

Preliminary communication

PREPARATION OF $(t\text{-BuNC})_5\text{MoX}_2$ ($X = \text{O}_2\text{CCF}_3, \text{Cl}$) AND $(t\text{-BuNC})_5\text{ReCl}$ BY CLEAVAGE OF THE QUADRUPLE BOND IN $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, $\text{K}_4\text{Mo}_2\text{Cl}_8$, AND $\text{Re}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$

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Summary

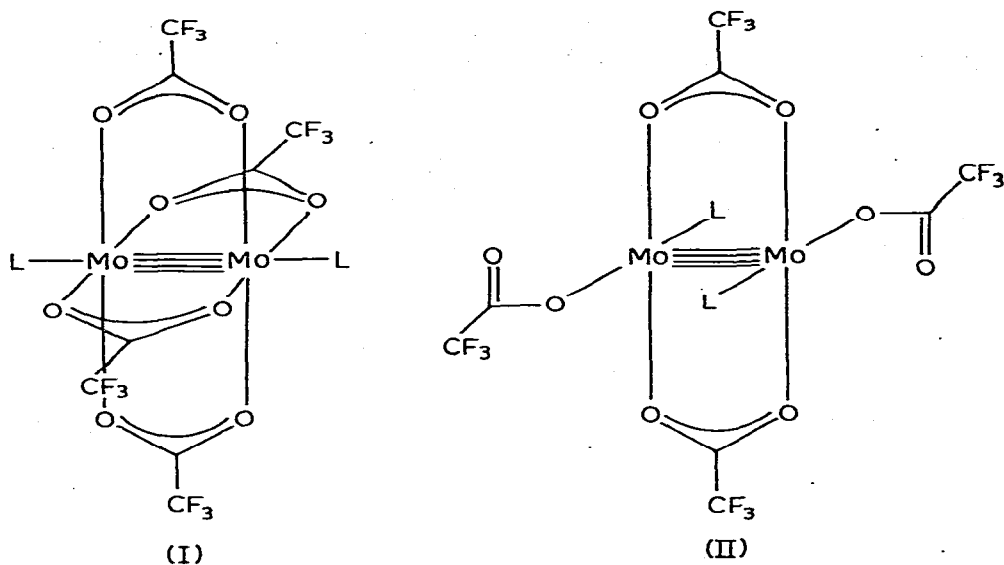
Addition of an excess of *t*-butyl isocyanide to solid $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ or $\text{Mo}_2(\text{O}_2\text{CMe})_4$ gives $(t\text{-BuNC})_5\text{Mo}(\text{O}_2\text{CCF}_3)_2$ or $(t\text{-BuNC})_4\text{Mo}(\text{O}_2\text{CMe})_2$, respectively. The quadruple bond in $\text{K}_4\text{Mo}_2\text{Cl}_8$ or $\text{Cl}_4\text{Mo}_2(\text{n-Bu}_3\text{P})_4$ also can be cleaved by an excess of *t*-butyl isocyanide to yield $(t\text{-BuNC})_5\text{MoCl}_2$. The anionic ligands can be exchanged with ammonium hexafluorophosphate in presence of excess *t*-BuNC to give the known $[(t\text{-BuNC})_7\text{Mo}][\text{PF}_6]_2$. *t*-Butyl isocyanide also cleaves the quadruple metal—metal bond in $\text{Re}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$ to give $(t\text{-BuNC})_5\text{ReCl}$.

Coordination complexes of tetra(trifluoroacetato)dimolybdenum of the type $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4\text{L}_2$ have recently been shown to be of two distinct types in solution, viz., those with axial coordination (I) and those with nonaxial coordination, one isomer being shown (II) [1].

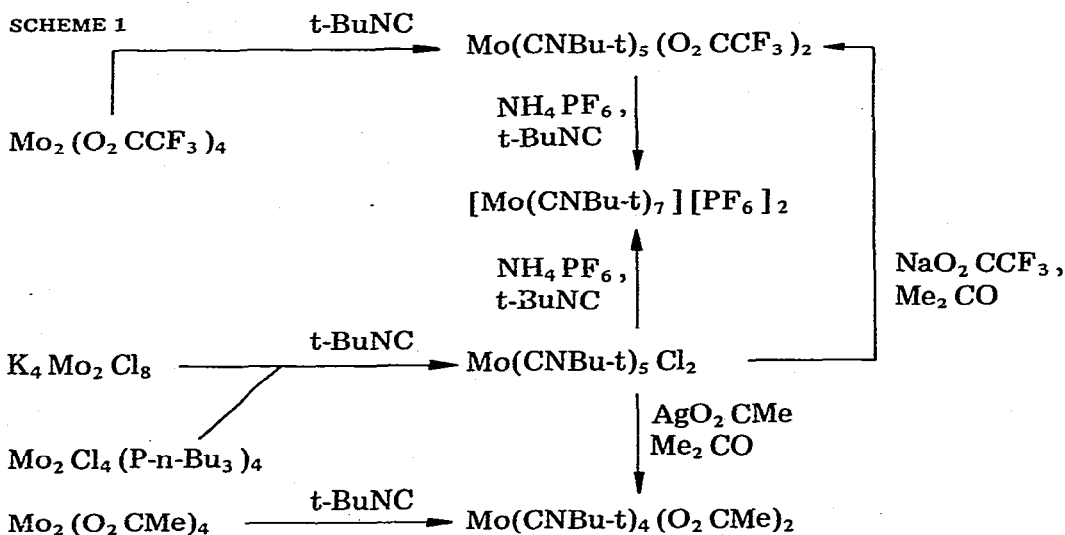
Both steric and electronic properties of the Lewis base (L) are important in determining the type of coordination complex that is observed. Only those ligands that are small and good σ -donors (PMe_3 , PMe_2Ph , or PEt_3) yield nonaxial complexes (II), whereas all others that we examined, e.g., PMe_2Ph_2 , PPh_3 , or $t\text{-Bu}_3\text{P}$, give axial complexes (I). Another set of ligands that are good σ -donors and sterically small are the isocyanides. We anticipated that these too would give nonaxial coordination complexes of type II.

