Reaction of Binuclear Carboxylate Complexes of Molybdenum, Rhenium, Ruthenium, and Rhodium with tert-Butyl Isocyanide: Metal-Metal Bond Cleavage vs. Bond Retention

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Received August 28, 1980

tert-Butyl isocyanide cleaves the quadruple metal–metal bonds in Mo$_2$(O$_2$CMe)$_4$, Mo$_2$(O$_2$CCF$_3$)$_4$, or K$_2$Mo$_3$Cl$_4$ to give the mononuclear, seven-coordinate species Mo(t-BuNC)$_2$(O$_2$CMe)$_2$ or [Mo(t-BuNC)$_2$]$X$[X], where $X$ is O$_2$CCF$_3$ or Cl. This reaction is consistent with the metal-metal bond cleavage reaction, as shown in the following equation:

$$\text{Mo}_2(\text{O}_2\text{CMe})_4 + 2\text{t-BuNC} \rightarrow 2\text{Mo(t-BuNC)}_2(\text{O}_2\text{CMe})_2$$

Intramolecular coordination of tert-Butyl isocyanide is monodentate and the other anionic O$_2$CCF$_3$ groups (Tables I and Table II). The $^1$H and $^{13}$C NMR spectra in CD$_3$CN show that the t-BuNC coordinate hydrogen is exchanged, indicating that the complex is best formulated as [Mo(t-BuNC)$_2$(O$_2$CMe)$_2$]. This complex is a nonelectrolyte in nitromethane, and the IR spectrum indicates terminal t-BuNC coordination, although a weak band at 1720 cm$^{-1}$ is observed. This low-energy absorption is most reasonably ascribed to bent monodentate$^{1}$ t-BuNC$^{-}$, rather than bridging t-BuNC groups, as has been shown crystallographically for Fe(t-BuNC)$_5$, though it might be due to a trace impurity. Some of the other complexes we have prepared also possess this IR absorption, although it may be obscured in the O$_2$CCF$_3$ complex by the intense, rather broad band at 1690 cm$^{-1}$. The IR spectrum of the O$_2$CCMe complex also shows two absorptions in the region typical of monodentate acetylacetonate group$^{14}$, although the $^1$H and $^{13}$C NMR spectra

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(5) Although (RNC)Ni(CO)$_5$ has not been described for R = Br, complexes with R = Br, Et, and n-Bu all have $v_{\nu}$(CO) $= 2072$ cm$^{-1}$.
Carboxylate Complexes of Mo, Re, Ru, and Rh


Table I. Analytical and Conductivity Data

<table>
<thead>
<tr>
<th>compd</th>
<th>color</th>
<th>mp, °C</th>
<th>% calcd</th>
<th>% found</th>
<th>Λ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(t-BuNC)₅(O₂CMe)₂</td>
<td>yellow</td>
<td>142-143</td>
<td>55.3</td>
<td>8.17</td>
<td>11.1</td>
</tr>
<tr>
<td>[Mo(t-BuNC)₅(O₂CCF₃)]₂[O₂CCF₃]</td>
<td>yellow</td>
<td>145-147</td>
<td>49.8</td>
<td>6.63</td>
<td>10.2</td>
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<tr>
<td>[Mo(t-BuNC)₅][PF₆]₂</td>
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<td>8.18</td>
<td>12.6</td>
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<tr>
<td>[Mo(t-BuNC)₅][Mo₂O₆]₂Me₂CO</td>
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<td>170 dec</td>
<td>43.4</td>
<td>6.56</td>
<td>10.1</td>
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<tr>
<td>Mo(t-BuNC)₅(O₂CCF₃)₂</td>
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<td>160-164</td>
<td>40.0</td>
<td>4.76</td>
<td>7.35</td>
</tr>
<tr>
<td>Re(t-BuNC)₅[Cl]</td>
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<td>188 dec</td>
<td>50.0</td>
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<td>11.7</td>
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<tr>
<td>trans-Ru(t-BuNC)₅(O₂CMe)₂</td>
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<td>147-148</td>
<td>52.2</td>
<td>7.67</td>
<td>10.2</td>
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<tr>
<td>Rh₂(O₂CMe)₆(t-BuNC)₅</td>
<td>red-orange</td>
<td>35.5</td>
<td>4.97</td>
<td>4.61</td>
<td>3.0</td>
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</tbody>
</table>

a 0.1-1 cm⁻¹ mol⁻¹ in MeCN at 25 °C, 10⁻³-10⁻⁴ M. b Zero in MeNO₃ (see text). c Cl: calcd, 10.7; found, 11.1. d P: calcd, 6.4; found, 7.1. e CI: calcd, 5.0; found, 5.5.

