2040 *Inorg. Chem.* **1981,** *20,* 2040-2044

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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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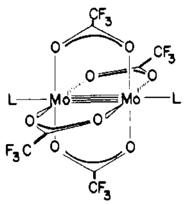
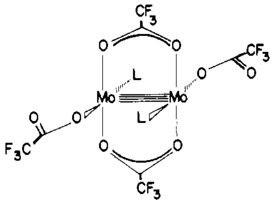
Received August 28, 1980

tert-Butyl isocyanide cleaves the quadruple metal–metal bonds in $Mo_2(O_2CMe)_4$, $Mo_2(O_2CCF_3)_4$, or $K_4Mo_2Cl_8$ to give the mononuclear, seven-coordinate species $Mo(t\text{-}BuNC)_5(O_2CMe)_2$ or $[Mo(t\text{-}BuNC)_6X][X]$, where X is O_2CCF_3 or Cl. These diamagnetic, 18-electron complexes may be converted into the known binary dication $[Mo(t\text{-}BuNC)_7][PF_6]_2$ by action of NH_4PF_6 and excess *t*-BuNC or into the polyoxoanion complex $[Mo(t\text{-}BuNC)_7][Mo_6O_{19}]\cdot 2Me_2CO$ by recrystallization from acetone in air. The rhenium and ruthenium acetates, $Re_2(O_2CMe)_4Cl_2$ and $Ru_2(O_2CMe)_4Cl$, are also cleaved by *t*-BuNC, yielding the mononuclear, six-coordinate species $[Re(t\text{-}BuNC)_6][Cl]$ and *trans*-$Ru(t\text{-}BuNC)_4(O_2CMe)_2$, respectively. In contrast, the singly bonded rhodium acetate, $Rh_2(O_2CMe)_4$, reacts with *t*-BuNC to give the binuclear axial diadduct, $Rh_2(O_2CMe)_4(t\text{-}BuNC)_2$, where the metal–metal bond has been retained.

It has been shown that tetrakis(trifluoroacetato)dimolybdenum, $Mo_2(O_2CCF_3)_4$, reacts with Lewis bases to form coordination complexes of two types: class I and class II.[1] Lewis bases such as triphenylphosphine or pyridine[2] form class I complexes, in which coordination occurs axially (A). Other Lewis bases such as triethylphosphine or dimethylphenylphosphine form nonaxial, class II adducts, one isomer of which is shown (B). Class II complexes are formed by those ligands which are relatively small (as measured by cone angle), are good σ bases (as measured by $\nu_{A_1}(CO)$ in $LNi(CO)_3$) and have some π-accepting capacity. The smallest class II ligand studied, trimethylphosphine, has a cone angle of 119° and $\nu_{A_1}(CO) = 2064$ cm^{-1}.[3] We were interested in extending the study to other ligands with similar properties. *tert*-Butyl isocyanide, *t*-BuNC, was chosen since it is extremely small (cone angle of 70°),[4] a good σ base ($\nu_{A_1}(CO)$ is 2072 cm^{-1}),[5] and a good π acceptor, suggesting that it might also form class II complexes with $Mo_2(O_2CCF_3)_4$.



A



B

Much to our surprise, we found that *t*-BuNC reacts with $Mo_2(O_2CCF_3)_4$ to give neither a class I nor a class II diadduct but instead gives a mononuclear product, $[Mo(t\text{-}BuNC)_6(O_2CCF_3)][O_2CCF_3]$, where metal–metal bond rupture has occurred.[6] This bond cleavage reaction is consistent with results obtained by Malatesta many years ago[7] in which reaction of tetrakis(acetato)dichromium, $Cr_2(O_2CMe)_4$, with phenyl isocyanide yielded mononuclear $Cr(PhNC)_6$. More recently Gray,[8] San Filippo,[9] Cotton,[10] and Walton[11] have also reported reaction of quadruple metal–metal bonded compounds with isocyanides. We have now completed a full investigation of the interaction of *tert*-butyl isocyanide with binuclear complexes of molybdenum, rhenium, ruthenium, and rhodium.

