Reversible Addition of Carbonyl Compounds to Parent Imido Complex: Preparation and Crystal Structures of *trans*-{Mo(NH)(OTf)(*syn*-Me_8[16]aneS_4)}OTf and *trans*-{Mo[NC(OH)RR′](OTf)(*syn*-Me_8[16]aneS_4)}OTf (R=R′=Me; R=H, R′=Ph)

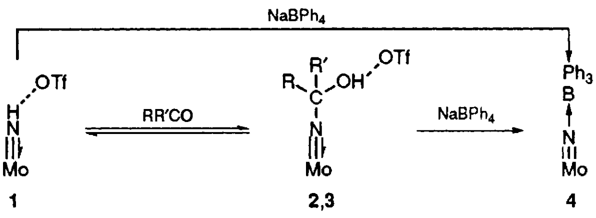
Toshikatsu Yoshida,* Tomohiro Adachi, Nobuhiro Yabunouchi, Tatsuo Ueda and Susumu Okamoto

Department of Chemistry, Faculty of Integrated Arts and Sciences, University of Osaka Prefecture, Sakai, Osaka 593, Japan

Reversible C–N bond formation of a parent imido complex *trans*-{Mo(NH)(OTf)(*syn*-Me_8[16]aneS_4)}OTf **1** proceeds through addition of acetone and benzaldehyde to give α-hydroxyalkylimido complexes *trans*-{Mo[NC(OH)RR′](OTf)(*syn*-Me_8[16]aneS_4)}OTf (**2**; R=R′=Me, **3**; R=H, R′=Ph); the structures of two imido complexes **1** and **3** as well as *trans*-Mo(N→BPh_3)(OTf)(anti-Me_8[16]aneS_4) **4** obtained by treating **1** and **2** with $NaBPh_4$ were elucidated by X-ray diffraction study.

Organoimido transition metal complexes[1] have received increasing interest in view of their versatile reactivities due to the ambiphilic character behaving as a nucleophile or electrophile.[2] In contrast, mononuclear parent imido (NH) complexes are relatively rare[2,3] and the reactivity of the N–H bond has remained virtually unexplored except the weakly acidic character of the NH hydrogen atom.[2,4] We present here the first transformation of a NH complex *trans*-{Mo(NH)(OTf)(*syn*-Me_8[16]aneS_4)}OTf **1** (Me_8[16]aneS_4 = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane, OTf = CF_3SO_3) into the organoimido complexes, *trans*-{Mo[NC(OH)Me_2](OTf)(*syn*-Me_8[16]aneS_4)}OTf **2** and *trans*-{Mo[NCH(OH)Ph](OTf)(*syn*-Me_8[16]aneS_4)}OTf **3** through addition of acetone and benzaldehyde, respectively (Scheme 1). An equilibration between **1** and α-hydroxyalkylimido complexes was established by isolating a BPh_3 adduct of nitride complex, *trans*-Mo(N→B-Ph_3)(OTf) (*anti*-Me_8[16]aneS_4) **4**, from both attempted metathesis reactions of **1** and **2** with $NaBPh_4$.

The parent imido complex **1** was prepared by protonation of *trans*-Mo(N)(N_3)(*syn*-Me_8[16]aneS_4)† with 4 equiv. of HOTf in toluene at room temp. and subsequent recrystallization of the precipitates from dimethoxyethane as air-stable, orange crystals (55% yield).‡ The ^{1}H NMR spectrum shows the NH proton signal at δ 7.49, which is extensively shielded compared to those found for *trans*-[W(NH)X(dppe)$_2$]$^+$ (δ 9.2)[3b] and [W(NH)Tp′(CO)$_2$]$^+$ (δ 11.0) [Tp′ = hydridotris(3,5-dimethyl-1-pyrazoyl)borate.[2] **1** is unequivocally characterized by an X-ray structural analysis [Fig. 1(*a*)].§ The NH ligand locates at the congested axial site surrounded by the ring C atoms of *syn*-Me_8[16]aneS_4, while the OTf anion is found at the opposite, uncongested site. The Mo–N distance [1.695(9) Å] is comparable with those in closely related imido complexes, *cis,mer*-M(NAr)Cl_2(PMe_3)$_3$ (M = Mo, Ar = *p*-MeC_6H_4 1.739(2);[6a] M = W, Ar = Ph 1.755(3) Å)[6b] and *trans*-[Mo(NR)X(dppe)$_2$]$^+$ (R = H 1.73(2),[7] R = Me 1.733(5)



