of mechanism B since it seems unlikely that a solvated FeCp(arene)$^+$ species in which the arene is η^2 or η^4 bound could have a lifetime long enough to undergo the required second-order reaction with L at the concentrations of L employed in these studies. Laser flash photolysis and low-temperature photolysis experiments are currently in progress to further resolve the mechanistic questions. We are also investigating the possible use of the reactive intermediate generated in these reactions with respect to photoassistance reactions and the synthesis of other FeCpL$_3^+$ complexes which are either unkown or difficult to synthesize by other routes.

Contribution from the Departments of Chemistry, Queen Mary College, London University, London E1 4NS, England, Indiana University, Bloomington, Indiana 47405, Princeton University, Princeton, New Jersey 08540, and Texas A&M University, College Station, Texas 77843

Hexaisopropoxydinitrosyldichromium and Its Reactions with Nitrogen Donor Ligands

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Cr(N-*i*-Pr$_2$)$_3$NO reacts with isopropyl alcohol to give the brick red crystalline compound Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$. An X-ray study shows this compound to be isostructural with the previously characterized molybdenum analogue, though a complete refinement of the chromium structure was not possible because crystals repeatedly and rapidly decomposed in the X-ray beam. The experimental data obtained from a number of physical and spectroscopic studies directly parallel those observed for Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$. The structure of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$ is thus shown to contain a central Cr$_2$O$_6$(NO)$_2$ skeleton with a rigorous inversion center and virtual C_{2h} symmetry; the σ_h plane contains the two chromium atoms, the axial NO groups, and the pair of oxygen atoms from the bridging alkoxy groups. Each chromium atom is in a local trigonal-bipyramidal environment and the two trigonal bipyramids are joined along a common axial–equatorial edge. The low-temperature limiting ^{1}H NMR spectrum is entirely consistent with the retention of this structure in solution. Above 80 °C in toluene-d_8, exchange of bridging and terminal isopropoxy ligands is rapid on the NMR time scale. The mixed-metal dimer CrMo(O-*i*-Pr)$_6$(NO)$_2$ is formed upon mixing the homonuclear dimers in hydrocarbon solvents and has been detected by ^{1}H NMR, IR, and mass spectroscopy. Variable-temperature NMR studies show that for solutions containing an equilibrium mixture of the Mo$_2$-, Cr$_2$-, and CrMo-containing dimers the exchange of isopropoxy groups between the dimers is slow on the NMR time scale. Addition of nitrogen donor ligands, L, to hydrocarbon solutions of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$ leads to an equilibrium mixture of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$, Cr(O-*i*-Pr)$_3$(NO)L, and free L, where L = ammonia, pyridine, and 2,4-lutidine. The equilibration of the above species is slow on the NMR time scale and the presence of free L does not influence the rate of exchange of bridging and terminal O-*i*-Pr ligands in Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$. By contrast the exchange between free and coordinated L in Cr(O-*i*-Pr)$_3$(NO)L is fast on the NMR time scale and is apparently independent of the concentration of free ligand, L. The compounds Cr(O-*i*-Pr)$_3$(NO)L have not been isolated as crystalline compounds because of the ready loss of L and formation of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$, but it is proposed that they are analogous to the previously characterized compound W(O-*t*-Bu)$_3$(py)(NO). A mechanism for bridge and terminal isopropoxy group exchange in Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$ is proposed involving the formation of a monobridged dimer in which one chromium atom is four-coordinate and lacks an O-*i*-Pr ligand trans to the nitrosyl group.

Introduction

The compounds Mo$_2$(OR)$_6$ (M≡M),[2] where R = *t*-Bu, *i*-Pr, and Me$_3$CCH$_2$, react[3] with nitric oxide (2 equiv) to give dimeric compounds Mo$_2$(OR)$_6$(NO)$_2$. In a formal sense, the metal-to-metal triple bond is cleaved and replaced by two metal-to-ligand triple bonds: the Mo-to-Mo distances are 2.222 (1) and 3.335 (1) Å in Mo$_2$(OCH$_2$CMe$_3$)$_6$[2] and Mo$_2$-(O-*i*-Pr)$_6$(NO)$_2$,[3] respectively. A similar cleavage of the tungsten-to-tungsten triple bond occurs in the reaction between W$_2$(O-*t*-Bu)$_6$[4] and nitric oxide (2 equiv), and by the addition of pyridine, a mononuclear compound W(O-*t*-Bu)$_3$(NO)(py) was isolated and structurally characterized.[5] Chromium, in its oxidation state +3, does not form dinuclear alkoxides with Cr-to-Cr triple bonds.[6] We show here, however, that chromium does form related nitrosyl compounds Cr$_2$(O-*i*-Pr)$_6$-(NO)$_2$ and Cr(O-*i*-Pr)$_3$(NO)L, where L = ammonia, pyridine, and 2,4-lutidine, and in the case of the bulky O-*t*-Bu ligand, a monomeric compound Cr(O-*t*-Bu)$_3$(NO) has been isolated. A preliminary report of some of this work has appeared.[7]