Table II. Infrared Data (cm⁻¹)

<table>
<thead>
<tr>
<th>compd</th>
<th>u(CN)</th>
<th>νₐ(CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(t-BuNC)₅(O₂CMe)₂</td>
<td>1770 (sh), 1715 (s), 1570 (s)</td>
<td>1630 (s), 1570 (s)</td>
</tr>
<tr>
<td>[Mo(t-BuNC)₅(O₂CCF₃)]₂[O₂CCF₃]</td>
<td>1740 (s), 1730 (m)</td>
<td>1690 (s)</td>
</tr>
<tr>
<td>[Mo(t-BuNC)₅][Cl]Cl</td>
<td>1750 (s), 1720 (m), 1610 (s)</td>
<td>1720 (m)</td>
</tr>
<tr>
<td>[Mo(t-BuNC)₅][PF₆]₂</td>
<td>1750 (s), 1720 (m)</td>
<td>1570 (m)</td>
</tr>
<tr>
<td>[Mo(t-BuNC)₅][Mo₂O₆]₂Me₂CO</td>
<td>1710 (m)</td>
<td>1690 (s)</td>
</tr>
<tr>
<td>Mo(t-BuNC)₅(O₂CCF₃)₂</td>
<td>1730 (s), 1720 (m)</td>
<td>1612(s)</td>
</tr>
<tr>
<td>Re(t-BuNC)₅[Cl]</td>
<td>2040 (s), 2020 (s)</td>
<td>1615 (m)</td>
</tr>
<tr>
<td>trans-Ru(t-BuNC)₅(O₂CMe)₂</td>
<td>2130 (s), 1710 (m)</td>
<td>1637 (m)</td>
</tr>
<tr>
<td>Rh₂(O₂CMe)₆(t-BuNC)₅</td>
<td>2150 (s), 2130 (s)</td>
<td>1590 (s)</td>
</tr>
</tbody>
</table>

Nujol mull. Key: s = strong, m = medium, w = weak, sh = shoulder.

tungsten analogue recently characterized crystallographically.

Multiple bonds in binuclear acetates of rhenium and ruthenium are also cleaved by t-BuNC. Addition of excess t-BuNC to Re₂(O₂CMe)Cl₂ in methanol yields a white, diamagnetic complex of stoichiometry Re(t-BuNC)₂Cl. In this case, the quadruple bond has been ruptured with current reduction of the oxidation state of the metal from three to one. The complex is a 1:1 electrolyte in acetonitrile and contains terminal and equivalent t-BuNC groups as shown by IR and NMR spectroscopy. Thus, this complex is best formulated as [n-Bu₄N][Re(t-BuNC)₂Cl]. Related rhenium(I) isocyanide complexes of this type have been prepared by other means.

In addition, the quadruple bond in [n-Bu₄N]₂[Re₂Cl₆] has been cleaved by methyl isocyanide, yielding the oxidized, rhenium(IV) product [n-Bu₄N][Re₂(MO₂Cl₄)]Cl₂.

The multiple bond in Ru₂(O₂CMe)₂Cl can also be cleaved by excess t-BuNC in methanol, giving colorless, diamagnetic Ru₂(t-BuNC)₂(O₂CMe)₂. This complex is a nonelectrolyte in acetonitrile, and the H and ¹³C[H] NMR spectra in CD₃CN show that the O₂CMe and t-BuNC groups are each equivalent. The IR spectrum has an absorption at 1710 cm⁻¹ due to bent t-BuNC groups, as discussed above for Mo(t-BuNC)₂(O₂CMe)₂, and two absorptions in the monodentate acetate region. The bent nature of at least some of the t-BuNC groups demands that the instantaneous point group symmetry of the ruthenium complex be lower than D₄h, and this in turn
The singly bonded compound Rh₂(O₂CMe)₄ is not cleaved by where only one would have been naively expected. The di-bonded molybdenum, rhenium, and ruthenium are readily cleaved synthesis of a number of t-BuNC derivatives. For molybdenum, the complexes Mo₂(~-BuNC)₂(O₂CMe)₂, [Mo(t-BuNC)₂(O₂CCF₃)] [O₂CCF₃] have been isolated. It is pertinent at this point to ask why the acetate is a better base than trifluoroacetate or chloride spectra are fully consistent with the binuclear formulation. We have also observed this phenomenon in [Mo(t-BuNC)₂][PF₆]₂ (see Table III). Similar behavior has been reported for other complexes of high symmetry.22

