Preliminary communication

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

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Summary

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

Coordination complexes of tetra(trifluoroacetato)dimolybdenum of the type Mo$_2$(O$_2$CCF$_3$)$_4$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$_2$Ph, or PEt$_3$) yield nonaxial complexes (II), whereas all others that we examined, e.g., PMe$_2$Ph$_2$, PPh$_3$, or t-Bu$_3$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 Mo$_2$(O$_2$CCF$_3$)$_4$ cleaves the molybdenum—molybdenum quadruple bond without changing the oxidation state of the metal atoms, giving yellow, mononuclear Mo(CNBu-t)$_5$(O$_2$CCF$_3$)$_2$ 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 (ν$_{as}$(CO$_2$)) groups. Tetraacetatodimolybdenum

*Anal. Found: C, 48.3; H, 6.35; N, 9.46. Caled: C, 47.2; H, 6.17; N, 9.49%
reacts similarly giving yellow Mo(t-BuNC)$_4$(O$_2$CMe)$_2$*. 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 $^1$H NMR spectrum at room temperature shows only two singlets at $\delta$ 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$_4$Mo$_2$Cl$_8$ or Mo$_2$Cl$_4$(n-Bu$_3$P)$_4$ can also be cleaved by t-butyl isocyanide, giving the mononuclear molybdenum(II) species Mo(t-BuNC)$_5$Cl$_2$**.

*Anal. Found: C, 53.2; H, 7.81; N, 10.4. Calcd.: C, 52.7; H, 7.79; 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)$_4$X$_2$ (X = Cl or Br) and RNC (R = p-tolyl and cyclohexyl) [2].

Reaction of (t-BuNC)$_3$Mo(O$_2$CCF$_3$)$_2$ or (t-BuNC)$_5$MoCl$_2$ with ammonium hexafluorophosphate in presence of excess t-butyl isocyanide gives the seven coordinate, capped trigonal prism [Mo(t-BuNC)$_7$]$_2$[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$_2$CMe)$_4$ and methyl isocyanide [4].

The quadruple bond in Re$_2$(O$_2$CMe)$_4$Cl$_2$ can also be cleaved by t-butyl isocyanide to give red, mononuclear ClRe(CNBu-t)$_5$ in 80% yield*. The infrared spectrum shows absorptions at 2040s and 2020s cm$^{-1}$ due to $\nu$(NC) and the $^1$H NMR shows a singlet at room temperature at $\delta$ 1.48 ppm. Analogous rhenium(I) isocyanides, IRe[CN(p-tolyl)]$_5$ from KReI$_6$ [6] and XRe[CN(p-tolyl)]$_5$ from Re(CO)$_5$X (X = Cl or Br), have been described [7].

Acknowledgment

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References

4 F.A. Cotton and R.A. Walton, unpublished work, as quoted in ref. 5.

*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%.