Results and Discussion

Syntheses. The monomeric compound Cr(N-*i*-Pr$_2$)$_3$NO[8] reacts with alcohols in hydrocarbon solvents. The bulky and relatively nonacidic alcohol *tert*-butyl alcohol reacts slowly[9]

(1) (a) Queen Mary College, London University. (b) Indiana University. (c) Princeton University. (d) Texas A&M University.
(2) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, **16**, 1801 (1977).
(3) M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, **100**, 3354 (1978).
(4) M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little, and P. E. Fanwick, *Inorg. Chem.*, **18**, 2266 (1979).
(5) M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *Inorg. Chem.*, **18** 116 (1979).
(6) D. C. Bradley, R. C. Mehrota, and D. P. Gaur in "Metal Alkoxides", Academic Press, London, New York, and San Francisco, 1978.
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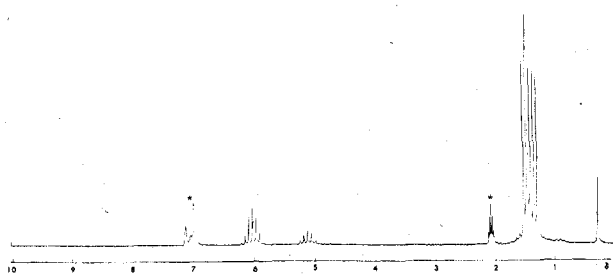
Figure 1. Low-temperature limiting ^1H NMR spectrum of $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ recorded in toluene-d_8 solvent at $-10\ °C$, 100 MHz. Signals marked with an asterisk are proton impurities in the solvent.
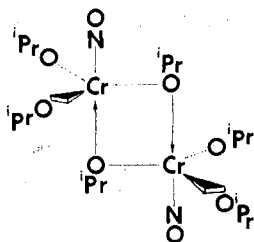

Figure 2. Schematic representation of the molecular structure of $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ emphasizing the pseudo-trigonal-bipyramidal coordination of the chromium atoms.

Table I. Values of $\nu(NO)$ in cm^{-1} for Compounds of the Form $MX_3(NO)L$ Where $M = Cr$, Mo, and W

compd	$\nu(NO)$	ref
$W(O\text{-}t\text{-}Bu)_3(NO)(py)$	1555	5
$Mo_2(O\text{-}t\text{-}Bu)_6(NO)_2$	1630	3
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6(NO)_2$	1632	3
$Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$	1640	3
$Cr(N\text{-}i\text{-}Pr_2)_3(NO)$	1641	this work
$Cr(2,6\text{-dimethylpiperidine})_3(NO)$	1673	7
$Cr(N\text{-}i\text{-}Pr)(O\text{-}t\text{-}Bu)_2(NO)$	1683	7
$Cr(NSi_2Me_6)_3(NO)$	1698	7
$Cr(O\text{-}t\text{-}Bu)_3(NO)$	1707	this work
$Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$	1720	this work

to give $Cr(O\text{-}t\text{-}Bu)_3NO$ which, on the basis of a cryoscopic molecular weight determination in benzene and spectroscopic data is shown to be a monomeric compound. Isopropyl alcohol reacts under similar conditions to give a brick red crystalline compound $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$, while the less sterically demanding and more acidic methyl and ethyl alcohols react to give the polymeric alkoxides $[Cr(OR)_3]_n$[10] with the elimination of the nitrosyl ligand.

Physical Properties. The diamagnetic crystalline compound $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ is air sensitive and must be handled in dry and oxygen-free atmospheres and solvents. It is appreciably soluble and quite stable in hydrocarbon solvents. A cryoscopic molecular weight determination confirmed that the compound is essentially dimeric, $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$, in solution. It is thermally quite stable and may be sublimed in vacuo at 90–100 °C (10^{-4} cmHg).

Spectroscopic Studies. $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ shows a single intense IR band at 1720 cm^{-1} assignable to $\nu(NO)$. In the mass spectrum, there is a weak molecular ion $Cr_2(O\text{-}i\text{-}Pr)_6\text{-}(NO)_2^+$, which is followed by a more intense ion corresponding to the loss of one NO ligand, $(M - 30)^+$. The most intense ion, however, corresponds to $Cr(O\text{-}i\text{-}Pr)_3NO^+$.

The low-temperature limiting ^1H NMR spectrum is attained below 0 °C in toluene-d_8 at 100 MHz and is shown in Figure 1. There are two septets in the integral ratio 2:1 assignable to terminal and bridging methyne proton resonances, $CH(C\text{-}H_3)_2$, respectively, and three partially overlapping doublets assignable to the isopropyl methyl groups. That there should be *three* doublets is entirely consistent with the fact that $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ maintains the $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ structure in solution: the methyl groups of the terminal O-i-Pr ligands are diastereotopic. When the temperature is raised, the resonances slowly broaden and then coalesce above 80 °C to give a sharp doublet and septet indicative of rapid (NMR time scale) bridge $\rightleftharpoons$ terminal O-i-Pr ligand exchange. This behavior is directly analogous to that reported for $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ which, taken together with the X-ray studies re-

ported in the Experimental Section, indicates that the compounds $M_2(O\text{-}i\text{-}Pr)_6(NO)_2$, where $M = Cr$ and Mo, not only share the same structure but also display a similar dynamic behavior.[11] We conclude that $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ has the structure shown schematically in Figure 2. Each chromium atom is in a trigonal-bipyramidal environment. There is a crystallographically imposed inversion center and the molecule has virtual C_{2h} symmetry. The σ_h plane contains the two chromium atoms, the two bridging oxygen atoms, and the two nitrosyl ligands.