Discussion

The multiple metal–metal bonds in binuclear compounds of molybdenum, rhodium, and ruthenium are readily cleaved by tert-butyl isocyanide, affording a convenient, high-yield synthesis of a number of t-BuNC derivatives. For molybdenum, the complexes Mo₂(t-BuNC)₂(O₂CMe)₂, [Mo₂(t-BuNC)₂(O₂CCF₃)] [O₂CCF₃] and [Mo₂(t-BuNC)₂Cl₂][Cl] have been isolated. It is pertinent at this point to ask why the acetato complex exists with five bound t-BuNC groups, while the O₂CCF₃ and Cl complexes have six. On the assumption that acetate is a better base than trifluoroacetate or chloride toward the molybdenum atom, the equilibrium constant for the reaction

\[
\text{Mo₄X}^+ + X^- = \text{Mo₃X}_2 + L
\]

will be largest for X = O₂CMe, thus favoring the species on the right. This assumption is reasonable in light of the relative pKₐ's of the conjugate acids, HX. Nevertheless, the equilibrium may be driven toward the left by addition of a large excess of a coordinating ligand, and indeed we find that the acetato complex, though a nonconductor in nitromethane, is a 1:1 electrolyte in acetonitrile; presumably [Mo₂(t-BuNC)₂](MeCN) [O₂CMe)] [O₂CCF₃] is formed in that solvent. Similar behavior has been observed for other molybdenum isocyanide complexes.22

We wished to determine whether intermediates could be isolated along the pathway leading to bond cleavage, in order to gain some insight into the mechanism of these reactions. Accordingly, we chose to study Mo₂(O₂CCF₃)₄ in more detail, since it reacts with t-BuNC under the mildest conditions. Addition of 2 equiv of t-BuNC per binuclear unit in diethyl ether at room temperature produces a deep red solution from which a yellow precipitate forms. This precipitate gives an elemental analysis consistent with the formulation Mo₂(t-BuNC)₂(O₂CCF₃)₂, and its infrared spectrum shows two different types of trifluoroacetate coordination: one bidentate and the other either monodentate or anionic. The conductivity and NMR data in acetonitrile are remarkably similar to those of [Mo₂(t-BuNC)₂(O₂CCF₃)] [O₂CCF₃], and it is reasonable to suggest that the complex exists in acetonitrile as [Mo₂(t-BuNC)₂(MeCN)] [O₂CCF₃] [O₂CCF₃]. Unfortunately we can say no more.24

For rhodium and ruthenium, we have isolated the complexes [Re₂(t-BuNC)₂][Cl] and trans-Ru₂(t-BuNC)₂(O₂CMe)₂, respectively. In both cases, reaction of the binuclear starting material with t-BuNC is accompanied by reduction of the metal. In the rhodium reaction, reduction is accomplished by loss of acetate ligands, whereas a chloride is lost in the ruthenium reaction. We know of no way to explain these observations except to point out that the lower oxidation states will be relatively stabilized due to more effective π-backbonding to the t-BuNC groups. For presumably similar reasons, Cr₂(O₂CMe)₄ reacts with aryl isocyanides to give reduced products via a disproportionation reaction.25 This leaves the question of why reduction does not occur in the molybdenum system. Other workers have shown that attempted reduction of [Mo₂(t-BuNC)₂][I] with zinc leads only to another molybdenum(II) species with reductively coupled t-BuNC groups. Apparently molybdenum(II)–alkyl isocyanides are stable relative to molybdenum(0)–alkyl isocyanide complexes.

In testing the generality of the bond cleavage reaction, we turned to the singly bonded rhodium compound Rh₂(O₂CMe)₄. We expected that rupture of the metal–metal bond would occur with reduction, giving a mononuclear complex of rhodium(I), of which many examples are known.22,26 Instead, the binuclear axial diaduct Rh₂(O₂CMe)₂(t-BuNC)₂ was obtained even in the presence of excess t-BuNC.