Much to our surprise, addition of *t*-butyl isocyanide to solid $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ cleaves the molybdenum—molybdenum quadruple bond without changing the oxidation state of the metal atoms, giving yellow, mononuclear $\text{Mo}(\text{CNBu-t})_5(\text{O}_2\text{CCF}_3)_2$ in high yield (72%)*. The infrared spectrum contains absorptions at 2140s, 2110s and 2060(sh) cm^{-1} due to $\nu(\text{NC})$ and at 1690s cm^{-1} due to monodentate trifluoroacetate ($\nu_{\text{as}}(\text{CO}_2)$) groups. Tetracetatodimolybdenum

*Anal. Found: C, 48.3; H, 6.35; N, 9.46. Calcd: C, 47.2; H, 6.17; N, 9.49%



reacts similarly giving yellow $\text{Mo}(\text{t-BuNC})_4(\text{O}_2\text{CMe})_2^*$. The infrared spectrum shows absorptions due to bi- and monodentate acetate groups, $\nu_{\text{as}}(\text{CO}_2)$ at 1552 and 1632 cm^{-1} and $\nu(\text{NC})$ at 2069s, 2040s and 2010 cm^{-1} , though the ^1H NMR spectrum at room temperature shows only two singlets at δ 2.31 and 1.54 ppm due to acetate and t-butyl isocyanide protons, respectively. These and other reactions are shown in Scheme 1. The quadruple bond in $\text{K}_4\text{Mo}_2\text{Cl}_8$ or $\text{Mo}_2\text{Cl}_4(\text{n-Bu}_3\text{P})_4$ can also be cleaved by t-butyl isocyanide, giving the mono-nuclear molybdenum(II) species $\text{Mo}(\text{t-BuNC})_5\text{Cl}_2^{**}$.



*Anal. Found: C, 53.2; H, 7.81; N, 10.4. Calcd.: C, 52.7; H, 7.75; N, 10.3%.

**Anal. Found: C, 52.4; H, 8.08; N, 12.1; Cl, 11.1. Calcd.: C, 51.5; H, 7.77; N, 12.0; Cl, 12.1%.

Similar isocyanide complexes of molybdenum(II) have been prepared from $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}$ or Br) and RNC ($\text{R} = p\text{-tolyl}$ and cyclohexyl) [2].

Reaction of $(t\text{-BuNC})_5\text{Mo}(\text{O}_2\text{CCF}_3)_2$ or $(t\text{-BuNC})_5\text{MoCl}_2$ with ammonium hexafluorophosphate in presence of excess *t*-butyl isocyanide gives the seven coordinate, capped trigonal prism $[\text{Mo}(t\text{-BuNC})_7][\text{PF}_6]_2$ previously prepared in low yield from $\text{Mo}(\text{CO})_6$, iodine, NaPF_6 , and the isocyanide in methanol [3]. The related methyl isocyanide complex was prepared similarly [3] and more recently from $\text{Mo}_2(\text{O}_2\text{CMe})_4$ and methyl isocyanide [4].

The quadruple bond in $\text{Re}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$ can also be cleaved by *t*-butyl isocyanide to give red, mononuclear $\text{ClRe}(\text{CNBu-}t)_5$ in 80% yield*. The infrared spectrum shows absorptions at 2040s and 2020s cm^{-1} due to $\nu(\text{NC})$ and the ^1H NMR shows a singlet at room temperature at δ 1.48 ppm. Analogous rhenium(I) isocyanides, $\text{IRe}[\text{CN}(p\text{-tolyl})]_5$ from KReI_6 [6] and $\text{XRe}[\text{CN}(p\text{-tolyl})]_5$ from $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}$ or Br), have been described [7].

Acknowledgment

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References

- 1 G.S. Girolami, V.V. Mainz and R.A. Andersen, *Inorg. Chem.*, in press.
- 2 F. Bonati and G. Minghetti, *Inorg. Chem.*, 9 (1970) 2642.
- 3 C.T. Lam, M. Novotny, D.L. Lewis and S.J. Lippard, *Inorg. Chem.*, 17 (1978) 2127.
- 4 F.A. Cotton and R.A. Walton, unpublished work, as quoted in ref. 5.
- 5 F.A. Cotton, P.E. Fanwick and P.A. McArdle, *Inorg. Chim. Acta*, 35 (1979) 289.
- 6 M. Freni and P. Romiti, *J. Organometal. Chem.*, 87 (1975) 241.
- 7 P.M. Treichel and J.P. Williams, *J. Organometal. Chem.*, 135 (1977) 39.

*Anal. Found: C, 47.5; H, 7.58; N, 12.1; Cl, 6.50. Calcd: C, 47.1; H, 7.12; N, 11.0; Cl, 5.86%.