Remarks on Bonding. In all of the compounds of formula $CrL_3(NO)$, where $L = NR_2$ or O-t-Bu, $M_2(OR)_6(NO)_2$, and $M(OR)_3(NO)L$ (e.g., $W(O\text{-}t\text{-}Bu)_3(NO)(py)$), the metal atoms are in either a local trigonal-pyramidal or -bipyramidal ligand field which splits the metal atom's orbitals into three sets: $a(d_{z^2})$, $e(d_{x^2-y^2}, d_{xy})$, and $e(d_{xz}, d_{yz})$. The latter e set is little involved in metal–ligand σ bonding and thus lies lowest in energy. The formal oxidation state of the metal is +2, and, irrespective of the formalism used to count valence electrons, the electronic ground-state configuration is $(d_{xz}, d_{yz})^4$. These four electrons are located in orbitals of the correct symmetry to be involved in metal-to-nitrosyl π^* back-bonding and this they do very well as evidenced by (i) the short M–N distances, (ii) the long N–O distances, and (iii) the relatively low values of $\nu(NO)$ found in the infrared spectra.[12] We previously pointed out that for a series of closely related compounds having linear M–N–O groups, the values of $\nu(NO)$ decrease as metal d–to–NO π^* bonding increases.

Table I lists values of $\nu(NO)$ for a series of compounds of the group 6 transition elements, all of which have trigonal symmetry and provide M $(d_{xz}, d_{yz})^4$-to-NO π^* back-bonding. Three points stand out clearly. (1) The degree of back-bonding increases down the group: W > Mo > Cr. This is readily understood, since the effective nuclear charge exerted on the valence electrons for these metals in formal oxidation state +2 is diminished by the completion of inner shells of electrons. The back-bonding ability of the metals in this +2 oxidation state may be contrasted, however, with that found in the zerovalent state as determined from studies of the degree of metal t_{2g}^6-to-CO π^* back-bonding in $M(CO)_6$ compounds.[13] (2) $\nu(NO)$ is appreciably sensitive to the nature of the ligands in the trigonal plane. Even the small change of going from O-t-Bu to O-i-Pr produces a shift of ca. 12 cm^{-1} in $\nu(NO)$ for both $M = Cr$ and Mo compounds. For the compounds of formula $CrX_3(NO)$, the change in $\nu(NO)$ as a function of X is quite remarkable: cf. 1641 ($X = N\text{-}i\text{-}Pr_2$), 1698 ($X = NSi_2Me_6$), and 1707 cm^{-1} ($X = O\text{-}t\text{-}Bu$). The value of $\nu(NO)$

(9) Intermediates in this alcoholysis reaction such as $Cr(N\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2NO$ have been isolated and are the subject of continuing studies: D. C. Bradley and G. Vuru, research in progress.

(10) In these the Cr^{3+} ion achieves its favored six-coordination. See ref 6.

(11) Tungsten, however, is somewhat different. $W_2(O\text{-}i\text{-}Pr)_6$ ($M\equiv M$) is not known. See ref 4 and M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, and D. Little, *J. Am. Chem. Soc.*, **101**, 2504 (1979).

(12) See table in ref 4 for a correlation of $\nu(NO)$ with M–N and N–O bond distances for compounds containing linear M–N–O groups.

(13) See F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, Chapter 22, Section 5, and references cited therein.

observed in $Cr(O-t-Bu)_2(N-i-Pr_2)(NO)$ is 1683 cm^{-1}, which is close to the weighted average (1685 cm^{-1}) of $Cr(N-i-Pr_2)_3NO$ and $Cr(O-t-Bu)_3NO$. (3) The value of $\nu(NO)$ is least influenced by the ligand in the trans position; indeed, even when it is absent, it does not seem to make any significant difference to this value.

The latter two observations indicate that the relative energies of the metal d_{xz}, d_{yz} atomic orbitals are principally influenced by the three ligands in the trigonal plane and hardly at all by the presence, or lack thereof, of a bond in the trans position. Structurally this is supported by the observation that the in-plane MX_3 bonds are short, while the M–L bond distances trans to the linear M–N–O moiety are long. Compare, for example, Mo–O(average, equatorial) = 1.88 Å with Mo–O(trans to M–NO) = 2.19 Å in $Mo_2(O-i-Pr)_6(NO)_2$. The changes in the values of $\nu(NO)$, which are observed as a function of X, are particularly interesting: $\nu(NO)$ decreases as the electronegativity of X decreases and as its π-donor properties increase. Although it is not possible to separate the σ- and π-donor effects of the ligand on metal d-to-NO π^* bonding, it should be noted that ligand (p)-to-metal (d_{xz}, d_{yz}) π bonding will have the effect of raising the energy of the metal $(d_{xz}, d_{yz})^4$ electrons from a position they would otherwise have had. This in turn will decrease the energy separation between the M $(d_{xy}, d_{yz})^4$ and NO π^* orbitals and thus favor metal-to-ligand back-bonding. This point has been recently emphasized[14] for the $Mo(O-t-Bu)_2(py)_2(CO)_2$ molecule, which shows the lowest average value of $\nu(CO)$ (1838 cm^{-1}) for a pair of cis-carbonyl groups coordinated to a six-coordinate Mo^{2+} center.[15]