Scheme 1 {Mo=Mo(OTf)(Me_8[16]aneS_4)}

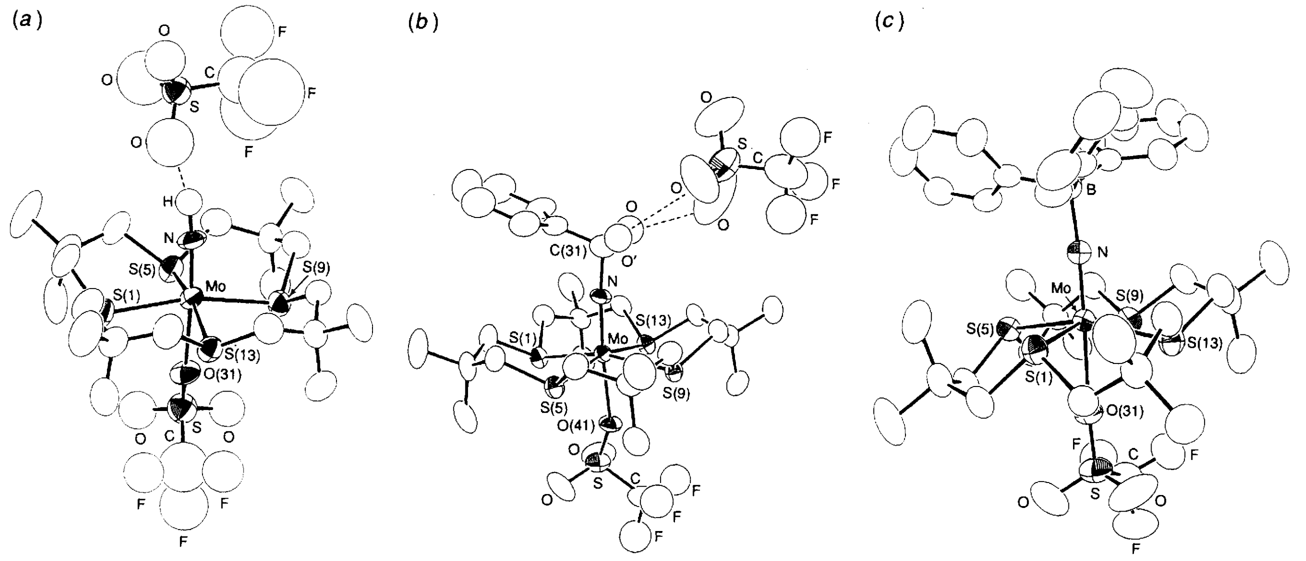


Fig. 1 Molecular structures of **1**, **3** and **4**. Selected bond distances (Å) and angles (°). (*a*) **1**: Mo-S1 2.451(4), Mo-S5 2.456(4), Mo-S9 2.458(4), Mo-S13 2.462(4), Mo-N 1.695(9), Mo-O31 2.182(8), N-H 1.07; S1-Mo-S5 88.9(1), S1-Mo-S9 165.3(1), S1-Mo-S13 88.8(1), S5-Mo-S9, 88.9(1), S5-Mo-S13 164.5(1), S9-Mo-S13 89.5(1), S1-Mo-N 95.8(3), S5-Mo-N 96.1(4), S9-Mo-N 98.9(3), S13-Mo-N 99.4(4), S1-Mo-O31 80.5(2), S5-Mo-O31 83.7(3), S9-Mo-O31 84.8(2), S13-Mo-O31 80.8(3), N-Mo-O31 176.3(4), Mo-N-H 172.1. (*b*) **3**: Mo-S1 2.455(3), Mo-S5 2.456(3), Mo-S9 2.454(3), Mo-S13 2.458(3), Mo-N 1.718(6), Mo-O41 2.194(5), N-C31 1.470(10); S1-Mo-S5 88.38(7), S1-Mo-S9 164.65(8), S1-Mo-S13 88.98(7), S5-Mo-S9 89.04(7), S5-Mo-S13 164.08(7), S9-Mo-S13 89.37(7), S1-Mo-N 99.6(2), S5-Mo-N 99.4(2), S9-Mo-N 95.8(2), S13-Mo-N 96.5(2), S1-Mo-O41 84.2(1), S5-Mo-O41 82.6(1), S9-Mo-O41 80.5(1), S13-Mo-O41 81.5(1), N-Mo-O41 175.(2), Mo-N-C31 174.4(5). (*c*) **4**: Mo-S1 2.4573(8), Mo-S5 2.459(1), Mo-S9 2.4592(8), Mo-S13 2.456(1), Mo-N 1.697(2), Mo-O31 2.375(2), N-B 1.624(4); S1-Mo-S5 92.98(3), S1-Mo-S9 164.35(3), S1-Mo-S13 87.28(3), S5-Mo-S9 87.24(3), S5-Mo-S13 162.99(3), S9-Mo-S13 87.98(3), S1-Mo-N 95.95(7), S5-Mo-N 95.92(7), S9-Mo-N 99.59(7), S13-Mo-N 100.97(7), S1-Mo-O31 84.69(5), S5-Mo-O31 81.85(5), S9-Mo-O31 79.86(5), S13-Mo-O31 81.24(5), N-Mo-O31 177.72(8), Mo-N-B 176.2(2).

