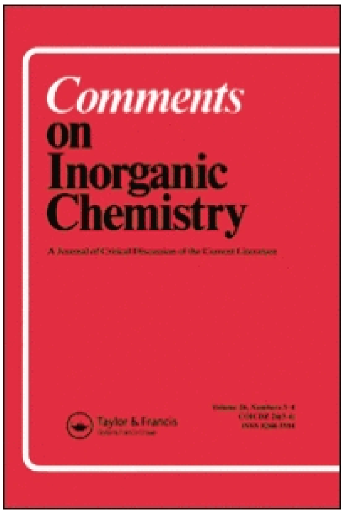

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Nitrosyl N-O Bond Cleavage During Reactions of Organometallic Nitrosyl Complexes of the Group 6 Elements

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To cite this Article Legzdins, Peter and Young, Michelle A.(1995) 'Nitrosyl N-O Bond Cleavage During Reactions of Organometallic Nitrosyl Complexes of the Group 6 Elements', Comments on Inorganic Chemistry, 17: 4, 239 — 254
To link to this Article: DOI: 10.1080/02603599508033859
URL: http://dx.doi.org/10.1080/02603599508033859

Nitrosyl N–O Bond Cleavage During Reactions of Organometallic Nitrosyl Complexes of the Group 6 Elements

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Received January 19, 1995

The nitrosyl ligands in organotransition-metal nitrosyl complexes usually stay intact during chemical transformations of these complexes. However, our continuing study of the characteristic reactivity of Group 6 organometallic nitrosyl complexes has recently revealed a number of new product complexes which result from N–O bond cleavage of the nitrosyl groups in the reactants. The various reactions and reaction conditions during which these complexes undergo facile nitrosyl N–O bond dissociation are summarized, and mechanistic ideas as to why these bond cleavages occur are also presented.

Key Words: *nitrosyl, nitrosyl bond cleavage, coordinatively unsaturated, bridging nitrosyl, Group 6*

Abbreviations Used: Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5), Cp′ (Cp* or Cp), R (alkyl or aryl), M (Mo or W), Me (CH_3), neopentyl (CH_2CMe_3), neophyl (CH_2CMe_2Ph), THF (tetrahydrofuran), Et_2O (diethyl ether), mes (2,4,6-$C_6H_2Me_3$), *o*-tolyl (2-Me-C_6H_4), *p*-tolyl (4-Me-C_6H_4), ESR (electron spin resonance), UV (ultraviolet; in electronic spectroscopy), VIS (visible, in electronic spectroscopy), k_{obs} (observed rate constant), $\Delta H\ddagger$ (enthalpy of activation), $\Delta S\ddagger$ (entropy of activation), NMR (nuclear magnetic resonance).

Comments Inorg. Chem.
1995, Vol. 17, No. 4, pp. 239–254
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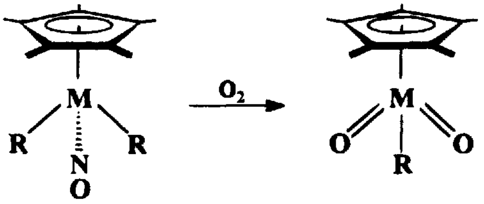
INTRODUCTION

Cleavage of the N–O bond in bound nitric oxide is both of fundamental significance in inorganic chemistry and of relevance to biological and environmental chemistry.[1] Such NO activation has been reported to occur in the gas-phase ion chemistry of metal clusters[2] as well as during their transformations in the condensed phase.[3] The degradation of the dinitrosyl complex $CpCr(NO)_2Cl$ monitored by mass spectroscopy has revealed fragmentation patterns consistent with nitrosyl N–O bond cleavage.[4] More recently, tandem mass spectrometry has demonstrated that $Cp_2Fe_2(NO)^+$ undergoes N–O bond cleavage, the resulting fragments being pyridine and $CpFe_2O^+$.[5] There have also been reports of the Lewis-acid induced conversion of terminal nitrosyl ligands into terminal oxo and nitrido groups.[6] Although nitrosyl metal cluster complexes have been shown to undergo dissociation of nitrosyl N–O bonds to afford nitrido clusters,[7] there is a scarcity of reports in the literature concerning monomeric or dimeric nitrosyl organometallic systems undergoing similar nitrosyl N–O bond-dissociation processes.

The principal focus of our research during the past few years has been the development of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten as unique synthetic reagents.[8] We have generally found during these studies that the nitrosyl ligand remains intact during various reactions involving these compounds, the utility of the nitrosyl group being its ability to regulate electron density at the metal center due to its strong π-acidity.[9] Recently we have encountered a new type of reactivity which involves nitrosyl N–O bond cleavage under a variety of mild conditions. This article focuses on those reactions of Group 6 organometallic nitrosyl complexes that result in nitrosyl N–O bond dissociation. Since the reaction conditions that prompt these cleavage reactions are variable and differ from metal to metal, each system is discussed separately. Then, the insights concerning bound N–O bond-dissociation processes provided by this work are collected at the end of the article.