$CrMo(O-i-Pr)_6(NO)_2$. In an attempt to gain insight into the mechanism of bridge $\rightleftharpoons$ terminal O-i-Pr group exchange, we sought ways to distinguish between inter- and intramolecular processes and, furthermore, possible catalytic processes. Both $Cr_2(O-i-Pr)_6(NO)_2$ and $Mo_2(O-i-Pr)_6(NO)_2$ show comparable energies of activation for bridge $\rightleftharpoons$ terminal group exchange, and since they are isostructural, we attempted to distinguish between intermolecular and intramolecular processes by mixing equimolar amounts of $Mo_2(O-i-Pr)_6(NO)_2$ and $Cr_2(O-i-Pr)_6(NO)_2$. Formation of $CrMo(O-i-Pr)_6(NO)_2$ would demonstrate the existence of intermolecular processes, while an investigation of the variable-temperature ^1H NMR spectra of a solution containing Cr_2-, CrMo-, and Mo_2-containing species should throw light on the threshold mechanism for bridge $\rightleftharpoons$ terminal O-i-Pr exchange.

Upon dissolving such a mixture in toluene-d_8, we observed a very complex ^1H NMR spectrum consisting of many overlapping septets and doublets. The methyne proton region of the spectrum was investigated by irradiating in the methyl region and spectra were recorded as a function of temperature in the range −10 to +100 °C. The low-temperature limiting spectrum of the methyne proton resonances is shown in Figure 3. There are three downfield resonances marked A, B, and C which correspond to terminal O-i-Pr groups and four upfield resonances D, E, F, and G corresponding to bridging O-i-Pr groups. A and D may be assigned to $Cr_2(O-i-Pr)_6(NO)_2$ and C and G to $Mo_2(O-i-Pr)_6(NO)_2$ on the basis of the chemical shifts of the pure compounds. The signal A is, however, broad, irrespective of the irradiation frequency, and has a disproportionately large integral area. Thus, we believe that the terminal O-i-Pr methyne resonances of the groups bonded to chromium in both Cr_2 and CrMo dimers have virtually the same chemical shift. The resonance B we assign to O-i-Pr
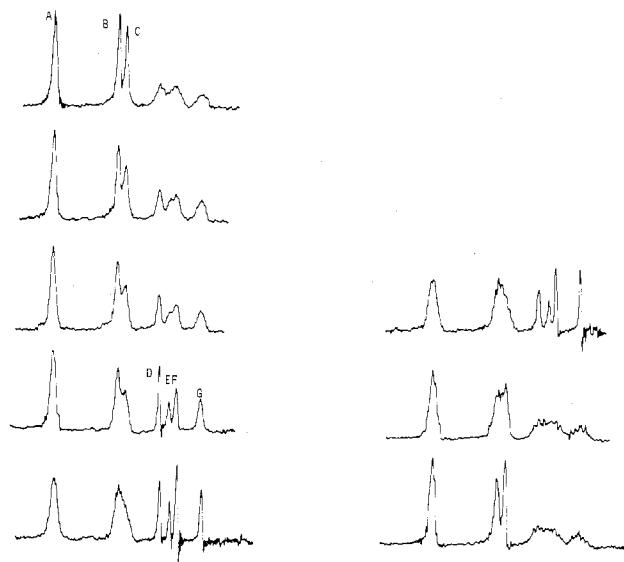
(14) M. H. Chisholm, J. C. Huffman, and R. L. Kelly, *J. Am. Chem. Soc.*, **101**, 7615 (1979).
(15) For values of $\nu(CO)$ in octahedral complexes containing cis-carbonyl ligands coordinated to Mo^{2+} see G. J. J. Chen, R. O. Yelton, and J. W. McDonald, *Inorg. Chim. Acta*, **22**, 249 (1977), and references therein.

Figure 3. Eight low-temperature limiting ^1H NMR spectra (−10 °C, 100 MHz) of the methyne signals of a toluene-d_8 solution containing $Cr_2(O-i-Pr)_6(NO)_2$, $Mo_2(O-i-Pr)_6(NO)_2$, and $CrMo(O-i-Pr)_6(NO)_2$ obtained by irradiating at various frequencies in the range of the methyl signals.