Å).[8] The Mo–N–H linkage (172°) is essentially linear. One salient structural feature of **1** is a hydrogen bond between the NH ligand and the OTf counter anion NH···O (1.70 Å) and N···O distances [2.75(2) Å]. Consistent with this, the N–H stretching frequency (3100 cm^{-1}) is considerably lower in energy than those (3163–3400 cm^{-1}) found for *trans*-$[M(NH)X(diphos)_2]^+$ (M = Mo, W; diphos = dppe, depe; X = halogen, N_3, MeO).[3a–c]

On dissolving **1** in acetone at room temp. a facile C–N bond formation took place to give the 1-hydroxy-1-methyethylimido complex **2** as red crystals (90% yield).‡ A similar reaction of **1** with PhCHO in tetrahydrofuran affords 1-hydroxybenzylimido complex **3** as deep red crystals (35% yield).‡ These α-hydroxyalkyl imido complexes **2** and **3** exhibit an O–H stretching frequency at 3380 and 3270 cm^{-1} and an OH proton signal at δ 6.24 (singlet) and 6.20 (broad singlet), respectively. **3** was again elucidated by an X-ray study.§ The molecular structure [Fig. 1(*b*)], including the geometry about the Mo atom, the Mo–N distance [1.718(6) Å], and Mo–N–C angle [174.4(5)°], is very similar to that of **1**. Due to asymmetry of the tertiary C atom in the NCH(OH)Ph group, the hydroxy O atom is disordered in two positions with an equal occupancy. The presence of an OH···OTf^- hydrogen bond is also suggested by the O···O distances [2.82(2) and 2.66(1) Å], which may be compared to the corresponding separation [2.63(1) Å] found for $[\eta^5\text{-}C_5H_5W(CO)_3(Pr^iOH)]$-OTf.[9]