Results

Addition of excess *t*-BuNC to $Mo_2(O_2CCF_3)_4$ in diethyl ether yields a yellow, diamagnetic, mononuclear complex of stoichiometry $Mo(t\text{-}BuNC)_6(O_2CCF_3)_2$. Thus, the quadruple molybdenum–molybdenum bond has been cleaved without change in oxidation state. The complex is a 1:1 electrolyte in acetonitrile[12] and possesses infrared absorptions characteristic of terminal *t*-BuNC groups and either monodentate[1] or anionic O_2CCF_3 groups (Tables I and Table II). The ^1H and $^{13}C\{^1H\}$ NMR spectra in CD_3CN show that the *t*-BuNC groups are equivalent on the NMR time scale. The ^{19}F NMR spectrum shows inequivalent O_2CCF_3 groups, two equal resonances being observed in the region indicative of either monodentate[1] or anionic coordination (Table III). All the data suggest that the complex is best formulated as $[Mo(t\text{-}BuNC)_6(O_2CCF_3)][O_2CCF_3]$, in which one O_2CCF_3 group is monodentate and the other anionic.

The quadruple bond in the acetate, $Mo_2(O_2CMe)_4$, is also cleaved by *t*-BuNC, giving yellow, diamagnetic $Mo(t\text{-}BuNC)_5(O_2CMe)_2$. 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 rather than bridging *t*-BuNC groups, as has been shown crystallographically for $Fe(t\text{-}BuNC)_5$,[13] 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_2CCF_3 complex by the intense, rather broad band at 1690 cm^{-1}. The IR spectrum of the O_2CMe complex also shows two absorptions in the region typical of monodentate acetate groups,[14] although the ^1H and $^{13}C\{^1H\}$ NMR spectra

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Table I. Analytical and Conductivity Data

			% calcd			% found			
compd	color	mp, °C	C	H	N	C	H	N	Λ^a
Mo(t-BuNC)$_5$(O$_2$CMe)$_2$	yellow	142–143	55.3	8.17	11.1	53.2	7.81	10.4	104^b
[Mo(t-BuNC)$_6$(O$_2$CCF$_3$)][O$_2$CCF$_3$]	yellow	145–147	49.8	6.63	10.2	48.3	6.35	9.46	128
[Mo(t-BuNC)$_6$Cl][Cl]	yellow	171–172	54.1	8.18	12.6^c	53.4	8.08	12.1	109
[Mo(t-BuNC)$_7$][PF$_6$]$_2$	yellow	197 dec	43.4	6.56	10.1^d	43.6	7.00	10.2	279
[Mo(t-BuNC)$_7$][Mo$_6$O$_{19}$]·2Me$_2$CO	orange	170 dec	29.4	4.52	5.86	28.9	4.37	6.20	
Mo(t-BuNC)$_3$(O$_2$CCF$_3$)$_2$	yellow	160–164	40.0	4.76	7.35	40.0	4.81	7.41	94
[Re(t-BuNC)$_6$][Cl]	white	188 dec	50.0	7.55	11.7^e	47.5	7.58	11.4	115
trans-Ru(t-BuNC)$_4$(O$_2$CMe)$_2$	colorless	147–148	52.2	7.67	10.2	50.9	7.72	10.2	0
Rh$_2$(O$_2$CMe)$_4$(t-BuNC)$_2$	red-orange		35.5	4.97	4.61	35.0	4.96	4.60	0