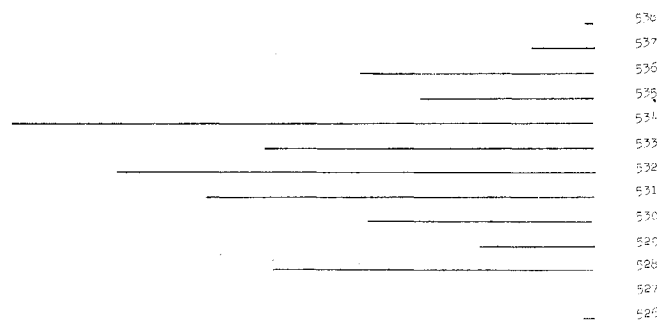**Figure 4.** Isotopic mass distribution observed for the heterodinuclear ion $CrMo(O-i-Pr)_6NO^+$ in the mass spectrum.

groups bonded to molybdenum in $CrMo(O-i-Pr)_6(NO)_2$.

The observation of four bridging $OCH(Me)_2$ resonances is particularly interesting. The signals at D and G may be assigned to homodinuclear compounds $Cr_2(O-i-Pr)_6(NO)_2$ and $Mo_2(O-i-Pr)_6(NO)_2$, respectively, on the basis of chemical shift values. An unambiguous assignment of E and F is not possible—but it should be noted that two bridging O-i-Pr groups are expected for a frozen-out heteronuclear dimer, $CrMo(O-i-Pr)_6(NO)_2$. One O-i-Pr group is axial to Cr and equatorial to Mo and the other is axial to Mo and equatorial to Cr.
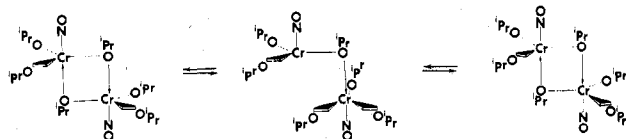
Further evidence for the existence of the heterodinuclear compound is seen in the mass spectrum of the solids obtained upon stripping the solvent of a solution containing $Mo_2(O-i-Pr)_6(NO)_2$ and $Cr_2(O-i-Pr)_6(NO)_2$. In addition to the homonuclear ions $Cr_2(O-i-Pr)_6(NO)_2^+$ and $Mo_2(O-i-Pr)_6(NO)_2^+$, there is a weak heterodinuclear ion $CrMo(O-i-Pr)_6(NO)_2^+$ and a more intense ion corresponding to loss of one nitrosyl ligand, $CrMo(O-i-Pr)_6NO^+$. The m/e isotopic distribution observed for the latter agreed well with that computed from the known isotopic natural abundances of the elements present. This is shown in Figure 4.

In the infrared spectrum (Nujol mull), the bands at 1720 and 1632 cm^{-1}, associated with the Cr_2- and Mo_2-containing dimers, were broadened in the presence of $CrMo(O-i-Pr)_6(NO)_2$, but no new bands were visible. Evidently the substitution of Mo for Cr and vice versa have a relatively small effect on Cr-to-NO and Mo-to-NO back-bonding in the

Scheme I. Proposed Mechanism for Bridge ⇌ Terminal Exchange in $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$

mixed-metal species. This, however, is to be expected on the basis of the arguments of bonding described earlier.

The formation of $CrMo(O\text{-}i\text{-}Pr)_6(NO)_2$ establishes that reaction 1 occurs readily in solution. The mechanism leading

$$Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2 + Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2 \rightleftharpoons$$
$$2CrMo(O\text{-}i\text{-}Pr)_6(NO)_2 \quad (1)$$
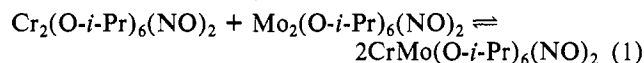
to the formation of $CrMo(O\text{-}i\text{-}Pr)_6(NO)_2$ could be either associative or dissociative and could conceivably be the mechanism leading to bridge ⇌ terminal O-i-Pr exchange. However, we discount the latter possibility since, when the solution containing the equilibrium mixture of homo- and heteronuclear dimers is heated to 100 °C in toluene-d_8, the ^{1}H NMR spectrum reveals three distinct types of O-i-Pr ligands readily assignable to time-averaged bridge ⇌ terminal O-i-Pr groups associated with the Cr_2-, CrMo-, or Mo_2-containing species. We conclude that the mechanism leading to bridge ⇌ terminal O-i-Pr exchange is intramolecular. Further support for this conclusion is seen in the following.

Addition of nitrogen donor ligands, such as pyridine, 2,4-lutidine, and ammonia, readily establishes the equilibrium shown in eq 2. $Mo(O\text{-}i\text{-}Pr)_3(NO)(py)$ has been isolated as

$$M_2(O\text{-}i\text{-}Pr)_6(NO)_2 + 2L \rightleftharpoons 2M(O\text{-}i\text{-}Pr)_3(NO)L \quad (2)$$
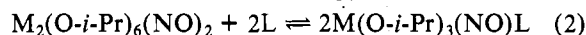
a crystalline compound and is believed to be structurally analogous to $W(O\text{-}t\text{-}Bu)_3(py)(NO)$.[5] The chromium analogues readily lose the nitrogen donor ligands and only $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ has ever been crystallized from solutions containing an excess of L.

Variable-temperature ^{1}H NMR studies of $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ in toluene-d_8 in the presence of varying concentrations of L reveal interesting mechanistic information.