As is the case of the NH addition of amines into carbonyl compounds, the formation of α-hydroxyalkylimido complexes is reversible. Although **2** is stable in $[^2H_6]$acetone at least for several hours, it transforms into the perdeuteriated methyl analogue *trans*-$\{Mo[NC(OH)(CD_3)_2]OTf)$(*syn*-$Me_8[16]aneS_4)\}OTf$ ($[^2H_6]$**2**) on prolonged standing (1 week) at ambient temperature. The ratio of **2** and $[^2H_6]$**2** estimated by the ^1H NMR spectrum is 1 : 6. The reverse reaction is facilitated in the presence of a non-polar solvent. Thus, addition of hexane to the $[^2H_6]$acetone solution of **2** resulted in an immediate precipitation of $[^2H_6]$**2**. Similar addition of hexane to an acetone solution of **3** gave **2**. These results suggest that the parent imido complex **1** is in an equilibrium with the α-hydroxyalkylimido complexes. This is manifested further by the attempted metathesis reactions of **1** and **2** with $NaBPh_4$ in MeOH at room temp., both afforded the same product **4** (63 and 55%, respectively) as yellow crystals rather than the corresponding BPh_4^- salts. **4** may be produced by deprotonation of the NH ligand of **1** by BPh_4^- to give a neutral nitrido complex $Mo(N)(OTf)(Me_8[16]aneS_4)$ together with $HBPh_4$ and subsequent addition of BPh_3 to the nitride. The adduct is fully characterized by the X-ray study [Fig. 1(*c*)] as well as the spectral data.‡§ In sharp contrast to the anti conformation of $Me_8[16]aneS_4$ in crystal, the ^1H NMR spectrum of **4** shows the presence of only *syn*-conformer in $CDCl_3$, suggesting a conformational flexibility of the macrocycle.

The reactivities of the parent imido complex **1** of the crown thioether thus revealed are totally different from those of the phosphine analogues *trans*-$[MoX(NH)(dppe)_2]X$ (X=Br, Cl), which give the BPh_4 salt on metathesis reaction with $NaBPh_4$[3a] and are inert toward addition of acetone under the similar conditions employed for **1**. We are currently studying the C–N bond formation through addition of oxiranes and olefins into the N–H bond of **1**.

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Footnotes

† The nitrido azido complex was obtained by treating *trans*-$Mo(N_2)_2$(*syn*-$Me_8[16]aneS_4)$[5] with Me_3SiN_3 in toluene at room temp. in 80% yield following by a similar procedure employed for preparation of the dppe analogue [dppe = 1,2-bis(diphenylphosphino)ethane].[3a] IR (Nujol, cm^{-1}) 2040 [ν(N_3)], 999 [ν(Mo≡N)]; ^1H NMR (C_6D_6, δ) 0.95 (s, 3H, Me), 1.25 (s, 3H, Me), 2.40 (d, *J* 11.6 Hz, 2H, CH_2), 2.80 (d, *J* 11.6 Hz, 2H, CH_2).

‡ Elemental analyses of all new complexes gave satisfactory results. Selected spectral data: Complex **1**: IR (cm^{-1}, Nujol) ν(NH) 3100; ^1H NMR (δ, $CDCl_3$) 1.28 (s, 12H, Me), 1.33 (s, 12H, Me), 2.93 (d, *J* 11.6 Hz, 8H, CH_2), 3.15 (d, *J* 11.6 Hz, 8H, CH_2), 7.49 (br, 1H, NH); FAB–MS (*m/z*) 670 ($[M]^+$). Complex **2**: IR (cm^{-1}, Nujol) ν(OH) 3380; ^1H NMR (δ, $[^2H_6]$acetone) 1.22 (s, 12H, Me), 1.32 (s, 12H, Me), 1.59 (s, 6H, NCMe), 2.97 (d, *J* 11.6 Hz, 8H, CH_2), 3.23 (d, *J* 11.6 Hz, 8H, CH_2), 6.49 (br, 1H, OH); FAB–MS (*m/z*) 728 ($[M]^+$). Complex **3**: IR (cm^{-1}, Nujol) ν(OH) 3270; ^1H NMR (δ, $CDCl_3$) 1.22 (s, 12H, Me), 1.27 (s, 12H, Me), 2.94 (br s, 16H, CH_2), 6.20 (br, 1H, OH), 7.2–7.6 (m, 5H, Ph), the CH proton signal was not detected; FAB–MS (*m/z*) 774 ($[M]^+$). Complex **4**: ^1H NMR (δ, $CDCl_3$) 1.08 (s, 12H, Me), 1.12 (s, 12H, Me), 2.71 (d, *J* 11.6 Hz, 8H, CH_2), 3.77 (d, *J* 11.6 Hz, 8H, CH_2), 6.9–7.6 (m, 15H, Ph); FAB–MS (*m/z*) 834 ($[M-Ph]^+$), 669 ($[M-BPh_3]^+$).