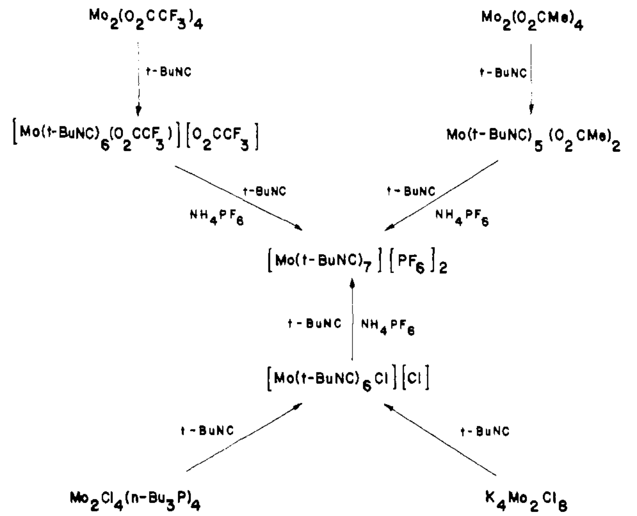
^{a} Ω^{-1} cm^2 mol^{-1} in MeCN at 25 °C, 10^{-3}–10^{-4} M. ^{b} Zero in MeNO$_2$ (see text). ^{c} Cl: calcd, 10.7; found, 11.1. ^{d} P: calcd, 6.4; found, 7.1. ^{e} Cl: calcd, 5.0; found, 5.5.

Table II. Infrared Data^a (cm^{-1})

compd	ν(CN)	ν_{as}(CO$_2$)
Mo(t-BuNC)$_5$(O$_2$CMe)$_2$	2170 (sh), 2115 (s), 1720 (m)	1630 (s), 1570 (s)
[Mo(t-BuNC)$_6$(O$_2$CCF$_3$)]-[O$_2$CCF$_3$]	2140 (s), 2110 (s)	1690 (s)
[Mo(t-BuNC)$_6$Cl][Cl]	2115 (s), 2040 (sh), 1712 (m)	
[Mo(t-BuNC)$_7$][PF$_6$]$_2$	2135 (s), 2042 (sh), 1710 (m)	
[Mo(t-BuNC)$_7$][Mo$_6$O$_{19}$]·2Me$_2$CO	2125 (s), 2040 (sh), 1708 (m)	
Mo(t-BuNC)$_3$(O$_2$CCF$_3$)$_2$	2130 (s), 2060 (sh)	1690 (s), 1612 (s)
[Re(t-BuNC)$_6$][Cl]	2040 (s), 2020 (s)	
trans-Ru(t-BuNC)$_4$(O$_2$CMe)$_2$	2130 (s), 1710 (m)	1637 (m), 1615 (m)
Rh$_2$(O$_2$CMe)$_4$(t-BuNC)$_2$	2150 (s), 2130 (s)	1590 (s)

^{a} Nujol mull. Key: s = strong, m = medium, w = weak, sh = shoulder.

Scheme I



in C$_6$D$_6$ show only one type of t-BuNC and O$_2$CMe environment. This behavior is doubtless due to the stereochemically rigid nature of the seven-coordinate species on the infrared but nonrigidity on the NMR time scale.

As a test of the generality of the molybdenum–molybdenum bond cleavage reaction, we allowed K$_4$Mo$_2$Cl$_8$ or Mo$_2$Cl$_4$(n-Bu$_3$P)$_4$ to react with excess t-BuNC. In both cases, a yellow, diamagnetic, mononuclear complex of stoichiometry Mo(t-BuNC)$_6$Cl$_2$ was obtained. The conductivity, IR, and ^{1}H and ^{13}C{^{1}H} NMR data all suggest that the compound is best formulated as [Mo(t-BuNC)$_6$Cl][Cl], similar to that of the O$_2$CCF$_3$ analogue. This chloro complex has been prepared previously by other means,[15] and the iodo analogue has been characterized crystallographically.[16]

All three of the molybdenum complexes Mo(t-BuNC)$_5$(O$_2$CMe)$_2$, [Mo(t-BuNC)$_6$(O$_2$CCF$_3$)][O$_2$CCF$_3$] and [Mo(t-BuNC)$_6$Cl][Cl] can be converted into the known binary dication [Mo(t-BuNC)$_7$][PF$_6$]$_2$ by action of NH$_4$PF$_6$ and excess t-BuNC in acetone (see Scheme I).[15,17] Other workers have also obtained this complex directly from Mo$_2$(O$_2$CMe)$_4$ or K$_4$Mo$_2$Cl$_8$ without isolation of the intermediate acetato or chloro species.[11]