1. The equilibrium shown in eq 2 is slow on the ^{1}H NMR time scale. Thus the spectra obtained are merely a superimposition of the signals associated with $Cr(O\text{-}i\text{-}Pr)_3(NO)L$ and $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$, and the rate of bridge ⇌ terminal O-i-Pr exchange is not at all influenced by added L.

2. In contrast to the above, there is a rapid (^{1}H NMR time scale) exchange between free and coordinated L of the type indicated by eq 3. See Figure 5.

$$Cr(O\text{-}i\text{-}Pr)_3(NO)L + L' \rightleftharpoons Cr(O\text{-}i\text{-}Pr)_3(NO)L' + L \quad (3)$$
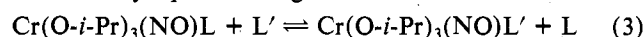
3. Studies of the latter exchange reaction reveal that for [Cr]:[L] concentration ratios within the range 6:1 to 1:6, the rate of exchange of free and coordinated L is not principally[16] determined by the concentration of free L but rather is dependent on the concentration of $Cr(O\text{-}i\text{-}Pr)_3(NO)L$. This is consistent with a rate-determining step involving dissociation of L as shown in eq 4.

$$Cr(O\text{-}i\text{-}Pr)_3(NO)(L) \xrightarrow{\text{rds}} Cr(O\text{-}i\text{-}Pr)_3(NO) + L \quad (4a)$$

$$Cr(O\text{-}i\text{-}Pr)_3(NO) + L' \xrightarrow{\text{fast}} Cr(O\text{-}i\text{-}Pr)_3(NO)(L') \quad (4b)$$

Thus a very plausible mechanism for bridge ⇌ terminal O-i-Pr exchange in $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ is implicated, namely,

Figure 5. ^{1}H NMR spectra, recorded at −40 (bottom), −20 (center), and +40 °C (top) and 270 MHz, of the equilibrium mixture formed upon adding 2 equiv of 2,4-lutidine to $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ in toluene-d_8. In the spectrum at −40 °C, the signals of coordinated 2,4-lutidine are labeled A, B, and C; those of free lutidine are marked A', B', and C'. The signals marked with an asterisk are those corresponding to $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$. The only other signals are due to the usual proton impurities in toluene-d_8, namely, the three aromatic resonances at δ ca. 7 and the methyl proton at δ 2.09. At −20 °C exchange between free and coordinated lutidine is fast enough to cause a single but still broad resonance for each of the three types of lutidine protons. The signals arising from $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ are not affected by this exchange, and bridge ⇌ terminal O-i-Pr exchange is frozen out. At +40 °C exchange between free and coordinated lutidine is fast, leading to three sharp signals, while bridge ⇌ terminal O-i-Pr exchange in $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ is now occurring sufficiently rapidly to cause broadening of the O-i-Pr resonances. The methyne proton resonances of terminal O-i-Pr ligands in $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ and $Cr(O\text{-}i\text{-}Pr)_3(NO)(\text{lutidine})$ are accidentally degenerate.

rupture of one of the long axial O-i-Pr bridges (the group trans to the nitrosyl ligand) followed by re-formation of the axial O-i-Pr bridge as shown in Scheme I. This mechanism involves the formation of a reactive four-coordinate chromium species, $Cr(O\text{-}i\text{-}Pr)_3(NO)$. Bulky alkoxy groups would be expected to stabilize the four-coordinate chromium species relative to the dimer, and, consistent with this view, changing O-i-Pr for O-t-Bu leads to the isolation of a monomer, $Cr(O\text{-}t\text{-}Bu)_3(NO)$. Conversely, decreasing the size of the alkoxy ligands or increasing the size of the metal would be expected to favor the formation of six-coordinate species. Recently we have isolated and characterized $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$ which is formed by addition of dimethylamine to $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ and contains six-coordinate molybdenum atoms.[17]

Experimental Section

General procedures involved the use of Schlenk techniques and a Vacuum Atmospheres Co. Dri-Lab system for the manipulation of the air-sensitive materials in this work. All solvents and atmospheres were dried and deoxygenated.

The following chemicals were purchased from commercial sources: diisopropylamine, *tert*-butyl alcohol, and isopropyl alcohol from BDH; anhydrous chromium trichloride (sublimed) from Alfa Inorganics; and *n*-butyllithium (hexane solutions) from both Alfa and Metallgesellschaft AG, Frankfurt, Germany.

Lithium dialkylamides were prepared by the addition of the dried amine to the hydrocarbon solution of butyllithium.

Elemental analyses were obtained from A. Bernhardt, Engelskirchen, Germany.

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(16) Though the concentrations of $Cr(O\text{-}i\text{-}Pr)_3(NO)L$ and $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ are influenced by added [L], the exchange between free and coordinated L in eq 3 is always frozen out on the NMR time scale at −40 °C and below. The latter observation is not influenced by [L] within the concentration range of these studies.