1. THE REACTIVITY OF $Cp'M(NO)R_2$ COMPLEXES WITH MOLECULAR OXYGEN

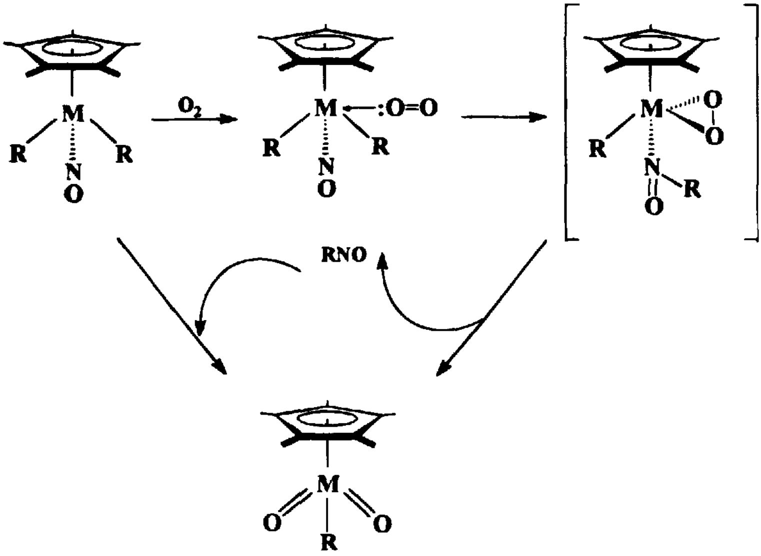
Treatment of solutions of the 16-valence-electron dialkyl or diaryl compounds, $Cp'M(NO)R_2$, with an excess of dioxygen at ambient temperatures and pressures produces alkyl or aryl dioxo complexes, $Cp'M(O)_2R$, which can be isolated in moderate yields (Eq. (1)).[10]



(1)

R = alkyl, aryl; M = Mo, W

The results of labeling studies with $^{18}O_2$ are consistent with the first steps of the reaction involving coordination of dioxygen to the metal center to form a simple 1:1 Lewis acid-base adduct. As shown in Scheme 1, migratory insertion of the bound nitrosyl group into



R = alkyl, aryl; M = Mo, W

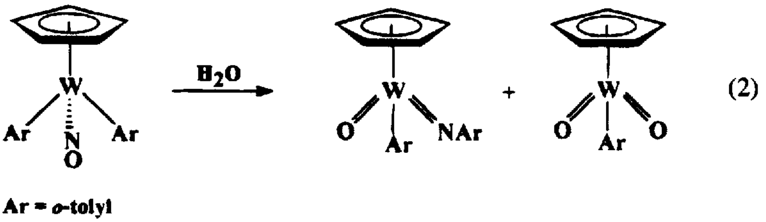
SCHEME 1

one of the W–C σ bonds would result in a peroxo alkyl- or aryl-nitroso complex. This complex could then expel the nitroso-alkane or -arene from the metal's coordination sphere in the final step and rearrange concomitantly to the final alkyl or aryl dioxo product. Unfortunately, no nitroso-containing byproducts have been detected during these conversions. However, this observation does not mean that they are not formed, since it is known that nitrosoalkanes do not persist for very long in solution given their potent oxidizing abilities.[11] For instance, we have established independently that PhNO in Et_2O consumes $Cp'W(NO)R_2$ complexes completely even at −60°C to produce $Cp'W(O)_2R$ as well as other products whose identities remain to be ascertained. In other words, nitroso-alkanes or -arenes produced during these reactions would be capable of functioning as an additional oxidant for these transformations, at least to some extent.

Although this reactivity does not involve nitrosyl N–O bond cleavage per se, it was our first experience with the nitrosyl ligand not remaining intact during our studies of the 16-valence-electron $Cp'M(NO)R_2$ systems. During the reactions summarized by Eq. (1), the nitrosyl ligand is lost in the form of a nitroso-alkane or -arene, and the oxo ligands in the organometallic product are derived from molecular oxygen. In this connection it may be noted that there has been a report of oxo ligands being derived intermolecularly from an external source of nitric oxide,[12] but the mechanism of this conversion is unclear.