§ The structures were solved by Patterson method and refined by full-matrix least-squares techniques of intensity data collected on a Rigaku AFC-5R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. *Crystal data* for **1**: $C_{22}H_{41}NO_6S_6F_6Mo$, $M = 817.86$, monoclinic, space group $C2/c$, $a = 35.615(15)$, $b = 9.557(5)$, $c = 21.036(11)$ Å, $\beta = 99.19(4)°$, $U = 7068(11)$ Å^3, $Z = 8$, $D_c = 1.537$ g cm^{-3}, μ(Mo-Kα) = 7.67 cm^{-1}, $F(000) = 3360$. Final R(R_w) = 0.065(0.061) for 2655 reflections $[I > 4.0\sigma(I)]$ and 298 variables. For **3**: $C_{29}H_{46}NO_7S_6F_6Mo\cdot 1/2PhCHO$, $M = 977.05$, monoclinic, space group $P2_1/n$, $a = 14.819(12)$, $b = 17.688(12)$, $c = 16.812(12)$, $\beta = 105.40(6)°$, $V = 4248(11)$ Å^3, Z = 4, $D_c = 1.527$ g cm^{-3}, μ(Mo-Kα) = 6.53 cm^{-1}, $F(000) = 2016$. Final R(R_w) = 0.050 (0.050) for 4337 reflections $[F > 3.0\sigma\ (F)]$ and 469 variables. For **4**: $C_{39}H_{55}NO_3S_5BF_3Mo$, $M = 909.91$, monoclinic, space group $P2_1/a$, $a = 18.991(4)$, $b = 11.484(2)$, $c = 20.438(6)$, $\beta = 104.66°$, $V = 4312(2)$ Å^3, Z = 4, $D_c = 1.401$ g cm^{-1}, μ(Mo-Kα) = 5.77 cm^{-1}, $F(000) = 1896$. Final $R(R_w) = 0.023\ (0.024)$ for 4414 reflections $[I > 4.0\sigma(I)]$ and 473 variables.

References

1 M. H. Chisholm and I. P. Rothwell, *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, pp. 161–188; W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, 1988.

2 P. J. Pérez, L. Luan, P. S. White, M. Brookhart and J. L. Templeton, *J. Am. Chem. Soc.*, 1992, **114**, 7928 and references cited therein.

3 (*a*) J. Chatt and J. R. Dilworth, *J. Indian Chem. Soc.*, 1977, **54**, 13; (*b*) P. C. Bevan, J. Chatt, J. R. Dilworth, R. A. Henderson and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1982, 821; (*c*) D. L. Hughes, M. Y. Mohammed and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1990, 2013; (*d*) R. R. Schrock, T. E. Glassman and M. G. Vale, *J. Am. Chem. Soc.*, 1991, **113**, 725; (*e*) J. Chatt, R. Choukroun, J. R. Dilworth, J. Hyde, P. Yella and J. Zubieta, *Trans. Met. Chem.*, 1979, **4**, 59.

4 R. A. Henderson, G. Davies, J. R. Dilworth and R. N. F. Thorrneley, *J. Chem. Soc., Dalton Trans.*, 1981, 40; R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1983, 51.

5 T. Yoshida, T. Adachi, T. Ueda, M. Kaminaka and T. Higuchi, *J. Am. Chem. Soc.*, 1988, **110**, 4872.

6 (*a*) C. Y. Chou, D. D. Devore, S. C. Huckett, E. A. Maatta, J. C. Huffman and F. Takusagawa, *Polyhedron*, 1986, **5**, 301; (*b*) D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2651.

7 J. R. Wentworth, P. L. Dahlstrom, J. R. Hyde and J. Zubieta, *Inorg. Chim. Acta*, 1983, **71**, 21.

8 D. L. Hughes, D. J. Kowe, M. Y. Mohammed, C. J. Pickett and N. M. Pinhal, *J. Chem. Soc., Dalton Trans.*, 1990, 2021.

9 J.-S. Song, D. J. Szalda, R. M. Bullock, C. J. C. Lawrie, M. A. Rodkin and J. R. Norton, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1233.