Interestingly, recrystallization of [Mo(t-BuNC)$_6$Cl][Cl] from acetone in air leads to the polyoxoanion complex (t-BuNC)$_7$][Mo$_6$O$_{19}$]·2Me$_2$CO. The infrared spectrum exhibits Mo–O absorptions at 950 and 795 cm^{-1}, and the ^{1}H NMR spectrum in benzonitrile shows the presence of acetone in the amount suggested. This compound is no doubt similar to the tungsten analogue recently characterized crystallographically.[18]

Multiple bonds in binuclear acetates of rhenium and ruthenium are also cleaved by t-BuNC. Addition of excess t-BuNC to Re$_2$(O$_2$CMe)$_4$Cl$_2$ in methanol yields a white, diamagnetic complex of stoichiometry Re(t-BuNC)$_6$Cl. In this case, the quadruple bond has been ruptured with concurrent 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 the 18-electron species [Re(t-BuNC)$_6$][Cl]. Related rhenium(I) isocyanide complexes of this type have been prepared by other means.[19–21] In addition, the quadruple bond in [n-Bu$_4$N]$_2$[Re$_2$Cl$_8$] has been cleaved by methyl isocyanide, yielding the oxidized, rhenium(IV) product [n-Bu$_4$N][Re(MeNC)Cl$_5$].[10]

The multiple bond in Ru$_2$(O$_2$CMe)$_4$Cl can also be cleaved by excess t-BuNC in methanol, giving colorless, diamagnetic Ru(t-BuNC)$_4$(O$_2$CMe)$_2$. This complex is a nonelectrolyte in acetonitrile, and the ^{1}H and ^{13}C{^{1}H} NMR spectra in C$_6$D$_6$ show that the O$_2$CMe and t-BuNC groups are each equivalent. The low-spin d^6 octahedral complex is most likely the trans isomer. The IR spectrum has an absorption at 1710 cm^{-1} due to bent t-BuNC groups, as discussed above for Mo(t-BuNC)$_5$(O$_2$CMe)$_2$, 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 D_{4h}, and this in turn

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Table III. NMR Data[a]

compd	^{1}H		^{13}C{^{1}H}					^{19}F
	$\mathrm{CNCMe_3}$	$\mathrm{O_2CMe}$	$\mathit{C}\mathrm{NCMe_3}$	$\mathrm{CN}\mathit{C}\mathrm{Me_3}$	$\mathrm{CNC}\mathit{Me}_3$	$\mathrm{O_2}\mathit{C}\mathrm{Me}$	$\mathrm{O_2C}\mathit{Me}$	$\mathrm{O_2CCF_3}$
$\mathrm{Mo}(t\text{-BuNC})_5(\mathrm{O_2CMe})_2$[b]	1.43 (45)	2.50 (6)	162.1	58.2	30.4	180.5	24.1	
$[\mathrm{Mo}(t\text{-BuNC})_6(\mathrm{O_2CCF_3})][\mathrm{O_2CCF_3}]$[c]	1.54		163.9	58.3	30.0			−73.9 (1), −74.7 (1)
$[\mathrm{Mo}(t\text{-BuNC})_6\mathrm{Cl}][\mathrm{Cl}]$[d]	1.49		164.3	57.8	31.0			
$[\mathrm{Mo}(t\text{-BuNC})_7][\mathrm{PF_6}]_2$[c]	1.64		152.9[f]	59.2[g]	29.5			
$[\mathrm{Mo}(t\text{-BuNC})_7][\mathrm{Mo_6O_{19}}]\cdot 2\mathrm{Me_2CO}$[e]	1.64							
$\mathrm{Mo}(t\text{-BuNC})_3(\mathrm{O_2CCF_3})_2$[c]	1.54		163.7	58.3	30.4			−74.7
$[\mathrm{Re}(t\text{-BuNC})_6][\mathrm{Cl}]$[d]	1.50		141.0	56.0	31.1			
trans-$\mathrm{Ru}(t\text{-BuNC})_4(\mathrm{O_2CMe})_2$[b]	1.36 (36)	2.23 (6)	151.8	56.6	30.5	177.7	23.9	
$\mathrm{Rh_2(O_2CMe)_4}(t\text{-BuNC})_2$[b]	1.21 (18)[h]	1.98 (12)	*i*	56.6[j]	30.0	192.9	23.9	