2. TREATMENT OF $CpW(NO)(o\text{-tolyl})_2$ WITH WATER

When a solid sample of the purple diaryl complex, $CpW(NO)(o\text{-tolyl})_2$, is exposed to deaerated water vapor for 5 min at ambient temperatures, the sample becomes an oily, brown solid. Workup produces a yellow product, $CpW(O)(N\text{-}o\text{-tolyl})(o\text{-tolyl})$, as well as the aryl dioxo compound, $CpW(NO)(o\text{-tolyl})(O)_2$ (Eq. (2)).[13]



(2)

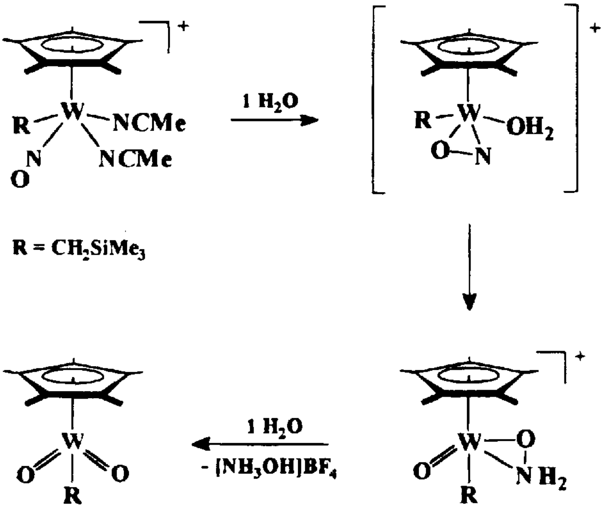
This novel isomerisation of a 16-valence-electron diaryl nitrosyl compound to a thermodynamically more stable 18-valence-electron oxo arylimido complex represents the first nitrosyl N–O bond cleavage reaction observed in our laboratories. Curiously, no dialkyl or diaryl complexes other than CpW(NO)(*o*-tolyl)$_2$ have been found to undergo this isomerization to their imido oxo analogues upon treatment with water. If CpW(NO)(*o*-tolyl)$_2$ is treated with ^{18}OH$_2$, the label is incorporated only into the dioxo product, CpW(NO)(O)$_2$·(*o*-tolyl). It thus appears that this isomerization occurs intramolecularly with the oxo and imido ligands having their origins in the initial nitrosyl ligand and that the dioxo aryl and arylimido oxo complexes are formed from CpW(NO)(*o*-tolyl)$_2$ via independent pathways.

This isomerization may proceed initially by the intramolecular insertion of the NO ligand into the tungsten–aryl bond. Although insertions of CO into metal–alkyl or–aryl bonds are far more common, there have been documented cases of NO ligand insertions into metal–alkyl bonds.[14] Ultimately, this isomerization reaction is thermodynamically driven by the propensity of tungsten to form strong multiple bonds with oxygen and nitrogen.[15]

3. REACTION OF [Cp*W(NO)(CH$_2$SiMe$_3$)(NCMe)$_2$]BF$_4$ WITH WATER

Treatment of either MeCN or CH$_2$Cl$_2$ solutions of [Cp*W(NO)·(CH$_2$SiMe$_3$)(NCMe)$_2$]BF$_4$ with one equivalent of water at room temperature results in the production of the intermediate complex,

$[Cp^*W(O)(\eta^2\text{-}NH_2O)(CH_2SiMe_3)]BF_4$ in 78% isolated yield. This hydroxylamido-containing cation reacts with a second equivalent of water to produce the dioxo alkyl complex, $Cp^*W(O)_2(CH_2SiMe_3)$, thereby completing the hydrolysis of the original nitrosyl ligand (Eq. (3))[16]

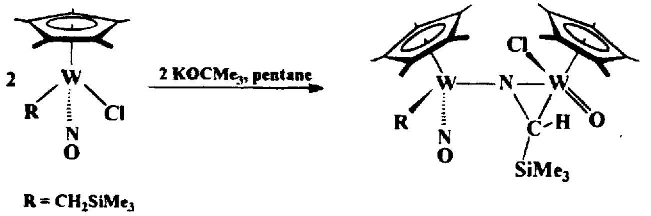


(3)

Reaction 3 represents the first observed stepwise hydrolysis of a nitrosyl ligand. In this reaction water probably functions as a Lewis base and initially displaces both acetonitrile ligands from the organometallic cation in a manner analogous to that observed with PMe_3.[16] This is then followed by hydrogen-atom transfer from the coordinated water to the nitrosyl nitrogen atom, a process that may be facilitated by the nitrosyl ligand adopting an η^2-mode of coordination to the electronically unsaturated tungsten center. Consistent with this mechanism is the fact that reaction of $[Cp^*W(NO)(CH_2SiMe_3)(NCMe)_2]BF_4$ with $^{18}OH_2$ yields $[Cp^*W(^{18}O)(\eta^2\text{-}NH_2O)(CH_2SiMe_3)]BF_4$. Other cationic aquo nitrosyl complexes of later transition metals do not undergo similar transformations,[17] probably due to the fact that these metal centers are not as oxophilic.

