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Preliminary communication

PREPARATION OF $(t\text{-BuNC})_5MoX_2$ (X = O_2CCF_3, Cl) AND $(t\text{-BuNC})_5ReCl$ BY CLEAVAGE OF THE QUADRUPLE BOND IN $Mo_2(O_2CCF_3)_4$, $K_4Mo_2Cl_8$, AND $Re_2(O_2CMe)_4Cl_2$

GREGORY S. GIROLAMI and RICHARD A. ANDERSEN*
Chemistry Department, University of California, Berkeley, California 94720 (U.S.A.)
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Summary

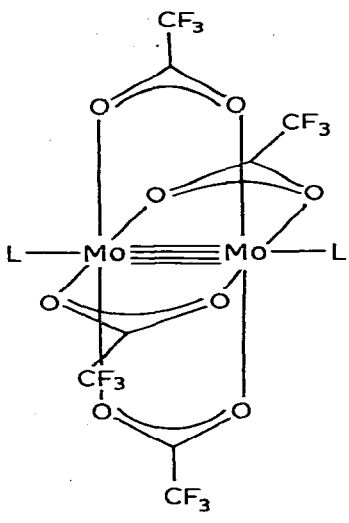
Addition of an excess of t-butyl isocyanide to solid $Mo_2(O_2CCF_3)_4$ or $Mo_2(O_2CMe)_4$ gives $(t\text{-BuNC})_5Mo(O_2CCF_3)_2$ or $(t\text{-BuNC})_4Mo(O_2CMe)_2$, respectively. The quadruple bond in $K_4Mo_2Cl_8$ or $Cl_4Mo_2(n\text{-}Bu_3P)_4$ also can be cleaved by an excess of t-butyl isocyanide to yield $(t\text{-BuNC})_5MoCl_2$. The anionic ligands can be exchanged with ammonium hexafluorophosphate in presence of excess t-BuNC to give the known $[(t\text{-BuNC})_7Mo][PF_6]_2$. t-Butyl isocyanide also cleaves the quadruple metal—metal bond in $Re_2(O_2CMe)_4Cl_2$ to give $(t\text{-BuNC})_5ReCl$.

Coordination complexes of tetra(trifluoroacetato)dimolybdenum of the type $Mo_2(O_2CCF_3)_4L_2$ 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].

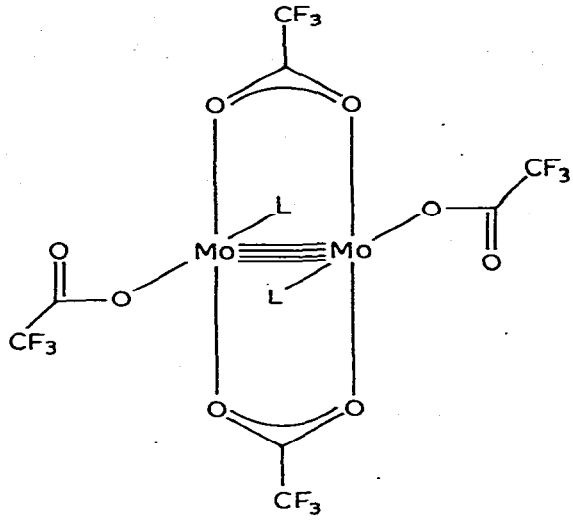
Both steric and electronic properties of the Lewis base (L) are important in determining the type of coordination complex that is observed. Only those ligands that are small and good σ-donors (PMe_3, PMe_2Ph, or PEt_3) yield nonaxial complexes (II), whereas all others that we examined, e.g., PMe_2Ph_2, PPh_3, or $t\text{-}Bu_3P$, 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 $Mo_2(O_2CCF_3)_4$ cleaves the molybdenum—molybdenum quadruple bond without changing the oxidation state of the metal atoms, giving yellow, mononuclear $Mo(CNBu\text{-}t)_5(O_2CCF_3)_2$ in high yield (72%)*. The infrared spectrum contains absorptions at 2140s, 2110s and 2060(sh) cm^{-1} due to ν(NC) and at 1690s cm^{-1} due to monodentate trifluoroacetate ($\nu_{as}(CO_2)$) groups. Tetraacetatodimolybdenum