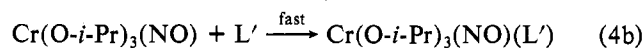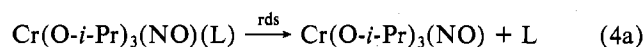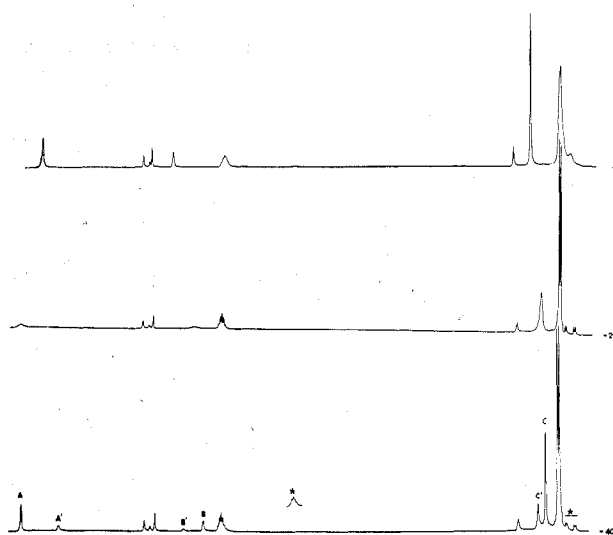(17) M. H. Chisholm, J. C. Huffman, and R. L. Kelly, *Inorg. Chem.*, **19**, 2762 (1980).

Molecular weight determinations were carried out by cryoscopic methods in an all-glass system and under an inert atmosphere using electrical circuits similar to those described elsewhere.[18]

Infrared spectra were obtained routinely by using Nujol mulls and CsI plates and Perkin-Elmer 337 or 287 spectrophotometers.

¹H NMR spectra were obtained on Varian HA and XL-100 and Bruker HX 270-MHz spectrometers with variable-temperature capabilities. Temperatures were calibrated with use of methyl alcohol (low temperatures) and ethylene glycol (high temperatures).

Mass spectra were obtained on an AEI MS902 by the method of direct insertion.

Preparation of Tris(diisopropylamido)nitrosylchromium. Purified nitric oxide was bubbled through a pentane (100 mL) solution of tris(diisopropylamido)chromium (6.6 g). The brown solution became red-orange, and red-orange crystals precipitated. The reaction was slightly exothermic. At completion of the reaction (no further color change), the solvent was distilled off under reduced pressure (50 °C (10⁻² mmHg)). Remaining was 7.1 g of orange-red crystals. These crystals were recrystallized from 60 mL of boiling cyclohexane. Cooling to 20 °C and filtration gave Cr(N-*i*-Pr₂)₃NO (3.4 g) as shiny bronze crystals. Anal. Calcd: Cr, 13.61; C, 56.55; H, 11.07; N, 14.66. Found: Cr, 13.59; C, 55.20; H, 10.96; N, 14.59. A cryoscopic determination of molecular weight in benzene gave $M_r = 371 \pm 16$ (required for ONCr(N-*i*-Pr₂)₃ $M_r = 382.56$).

This compound gave a strong molecular ion, $m/e(^{52}Cr) = 382$, in the mass spectrum at 140 °C (5 × 10⁻⁷ mmHg). The ¹H NMR spectrum was temperature independent in toluene-d_8 in the range +30 to −60 °C and showed a doublet, $\delta(CH_3)$ 1.26, and a septet, $\delta(CH)$ 3.46, in the expected integral ratio 6:1, respectively; $J_{HH} = 6.2$ Hz (δ relative to Me₄Si). IR data (Nujol mull): 449 (m), 532 (w), 575 (m), 624 (w), 689 (w), 828 (m), 864 (w), 932 (m, sh), 940 (m), 1005 (w), 1103 (s), 1125 (w), 1158 (m), 1198 (m), 1296 (w), 1342 (m), 1358 (m), 1374, 1641 cm⁻¹.

Preparation of Tri-*tert*-butoxynitrosylchromium. Cr(N-*i*-Pr₂)₃(NO) (5.2 g) was heated to reflux in *tert*-butyl alcohol (70 mL) for 30 h. The amido compound is not very soluble in *tert*-butyl alcohol and dissolved with reaction. After 30 h the solvent was stripped, yielding a red solid which was purified by sublimation (40 °C (10⁻³ cmHg)) and yielded Cr(O-*t*-Bu)₃(NO) (3.2 g, 78% yield based on Cr) as a red solid, mp 62–63 °C. Anal. Calcd: Cr, 17.3; C, 48.0; H, 9.06; N, 4.66. Found: Cr, 17.2; C, 4.79; H, 8.93; N, 4.51.

¹H NMR data recorded in benzene (10–50 °C): $\delta(CH_3)$ 1.50 (relative to Me₄Si).

IR data obtained from a Nujol mull between KBr plates: 484 (w, br), 572 (w), 588 (w), 628 (m), 709 (m), 793 (s), 912 (m, sh), 932 (s, sh), 953 (vs), 1027 (w), 1158 (s), 1239 (m), 1263 (w), 1372 (s), 1707 (s) cm⁻¹.

A cryoscopic molecular weight determination in benzene gave $M_r = 307 \pm 12$ (calculated for Cr(O-*t*-Bu)₃(NO) $M_r = 301.4$).

