida*

Department of Chemistry, Faculty of Integrated Arts and Sciences, University of Osaka Prefecture, Sakai, Osaka 591, Japan

Reaction of *trans*-$\mathrm{Mo(N_2)_2(Me_8[16]aneS_4)}$ with PhNC gave *trans*-$\mathrm{Mo(PhNC)_2(Me_8[16]aneS_4)}$, the first extensively bent aryl isocyanide complex, while a similar reaction with Bu^{t}NC took place with dealkylation affording *trans*-$\mathrm{Mo(CN)_2(Me_8[16]aneS_4)}$; the *X*-ray crystal structures of both complexes have been determined.

We have recently reported the synthesis of an electron rich molybdenum(0) dinitrogen complex containing a crown thioether, *trans*-$\mathrm{Mo(N_2)_2(Me_8[16]aneS_4)}$ (**1**)[1] and the facile N-arylation and -benzylation of the co-ordinated dinitrogen in (**1**) with aryl and benzyl halides to give aryldiazenido and *N*,*N*-dibenzylhydrazido complexes, respectively.[2] Neither of these C–N bond forming reactions has been achieved with the phosphine analogues, *e.g.*, *trans*-$\mathrm{Mo(N_2)_2(dppe)_2}$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$).[3] The electron richness and novel reactivities of (**1**) may arise from the $\mathrm{p_\pi}$-donor ability of $\mathrm{Me_8[16]aneS_4}$.[1] To delineate the electronic features of this crown thioether further, we have examined reactions of (**1**) with isocyanides and found the formation of the first example of an extensively bent aryl isocyanide complex, *trans*-$\mathrm{Mo(PhNC)_2(Me_8[16]aneS_4)}$ (**2**), and the facile dealkylation of Bu^{t}NC to give *trans*-$\mathrm{Mo(CN)_2(Me_8[16]aneS_4)}$ (**3**).

Treatment of (**1**) with PhNC (2 mol equiv.) in toluene at room temperature for 10 h quantitatively gave *trans*-$\mathrm{Mo(PhNC)_2(Me_8[16]aneS_4)}$ (**2**) as diamagnetic dark green crystals.[†] The i.r. spectrum shows two strong bands due to ν_{NC} at 1658 and 1959 cm^{-1}. The former band is at a much lower wavenumber than that (1853 cm^{-1}) for *trans*-$\mathrm{Mo(PhNC)_2(dppe)_2}$,[4] while the latter is in the region expected for linear PhNC co-ordination. Two types of PhNC co-ordination in (**2**) are also retained in toluene solution as shown by two isocyanide ^{13}C n.m.r. signals at δ 197.6 and 233.2. The latter chemical shift is the largest reported for aryl isocyanide complexes and is close to the region of carbene carbon (δ 250—400).[5]

The crystal structure of (**2**) (Figure 1)[‡] shows a slightly distorted octahedral geometry around the Mo atom with four S atoms in the equatorial plane and two PhNC ligands at the axial sites. The conformation of $\mathrm{Me_8[16]aneS_4}$ is all-up, as also observed for the isoelectronic *trans*-$\mathrm{MoL_2(Me_8[16]aneS_4)}$ (L = CO,[6] $\mathrm{N_2}$[1]). The PhNC molecule co-ordinated on the same side as the ring C atoms of $\mathrm{Me_8[16]aneS_4}$ with respect to the 4S equatorial plane is extensively bent at N(20) [139.3(8)°], while

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[†] All new compounds gave satisfactory elemental analyses.

[‡] *Crystal data* for (**2**): $\mathrm{C_{34}H_{50}N_2S_4Mo}$, M = 711.04, monoclinic, space group $P2_1/c$, a = 9.123(3), b = 19.027(6), c = 20.527(5) Å, β = 91.30(2)°, U = 3562(2) Å^3, Z = 4, D_c = 1.33 g cm^{-3}, μ(Mo-K_α) = 6.0 cm^{-1}, crystal size 0.1 × 0.1 × 0.3 mm.

Crystal data for (**3**): $\mathrm{C_{22}H_{40}N_2S_4Mo}$, M = 556.82, monoclinic, space group $P2_1/c$, a = 13.982(2), b = 10.719(2), c = 8.737(2) Å, β = 92.71(2)°, U = 1308(1) Å^3, Z = 2, D_c = 1.41 g cm^{-3}, μ(Mo-K_α) = 8.0 cm^{-1}, crystal size 0.2 × 0.2 × 0.2 mm. Intensity data were collected on a Rigaku AFC-6 diffractometer with Mo-K_α radiation and corrected for Lorentz and polarization effects. The structures were solved by Patterson and Fourier methods and refined by block-diagonal least squares to final residuals R = 0.059 (R_w = 0.057) from 4161 observed reflections [$|F_o| > 3\sigma(F_o)$] for (**2**) and R = 0.054 (R_w = 0.068) from 1483 observed reflections [$|F_o| > 6\sigma(F_o)$] for (**3**). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