At first glance, it is surprising that a bond of order one remains intact under reaction conditions which cleave bonds of higher order, but in fact this behavior is easily explained. As Christoph has shown for Rh₂(O₂CMe)₄, coordination by Lewis bases which are good π-acceptors strengthens the Rh–Rh bond by effectively delocalizing electron density from

\[
\begin{align*}
\text{Acetonitrile is not itself capable of cleaving quadruple bonds, as Mo₄(O₂CCF₃)₄ simply dissolves in this solvent. It is possible that the} \\
\text{structure of Mo₂(t-BuNC)₂(O₂CCF₃)₂ in the solid state is similar to that of} \\
\end{align*}
\]

(24) Acetonitrile is not itself capable of cleaving quadruple bonds, as Mo₄(O₂CCF₃)₄ simply dissolves in this solvent. It is possible that the structure of Mo₂(t-BuNC)₂(O₂CCF₃)₂ in the solid state is similar to that of Re₂Cl₆(dppe)·2MeCN: Jaeger, J. A.; Robinson, W. R.; Walton, R. A. J. Chem. Soc., Dalton Trans. 1975, 698.
Carboxylate Complexes of Mo, Re, Ru, and Rh

HOMO's which are metal-metal antibonding (Figure 1a). Conversely, for molybdenum and rhenium, the HOMO's are also from the metal-metal bonding orbitals of proper symmetry under view of the electron delocalization mechanism discussed above.36

The IR spectra were recorded on a Perkin-Elmer 257 instrument. The NMR spectra were recorded on a modified Bruker spectrometer operating at 180 MHz for proton, 69.14 MHz for fluorine, and 45.29 MHz for carbon. The conductivities were measured with use of a standard cell. All manipulations were performed under argon.

Experimental Section

All analyses were by the microanalytical laboratory of this department. The IR spectra were recorded on a Perkin-Elmer 257 instrument. The NMR spectra were recorded on a modified Bruker 1100 machine operating at 180 MHz for proton, 69.14 MHz for fluorine, and 45.29 MHz for carbon. The conductivities were measured with use of a standard cell. All manipulations were performed under argon.

(37) Heating in the neat hydrocarbon for 1 h.

Figure 1. (a) Electron delocalization from filled Rh–Rh antibonding orbital into empty ligand π* orbital. (b) Electron delocalization from filled Mo–Mo bonding orbital into empty ligand π* orbital.

Mo(t-BuNC)₂(OCMe)₂, tert-Butyl isocyanide (1.9 mL, 0.017 mol) was added to a suspension of tetrakis(acetato)dimolybdenum (0.65 g, 0.015 mol) in diethyl ether (30 mL) and methanol (5 mL). After being refluxed for 48 h, the solvent was removed under reduced pressure. The residue was stirred (30 min), filtered, and the filtrate was concentrated to ca. 5 mL, and the residue was washed with diethyl ether (2 × 20 mL), and dried under vacuum. The residue was extracted with boiling toluene (3 × 50 mL), and the combined extracts were filtered, washed with diethyl ether (2 × 20 mL), and dried under vacuum. The residue was extracted with hot toluene (3 × 40 mL), and the combined extracts were filtered, concentrated to ca. 15 mL, and cooled (−10 °C). The yellow crystals (0.85 g, 66%) were collected and dried under vacuum.

[Mo(t-BuNC)₂(OCCF₃)₂]Cl₂. (e) From K₂Mo₂Cl₄. tert-Butyl isocyanide (1.3 mL, 0.012 mol) was added to a suspension of tetrakis(acetoxyethyl)dimolybdenum (0.52 g, 0.0081 mol) in diethyl ether (30 mL). After the solution was stirred for 6 h, the yellow precipitate was collected by filtration, washed with diethyl ether (2 × 20 mL), and dried under vacuum. The residue was extracted with hot toluene (3 × 40 mL), and the combined extracts were filtered, concentrated to ca. 15 mL, and cooled (−10 °C). The yellow crystals (0.81 g, 71%) were collected and dried under vacuum.

[Mo(t-BuNC)₂Cl₄]Cl₄. The chloro complex [Mo(t-BuNC)₂Cl₄]Cl₄ (1.0 g, 0.0015 mol) and ammonium hexafluorophosphate (0.05 g, 0.00031 mol) were mixed with tert-butyl isocyanide (0.16 mL, 0.00090 mol). Acetone (30 mL) was added, and the solution was stirred for 6 h. After filtration and concentration of the filtrate to ca. 10 mL, cooling (−10 °C) yielded yellow prisms (0.11 g, 78%). The hexafluorophosphate salt may also be prepared from [Mo(t-BuNC)₂(OCCF₃)₂]Cl₂ [OCCF₃] or [Mo(t-BuNC)₂(OCCMe)₂] in a similar manner.

[Mo(t-BuNC)₂][Mo₂O₇]Cl₂. The chloro complex [Mo(t-BuNC)₂Cl₄]Cl₄ (0.32 g, 0.00048 mol) was dissolved in acetone (30 mL), and the acetone was allowed to evaporate in air, depositing orange crystals (0.09 g, 44%) identified by mp and IR as [Mo(t-BuNC)₂Cl₄]Cl₄.