Preparation of Hexaisopropoxydinitrosyldichromium. Cr(N-*i*-Pr₂)₃(NO) (5.3 g) was added to isopropyl alcohol (60 mL). There was a mild heat of reaction as the solution turned from dark brown to orange-red. The solution was heated to reflux for 10 min and then the isopropyl alcohol was stripped, yielding an orange-red solid which was sublimed at 90 °C (10⁻⁴ cmHg); yield 3.1 g (86% based on Cr).

Anal. Calcd: Cr, 20.1; C, 41.7; H, 8.16; N, 5.4. Found: Cr, 19.9; C, 41.5; H, 7.99; N, 5.1.

A cryoscopic molecular weight determination in benzene gave $M_r = 456 \pm 38$ (calculated for Cr₂(O-*i*-Pr)₆(NO)₂ $M_r = 518.6$).

¹H NMR data obtained in toluene-d_8: at +100 °C, $\delta(CH)$ 5.72, $\delta(CH_3)$ 1.44; at −5 °C, $\delta(CH)$ 6.00 (terminal) and 5.08 (bridging), $J_{HH} = 6.5$ Hz.

IR data obtained from a Nujol mull between KBr plates: 470 (vw), 488 (m), 592 (vw, sh), 638 (vs, br), 675 (vs), 840 (s), 853 (s), 953 (vs, sh), 971 (vs), 1078 (m, sh), 1109 (vs), 1120 (m, sh), 1135 (m, sh), 1068 (m), 1322 (s), 1370 (s), 1390 (s), 1720 (vs) cm⁻¹.

Cr₂(O-*i*-Pr)₆(NO)₂ + Nitrogen Donor Ligands. All attempts to isolate crystalline Cr(O-*i*-Pr)₃(NO)L compounds, where L = ammonia, pyridine, and 2,4-lutidine, by the addition of excess free ligand to a hydrocarbon solution of Cr₂(O-*i*-Pr)₆(NO)₂, failed; only Cr₂(O-*i*-Pr)₆(NO)₂ crystallized from such solutions as the solvent was removed.

¹H NMR studies of the reaction Cr₂(O-*i*-Pr)₆(NO)₂ + 2L ⇌ Cr(O-*i*-Pr)₃(NO)L were carried out by preparing the solutions in the Dri-Lab system. All NMR tubes were ultimately sealed under a partial vacuum.

X-ray Crystallography. A great many crystals of Cr₂(O-*i*-Pr)₆(NO)₂ were mounted in capillaries filled with epoxy resin. Crystals so mounted were stored for periods as long as 2 weeks with no noticeable decomposition. However, all crystals began to decay immediately when exposed to X-ray radiation. The majority of the crystals displayed counting intensity changes of 10–25% during the alignment procedure alone. After several hours of irradiation, the crystals had changed color, from dark orange to pale lime green. For several crystals, the decay process seemed slow enough that data collection was commenced. However, in all cases, after 7–20 h of exposure to radiation, the crystals had decomposed to the extent that they were no longer suitable. It was then decided to attempt to obtain a data set by combining the data from several crystals, with proper scaling ratios. However, from that point on, no further crystals were found that were suitable; all displayed pronounced decay after less than 2 h of irradiation.

The best data set obtained was for a large crystal, approximately 0.5 × 0.5 × 0.3 mm. The unit cell was determined, and data were collected on a Syntex P1̄ four-circle automated diffractometer. Cell constants as determined from the least-squares fit of 15 reflections in the range 10° < 2θ < 25° were $a = 10.685$ (7) Å, $b = 15.727$ (11) Å, $c = 9.805$ (5) Å, $\alpha = 90.29$ (5)°, $\beta = 116.59$ (4)°, $\gamma = 84.48$ (5)°, and $V = 1465$ Å³, which are quite similar to those of molybdenum compounds with the same formula.[3] The space group is P1̄ (No. 2) with $Z = 2$. Data were collected with the use of a variable-scan technique with speeds from 4° to 24° min⁻¹ and a scan range from 0.9° below Kα₁ to 0.9° above Kα₂. Reflections determined to be weak during the prescan were omitted entirely. Other procedures used were as previously described.[19] Three standard reflections were collected after every 97 reflections and displayed a steady drop in intensity. At the end of data collection, the intensities of the standards were less than 20% of their original values. A total of 1842 unique data were collected, of which only 683 were greater than 1 esd. This amount of data is insufficient for a complete structure determination. However, to ensure that the chromium compound is truly isostructural with the analogous molybdenum compound, we used the atomic positions for the molybdenum compound as initial parameters for three cycles of least-squares refinement employing the decay-corrected data. All atoms refined satisfactorily with the discrepancy indices falling to

$$R_1 = \sum ||F_o| - |F_c||/\sum |F_o| = 0.126$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.158$$

No attempt was made to continue the refinement because of the poor quality and quantity of the data.

(18) M. W. Extine, Ph.D. Thesis, Princeton University, 1976.

(19) A. Bino and F. A. Cotton, *Inorg. Chem.*, **18**, 1381 (1979).