[a] All NMR data reported in δ units (positive values to low field) relative to Me_4Si (^{1}H and ^{13}C) or $CFCl_3$ (^{19}F) at 25 °C. Relative intensities are reported in parentheses. ^{13}C{^{1}H} spectra were obtained with use of $Cr(acac)_3$ as a spin relaxation agent. [b] In C_6D_6. [c] In CD_3CN. [d] In $CDCl_3$. [e] In PhCN. [f] Triplet, $J_{NC} = 17$ Hz. [g] Triplet, $J_{NC} = 4.7$ Hz. [h] Triplet, $J_{NH} = 2$ Hz. [i] Not observed. [j] Triplet, $J_{NC} = 5.5$ Hz.

might account for the two acetate absorptions in the infrared, where only one would have been naively expected. The dichloro analogue of this complex has been described.[13]

In contrast to all of the results obtained with multiply bonded molybdenum, rhenium, and ruthenium systems, the singly bonded compound $Rh_2(O_2CMe)_4$ is not cleaved by *t*-BuNC. Instead, the red-orange axial diadduct $Rh_2(O_2CMe)_4(t\text{-BuNC})_2$ is obtained. The complex is a nonelectrolyte in acetonitrile, and the IR and ^{1}H and ^{13}C{^{1}H} NMR spectra are fully consistent with the binuclear formulation. One interesting feature of this complex is that coupling of the nitrogen nuclei ($I = 1$) to the *t*-BuNC hydrogen and carbon atoms is observed in the ^{1}H and ^{13}C NMR spectra. We have also observed this phenomenon in $[Mo(t\text{-BuNC})_7][PF_6]_2$ (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, rhenium, 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 $Mo(t\text{-BuNC})_5(O_2CMe)_2$, $[Mo(t\text{-BuNC})_6(O_2CCF_3)][O_2CCF_3]$ and $[Mo(t\text{-BuNC})_6Cl][Cl]$ have been isolated. It is pertinent at this point to ask why the acetato complex exists with five bound *t*-BuNC groups, while the O_2CCF_3 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

$$MoL_6X^+ + X^- \rightleftharpoons MoL_5X_2 + L$$

will be largest for $X = O_2CMe$, thus favoring the species on the right. This assumption is reasonable in light of the relative pK_a'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 $[Mo(t\text{-BuNC})_5(MeCN)(O_2CMe)][O_2CMe]$ is formed in that solvent. Similar behavior has been observed for other molybdenum isocyanide complexes.[23]

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 $Mo_2(O_2CCF_3)_4$ 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 $Mo(t\text{-BuNC})_3(O_2CCF_3)_2$, 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 $[Mo(t\text{-BuNC})_6(O_2CCF_3)][O_2CCF_3]$, and it is reasonable to suggest that the complex exists in acetonitrile as $[Mo(t\text{-BuNC})_3(MeCN)_3(O_2CCF_3)][O_2CCF_3]$. Unfortunately we can say no more.[24]

For rhenium and ruthenium, we have isolated the complexes $[Re(t\text{-BuNC})_6][Cl]$ and *trans*-$Ru(t\text{-BuNC})_4(O_2CMe)_2$, respectively. In both cases, reaction of the binuclear starting material with *t*-BuNC is accompanied by reduction of the metal. In the rhenium 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, $Cr_2(O_2CMe)_4$ reacts with aryl isocyanides to give reduced products via a disproportionation reaction.[7] This leaves the question of why reduction does not occur in the molybdenum system. Other workers have shown that attempted reduction of $[Mo(t\text{-BuNC})_6I][I]$ with zinc leads only to another molybdenum(II) species with reductively coupled *t*-BuNC groups.[25] 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 $Rh_2(O_2CMe)_4$. 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.[4,22,26] Instead, the binuclear axial diadduct $Rh_2(O_2CMe)_4(t\text{-BuNC})_2$ 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[27] for $Rh_2(O_2CMe)_4$, coordination by Lewis bases which are good π-acceptors strengthens the Rh–Rh bond by effectively delocalizing electron density from