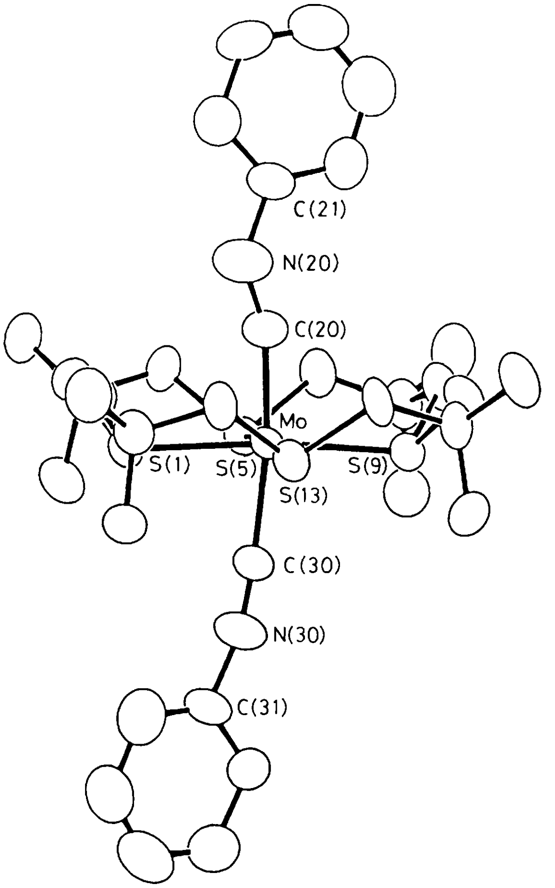

Figure 1. Molecular structure of *trans*-Mo(PhNC)$_2$(Me$_8$[16]aneS$_4$) (**2**). Selected bond distances (Å) and angles (°): Mo–S(1) 2.428(2), Mo–S(5) 2.418(2), Mo–S(9) 2.409(2), Mo–S(13) 2.416(2); S(1)–Mo–S(5) 87.4(1), S(5)–Mo–S(9) 92.0(1), S(9)–Mo–S(13) 87.4(1), S(1)–Mo–S(13) 92.6(1), S(1)–Mo–S(9) 173.8(1), S(5)–Mo–S(13) 175.8(1), C(20)–Mo–C(30) 171.4(3), Mo–C(20)–N(20) 163.4(6), Mo–C(30)–N(30) 174.0(6).

that located on the opposite side is essentially linear [C(30)–N(30)–C(31) 167.4(7)°]. The bending can be ascribed to a strong d_π(Mo)–p_π*(NC) interaction. Thus, the Mo–C(20) length [1.987(7) Å] is significantly shorter than Mo–C(30) [2.088(7) Å], and the C(20)–N(20) distance [1.236(11) Å] is longer than C(30)–N(30) [1.197(10) Å]. It is noteworthy that the angle at N(20) and the Mo–C(20) length are more acute and shorter than the respective values [156(1)° and 2.101(7) Å] for *trans*-Mo(MeNC)$_2$(dppe)$_2$.[4] Similar extensive bending has been established for bulky alkyl isocyanide complexes, Fe(Bu^{t}NC)$_5$ [135(1)°],[7] Ru(Bu^{t}NC)$_4$(PPh$_3$) [130(2)°],[7] and [Mo(Bu^{t}N=CCH$_2$Ph)(Bu^{t}NC)$_5$]Br [137(2)°].[8] By contrast, aryl isocyanides seem to resist bending as deduced from the high ν_{NC} (1965 cm^{-1}) of Fe(2,6-Me$_2$C$_6$H$_3$NC)$_5$ compared to the Bu^{t}NC analogue cited above.[7] Thus, (**2**) may represent the first well-characterized example of an extensively bent aryl isocyanide complex.

trans-Mo(L)$_2$(Me$_8$[16]aneS$_4$)
(**1**) L = N$_2$
(**2**) L = PhNC
(**3**) L = CN

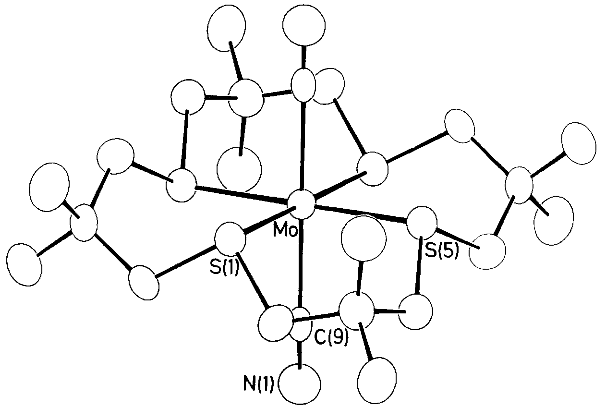

Figure 2. Molecular structure of *trans*-Mo(CN)$_2$(Me$_8$[16]aneS$_4$) (**3**). Selected bond distances (Å) and angles (°): Mo–S(1) 2.430(2), Mo–S(5) 2.433(3), Mo–C(9) 2.219(7), C(9)–N(1) 1.086(10); S(1)–Mo–S(5) 91.5(1), S(5)–Mo–S(1′) 88.5(1), Mo–C(9)–N(1) 178.5(8), S(1)–Mo–C(9) 90.8(2), S(5)–Mo–C(9) 92.2(2).