Reaction of Mo₂O₇(OCMe)₃ with 2 Molar Equiv of t-BuNC. tert-Butyl isocyanide (0.20 mL, 0.0018 mol) was added dropwise to tetrakis(trifluoroacetato)dimolybdenum (0.58 g, 0.00090 mol) in diethyl ether (25 mL). The red solution yielded yellow microcrystals on standing for 1 h. The product was collected, washed with diethyl ether (10 mL), and dried under vacuum (0.23 g, 22%).

[Re(t-BuNC)₂Cl₄]Cl₂. tert-Butyl isocyanide (0.95 mL, 0.0088 mol) was added to bis(acetato)dichlororidene (0.30 g, 0.0044 mol) in methanol (15 mL) and dichloromethane (15 mL). After the solution was refluxed (6 h), the volatile material was removed under reduced pressure, and the residue was exposed to vacuum for 12 h. Diethyl ether (5 mL) and pentane (5 mL) were added to the residue, and the suspension was stirred (30 min). The brown-red powder was collected by filtration and dried under reduced pressure. The residue was extracted with hot toluene (20 mL) and filtered, and the filtrate was discarded. The off-white residue was dissolved in toluene (25 mL) and acetone (10 mL) and filtered, and the filtrate was concentrated to ca. 25 mL. The white precipitate yield increased with time (ca. 25 mL) and stirred overnight in diethyl ether (15 mL) and methanol (15 mL). The volatile material was removed under reduced pressure, and the residue was extracted with warm diethyl ether (2 × 20 mL). After filtration the extract was concentrated to ca. 10 mL and cooled (−10 °C). The white precipitate (0.65 g, 87%) was collected.

[Rh(OCMe)₃(t-BuNC)₂]. Tetrakis(acetato)dihydride–bis(methanol) (0.085 g, 0.00017 mol) was suspended in diethyl ether (30 mL),
Metal-Promoted Reactivity of Cyanogen toward Compounds Containing Active Hydrogen Atoms on Carbon. 2. Synthesis of a Fully Functionalized Substituted Pyrimidine from Cyanogen and Acetylacetone Catalyzed by Acetylacetonate Complexes of Transition Metals

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Received April 17, 1980

The reactivity of various metal acetylacetonate complexes [M(acac)₃] (n = 2 for M = MnIII, FeIII, CoII, CuII, PdII; n = 3 for M = CrIII, MnIII, FeIII) has been tested toward C₂N₂ at ambient conditions in CH₂Cl₂. All [M(acac)₃] complexes, except [Pd(acac)₂], react with cyanogen to give addition compounds which are found to be unstable for Mn, Fe, and Co and quite stable for Cu. The Cu complex displays a stoichiometric composition [Cu(acac)₂C₂N₂] and is found to be isostuctural with the complex bis(3-cyanomethyl)-2,4-pentanedionato nickel(II). CrIII and FeIII complexes are found to be reactive with cyanogen are seen to be effective catalysts for the addition reaction of cyanogen to Hacac in mild conditions. On the basis of X-ray data, the organic compound obtained has been identified as a heavily functionalized pyrimidinic compound of stoichiometry (H-C=C'C=N)ₓ. X-ray structure and IR, NMR, visible-W, and mass spectra, referring to this novel compound, are given and discussed.

Introduction

The reaction between cyanogen and acetylacetone at ambient conditions in ethanol in the presence of cat-

Note Added in Proof. Some phosphine complexes of the Mo(II) dications have been described recently.38

Contribution from the Centro di Studio sulla Stabilita e Reattivi di Composti di Coordinazione, CNR, Istituto di Chimica Analitica, and the Centro di Studio sui Biopolimeri, CNR, Istituto di Chimica Organica, 35100 Padova, Italy

by Traube in 1899.1c Doubts on the correct identification of this compound have been advanced in the literature,2 but very recent data published by us3 confirm Traube's original proposal. It is worthwhile to underline the fact that the reaction does not occur thermally and it requires the presence of catalytic amounts of C₂H₅O⁻.

We have recently reported4-6 that a compound with the minimal elemental composition CₓHᵧN₂O₂, i.e., the same as that of αH, but with a completely different nature, can be obtained by reacting cyanogen and acetylacetone in CH₂Cl₂ at ambient conditions in the presence of catalytic amounts of [Ni(acac)₃].

It is pertinent to point out that this organic synthesis was originated by an inorganic investigation, which led to the discovery1-6 of a new "reaction mode" of cyanogen in its coordination chemistry.7 We have found, in fact, that cyanogen, in addition to its behavior as an oxidative addition reagent and