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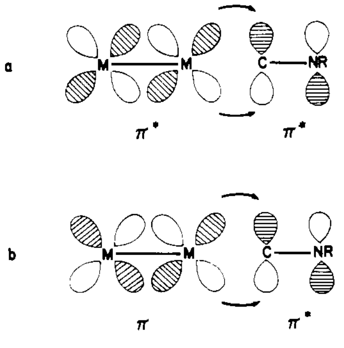

Figure 1. (a) Electron delocalization from filled Rh–Rh antibonding orbital into empty ligand π* orbital. (b) Electron delocalization from filled Mo–Mo bonding orbital into empty ligand π* orbital.

HOMO's which are metal–metal antibonding (Figure 1a). Conversely, for molybdenum and rhenium, the HOMO's are metal–metal bonding and coordination by good π acceptors leads to bond weakening (Figure 1b). Apparently for $Ru_2(O_2CMe)_4Cl$, coordination by *t*-BuNC is able to delocalize electron density not only from the antibonding HOMO's but also from the metal–metal bonding orbitals of proper symmetry which lie just slightly lower in energy, leading to net weakening of the bond.[28] Reduction in metal–metal bond strength leads ultimately to mononuclear products, whereas increasing the metal–metal bond strength during *t*-BuNC coordination favors retention of the binuclear unit. This rationalization accounts for the observed behavior of the various binuclear complexes in this study toward *t*-BuNC.

Cleavage of multiple metal–metal bonds has been observed with other π-accepting ligands isoelectronic with *t*-BuNC such as MeCN,[29] CO,[30,31] NO^+,[32] CN^-,[33] and also NO.[34,35] An understanding of the ability of π-accepting ligands in general to cleave multiple metal–metal bonds may be obtained in view of the electron delocalization mechanism discussed above.[36] As a final note, we have attempted reaction of $Mo_2(O_2CCF_3)_4$ with other sterically small, good π-accepting ligands. We have found that no reaction is observed toward CO (18 atm in toluene at 120 °C), 1,5-cyclooctadiene,[37] or the alkynes[37] (RC≡CR where R = Et, Ph, $SiMe_3$, or CO_2Me). We ascribe these results to the fact that none of these ligands is a good enough σ base[1] to allow coordination.

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 1180 machine operating at 180 MHz for proton, 169.4 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.

$Mo(t\text{-}BuNC)_5(O_2CMe)_2$. *tert*-Butyl isocyanide (1.9 mL, 0.017 mol) was added to a suspension of tetrakis(acetato)dimolybdenum (0.65 g, 0.0015 mol) in diethyl ether (30 mL) and methanol (5 mL). After being refluxed for 48 h, the solvent was removed under reduced pressure. To the red oil was added boiling octane (50 mL), and the solution was stirred for 30 min, then filtered, and discarded. The residue was stirred with diethyl ether (10 mL) for 6 h. The orange solid was collected, dried under vacuum, and then extracted with boiling toluene (3 × 50 mL). The extracts were combined, concentrated to ca. 15 mL and cooled (−70 °C). The yellow needles (0.72 g, 38%) were collected. *t*-BuNC must be free from CH_2Cl_2.

$[Mo(t\text{-}BuNC)_6(O_2CCF_3)][O_2CCF_3]$. *tert*-Butyl isocyanide (1.0 mL, 0.0090 mol) was added to tetrakis(trifluoroacetato)dimolybdenum (0.52 g, 0.000 81 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 (0.85 g, 66%) were collected and dried under vacuum.