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



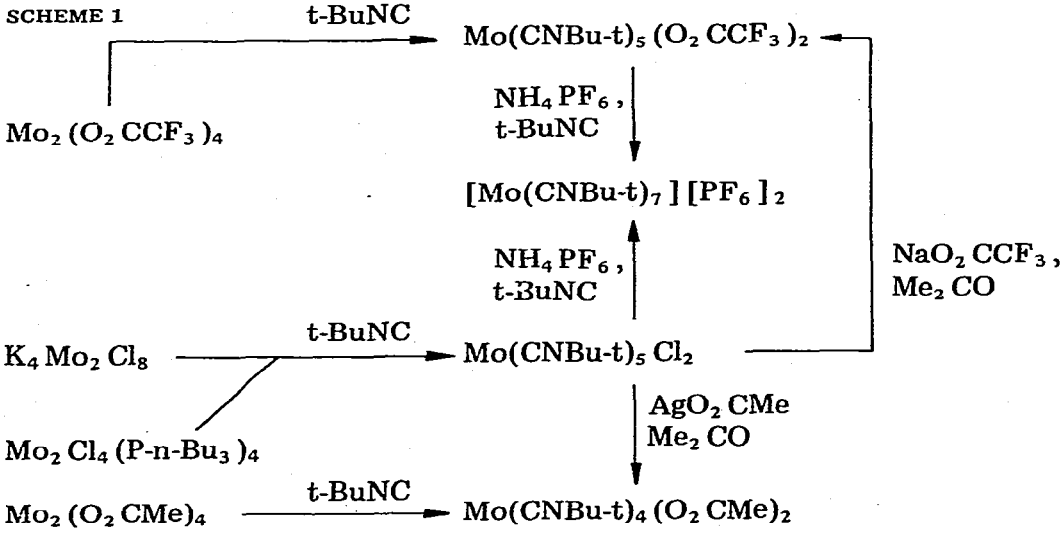
(I)



(II)

reacts similarly giving yellow $Mo(t\text{-}BuNC)_4(O_2CMe)_2$*. The infrared spectrum shows absorptions due to bi- and monodentate acetate groups, $\nu_{as}(CO_2)$ at 1552 and 1632 cm^{-1} and $\nu(NC)$ 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 $K_4Mo_2Cl_8$ or $Mo_2Cl_4(n\text{-}Bu_3P)_4$ can also be cleaved by t-butyl isocyanide, giving the mononuclear molybdenum(II) species $Mo(t\text{-}BuNC)_5Cl_2$**.

SCHEME 1



*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 $Mo(CO)_4X_2$ (X = Cl or Br) and RNC (R = *p*-tolyl and cyclohexyl) [2].

Reaction of $(t\text{-BuNC})_5Mo(O_2CCF_3)_2$ or $(t\text{-BuNC})_5MoCl_2$ with ammonium hexafluorophosphate in presence of excess t-butyl isocyanide gives the seven coordinate, capped trigonal prism $[Mo(t\text{-BuNC})_7][PF_6]_2$ previously prepared in low yield from $Mo(CO)_6$, iodine, $NaPF_6$, and the isocyanide in methanol [3]. The related methyl isocyanide complex was prepared similarly [3] and more recently from $Mo_2(O_2CMe)_4$ and methyl isocyanide [4].

The quadruple bond in $Re_2(O_2CMe)_4Cl_2$ can also be cleaved by t-butyl isocyanide to give red, mononuclear $ClRe(CNBu\text{-}t)_5$ in 80% yield*. The infrared spectrum shows absorptions at 2040s and 2020s cm^{-1} due to ν(NC) and the ^1H NMR shows a singlet at room temperature at δ 1.48 ppm. Analogous rhenium(I) isocyanides, $IRe[CN(p\text{-tolyl})]_5$ from $KReI_6$ [6] and $XRe[CN(p\text{-tolyl})]_5$ from $Re(CO)_5X$ (X = Cl or Br), have been described [7].

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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%.