The coexistence of both bent and linear PhNC ligands may be ascribed to the deviation of the Mo atom by 0.110(1) Å from the 4S equatorial plane towards the macrocyclic ring C atoms, the mean deviation of the four S atoms from the 4S plane being 0.020(2) Å. E.H.M.O. calculations on the hypothetical model *trans*-Mo(HNC)$_2$(SH$_2$)$_4$§ indicated that both σ- and π-Mo–C overlap populations (0.5700 and 0.2402, respectively) of the HNC ligand on the same side as the Mo atom with respect to the 4S plane are larger than the respective values (0.5026 and 0.1137) on the opposite side. This stereoelectronic effect due to the Mo atom deviation from the 4S plane is borne out by the equidistance of Mo–C(20) in (**2**) and the Mo–CO bonds [1.979(8), 2.002(8) Å] found for *trans*-Mo(CO)$_2$(Me$_8$[16]aneS$_4$) where the deviation of the Mo atom is 0.093(2) Å;[6] in the absence of the stereoelectronic effect a stronger d_π–p_π* back-bonding is expected for CO than PhNC.[9] Compound (**2**) is extremely air-sensitive, decomposing to liberate free PhNC and Me$_8$[16]aneS$_4$, no oxidation products of either ligand being detected.

A similar reaction of (**2**) with an excess of Bu^{t}NC in hexane at room temperature for 4 h gave the paramagnetic Mo(CN)(Bu^{t}NC)(Me$_8$[16]aneS$_4$) (**4**) as very air-sensitive yellow needles (79%, ν_{CN} 2090w, ν_{NC} 1718s, 1745s cm^{-1}). Complex (**4**) is also thermally unstable and on prolonged standing (10 days) in toluene even at −30 °C decomposed affording *trans*-Mo(CN)$_2$(Me$_8$[16]aneS$_4$) (**3**) as paramagnetic orange crystals (73%, ν_{CN} 2080 cm^{-1}). The fate of the Bu^t group has not been determined. Similar dealkylation of alkyl isocyanides to give cyanides has a precedent with cationic Pt^{II} complexes, [Pt(R′)(RNC)(PPh$_3$)$_2$]$^+$ (R = Me, Bu^t; R′ = Me, C$_6$F$_5$)[10] and [Pt(Me)(Bu^{t}NC)(PMe$_2$Ph)$_2$]$^+$,[11] but they require more forcing conditions.

The crystal structure of (**3**) (Figure 2)‡ shows that the Mo atom achieves slightly distorted octahedral co-ordination with two CN ligands occupying the axial sites. In contrast with the all-up conformation of the Me$_8$[16]aneS$_4$ unit of (**2**), the crown thioether in the equatorial plane assumes an up–up–down–down conformation where four $\overline{\text{MoSCH}_2\text{CMe}_2\text{CH}_2\text{S}}$ rings adopt chair and twist-boat forms. Thus, the molecule possesses virtually D_{2h} symmetry and the Mo atom lies strictly in the 4S plane. The facile dealkylation of Bu^{t}NC on reaction

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§ Ref. 1 gives the details of the type of E.H.M.O. calculations used and the relevant parameters. The structural data of the model were based on those observed for (**2**).

with (**1**) is rather remarkable since the corresponding reaction of *trans*-$Mo(N_2)_2(dppe)_2$ has been shown to give *trans*-$Mo(Bu^tNC)_2(dppe)_2$ exclusively.[4]

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References

1 T. Yoshida, T. Adachi, M. Kaminaka, T. Ueda, and T. Higuchi, *J. Am. Chem. Soc.*, 1988, **110**, 4872.
2 T. Yoshida, T. Adachi, T. Ueda, M. Kaminaka, N. Sasaki, T. Higuchi, T. Aoshima, I. Mega, Y. Mizobe, and M. Hidai, *Angew. Chem.*, in the press.
3 J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1978, 1638.
4 J. Chatt, C. M. Elson, A. J. L. Pomberio, R. L. Richards, and G. H. D. Royston, *J. Chem. Soc., Dalton Trans.*, 1978, 165.
5 R. H. Crabtree, 'The Organometallic Chemistry of the Transition Metals,' Wiley, New York, 1988, p. 218.
6 T. Yoshida, T. Adachi, T. Ueda, M. Watanabe, M. Kaminaka, and T. Higuchi, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1171.
7 J.-M. Bassett, D. E. Very, G. K. Barker, M. Green, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1003.
8 T. Yoshida, K. Hirotsu, T. Higuchi, and S. Otsuka, *Chem. Lett.*, 1982, 1017.
9 G. R. Knox, G. A. Sim, J. G. Sime, and D. I. Woodhouse, *J. Organometal. Chem.*, 1974, **74**, C7.
10 P. M. Treichel, K. P. Wagner, and R. W. Hess, *Inorg. Chem.*, 1973, **12**, 1471.
11 Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1873.