$[Mo(t\text{-}BuNC)_6Cl][Cl]$. (a) From $K_4Mo_2Cl_8$. *tert*-Butyl isocyanide (1.3 mL, 0.012 mol) was added to a suspension of tetrapotassium octachlorodimolybdate (0.54 g, 0.000 85 mol) in methanol (30 mL), and the suspension was refluxed (2 h). The volatile material was removed under reduced pressure, and the residue was washed with diethyl ether (30 mL). Acetone (30 mL) was added to the residue, the solution was filtered, and the filtrate was concentrated to ca. 10 mL and cooled (−10 °C). The yellow crystals (0.81 g, 71%) were collected and dried under vacuum.

(b) From $Mo_2Cl_4[P(n\text{-}Bu)_3]_4$. The phosphine complex (0.35 g, 0.000 31 mol) was dissolved in pentane (30 mL), and *tert*-butyl isocyanide (0.50 mL, 0.0045 mol) was added. After the solution was stirred for 6 h, the yellow precipitate was collected and dried under vacuum. Crystallization from acetone–diethyl ether yielded yellow needles (0.18 g, 44%) identified by mp and IR as $[Mo(t\text{-}BuNC)_6Cl][Cl]$.

$[Mo(t\text{-}BuNC)_7][PF_6]_2$. The chloro complex $[Mo(t\text{-}BuNC)_6Cl][Cl]$ (0.10 g, 0.000 15 mol) and ammonium hexafluorophosphate (0.05 g, 0.000 31 mol) were mixed with *tert*-butyl isocyanide (0.10 mL, 0.000 90 mol). Acetone (30 mL) was added, and the solution was stirred for 1 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 $[Mo(t\text{-}BuNC)_6(O_2CCF_3)][O_2CCF_3]$ or $Mo(t\text{-}BuNC)_5(O_2CMe)_2$ in a similar manner.

$[Mo(t\text{-}BuNC)_7][Mo_6O_{19}][Me_2CO]_2$. The chloro complex $[Mo(t\text{-}BuNC)_6Cl][Cl]$ (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, 78%).

Reaction of $Mo_2(O_2CCF_3)_4$ 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, 0.000 90 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%).

$[Re(t\text{-}BuNC)_6][Cl]$. *tert*-Butyl isocyanide (0.95 mL, 0.0088 mol) was added to bis(acetato)dichlorodirhenium (0.30 g, 0.000 44 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 under vacuum to ca. 25 mL. Cooling (−70 °C) yielded white prisms (0.25 g, 40%) which were collected and dried under reduced pressure.

***trans*-$Ru(t\text{-}BuNC)_4(O_2CMe)_2$.** *tert*-Butyl isocyanide (1.0 mL, 0.0090 mol) and tetrakis(acetato)chlorodiruthenium (0.32 g, 0.000 68 mol) were 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 prisms (0.65 g, 87%) were collected.

$Rh_2(O_2CMe)_4(t\text{-}BuNC)_2$. Tetrakis(acetato)dirhodium-bis(methanol) (0.085 g, 0.000 17 mol) was suspended in diethyl ether (30 mL),

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

and *tert*-butyl isocyanide (0.25 mL, 0.0022 mol) was added. The orange suspension was stirred for 4 h, and the precipitate was collected by filtration. The residue was dissolved in toluene (10 mL) and filtered, and the filtrate was concentrated to ca. 5 mL. Cooling (−10 °C) yielded orange-red needles (0.10 g, 91%).

Acknowledgment. We thank the Regents of the University of California for a fellowship (G.S.G.) and the National Science Foundation for a departmental grant used to purchase the NMR spectrometer used in this work.

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

Registry No. $Mo(t\text{-}BuNC)_5(O_2CMe)_2$, 77136-36-8; $[Mo(t\text{-}BuNC)_6(O_2CCF_3)][O_2CCF_3]$, 77136-38-0; $[Mo(t\text{-}BuNC)_6Cl][Cl]$, 66652-50-4; $[Mo(t\text{-}BuNC)_7][PF_6]_2$, 41982-05-2; $[Mo(t\text{-}BuNC)_7][Mo_6O_{19}]$, 77209-24-6; $[Mo(t\text{-}BuNC)_3(O_2CCF_3)_2]_2$, 77136-39-1; $[Re(t\text{-}BuNC)_6][Cl]$, 77152-63-7; *trans*-$Ru(t\text{-}BuNC)_4(O_2CMe)_2$, 77136-40-4; $Rh_2(O_2CMe)_4(t\text{-}BuNC)_2$, 77136-41-5; $Mo_2(O_2CMe)_4$, 14221-06-8; $Mo_2(O_2CCF_3)_4$, 36608-07-8; $K_4Mo_2Cl_8$, 25448-39-9; $Mo_2Cl_4[P(n\text{-}Bu)_3]_4$, 39306-31-5; $Re_2(O_2CMe)_4Cl_2$, 14126-96-6; $Ru_2(O_2CMe)_4Cl$, 38833-34-0; $Rh_2(O_2CMe)_4(MeOH)_2$, 41772-64-9.

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Contribution from the Centro di Studio sulla Stabilità e Reattività di Composti di Coordinazione, CNR, Istituto di Chimica Analitica,
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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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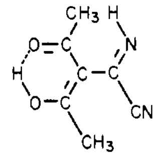
Received April 17, 1980

The reactivity of various metal acetylacetonate complexes $[M(acac)_n]$ ($n = 2$ for M = Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, Pd^{II}; $n = 3$ for M = Cr^{III}, Mn^{III}, Fe^{III}) has been tested toward C_2N_2 at ambient conditions in CH_2Cl_2. All $[M(acac)_2]$ 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 $[Cu(acac{\cdot}C_2N_2)_2]$ and is found to be isostructural with the complex bis(3-(cyanoiminomethyl)-2,4-pentanedionato)nickel(II). Cr^{III} and Fe^{III} complexes are found to be unreactive in the employed conditions, and $[Mn(acac)_3]$ behaves similarly to $[Mn(acac)_2]$. The complexes 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 $(Hacac{\cdot}C_2N_2)_2$. X-ray structure and IR, NMR, visible–UV, and mass spectra, referring to this novel compound, are given and discussed.

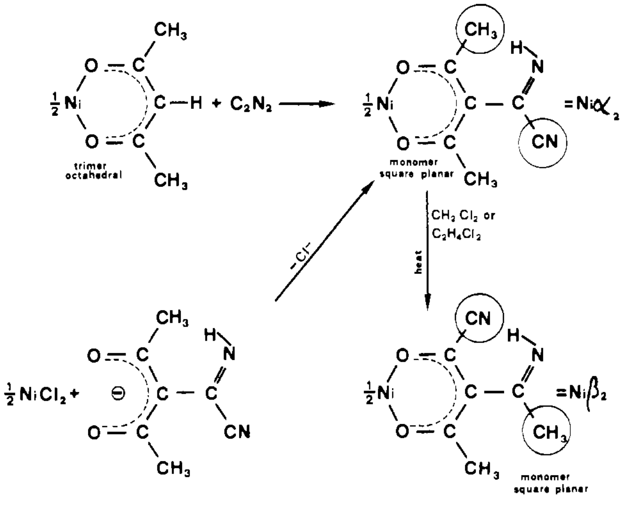
Introduction

The reaction between cyanogen and acetylacetone at ambient conditions in ethanol in the presence of $C_2H_5O^-$ to give 3-(cyanoiminomethyl)acetylacetone (αH) has been described 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 us[3] 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 $C_2H_5O^-$.



αH

Scheme I



We have recently reported[4-6] that a compound with the minimal elemental composition $C_7H_8N_2O_2$, i.e., the same as that of αH, but with a completely different nature, can be obtained by reacting cyanogen and acetylacetone in CH_2Cl_2 at ambient conditions in the presence of catalytic amounts of $[Ni(acac)_2]$.

It is pertinent to point out that this organic synthesis was originated by an inorganic investigation, which led to the discovery[3-6] 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

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