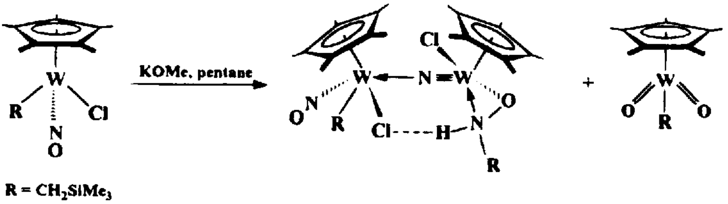
4. REACTION OF Cp*W(NO)(CH$_2$SiMe$_3$)Cl WITH EITHER KOCMe$_3$ OR KOMe IN PENTANE

The bimetallic compound, [Cp*W(NO)(CH$_2$SiMe$_3$)][Cp*W(Cl)·(O)]-(μ_2-η^1:η^2-NC{H}SiMe$_3$), is produced in low yield by the heterogeneous reaction between Cp*W(NO)(CH$_2$SiMe$_3$)Cl and KOCMe$_3$ in pentane (Eq. (4)).[18]



(4)

However, when this reaction is performed in THF or Et$_2$O, the expected metathesis product, Cp*W(NO)(CH$_2$SiMe$_3$)(OCMe$_3$), is obtained rather than the bimetallic complex shown in Eq. (4). When Cp*W(NO)(CH$_2$SiMe$_3$)Cl is treated with KOMe in pentane, another bimetallic compound, [Cp*W(NO)(CH$_2$SiMe$_3$)Cl][Cp*W(Cl)(η^2-NO{N}CH$_2$SiMe$_3$)](μ-N), as well as the dioxo alkyl complex, Cp*W(NO)(O)$_2$(CH$_2$SiMe$_3$), are produced (Eq. (5)).[18] Similarly, the expected alkyl alkoxide product, Cp*W(NO)(CH$_2$SiMe$_3$)(OMe), is produced when the reaction is effected in THF or Et$_2$O.

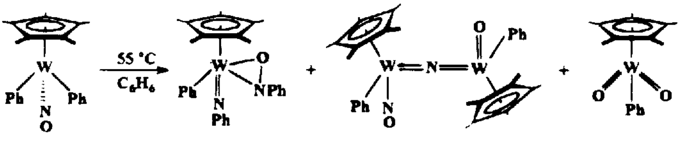


(5)

The role of KOCMe$_3$ or KOMe in the latter two conversions is unclear. It may be noted, however, that when the reactions are performed using the Li or Na alkoxide salts, the expected metatheses products, namely the alkyl alkoxide complexes, are indeed produced. Similarly, the reactions appear to be solvent dependent since the bimetallic species are only produced when the reactions are performed in pentane. The transformation depicted in Eq. (4) probably proceeds via initial deprotonation of the starting material by the butoxide anion, but the detailed reaction mechanisms of the transformations presented in Eqs. (4) and (5) are currently unknown.

5. THERMOLYSIS OF Cp*W(NO)Ph_2

Thermolysis of the diphenyl complex, Cp*W(NO)Ph_2, in benzene at 55°C affords three isolable products as shown in Eq. (6).[19]



(6)

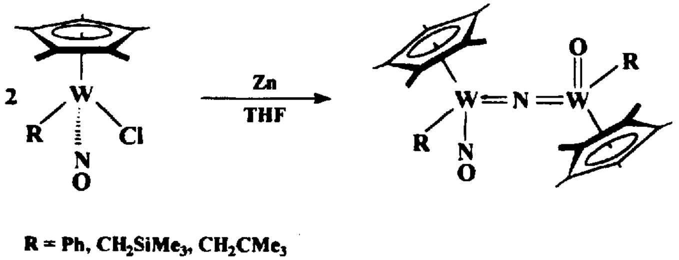
Each of these products formally results from nitrosyl N–O bond cleavage. They are probably formed via an initial M–C bond homolysis in the original reactant which results in the formation of the reactive transient radical, Cp*W(NO)Ph. This event is then followed by subsequent intramolecular rearrangement and trapping. Evidence for the formation of this radical comes from the fact that when this thermolysis is performed in the presence of PhSSPh, the aryl sulfide complex, Cp*W(NO)(Ph)(SPh), is formed quantitatively.

Oxo nitrido bimetallic complexes of the the type [Cp*W(NO)(R)](μ-N)[Cp*W(O)(R)] shown in Eq. (6) have also been prepared by the zinc reduction of Cp*W(NO)(R)Cl (vide infra). These reactions are also viewed as proceeding via the initial generation of Cp*W(NO)(R) radicals. If any PhNO is generated during the thermolysis of Cp*W(NO)Ph_2, it would quickly react with the starting diaryl complex to produce the dioxo aryl compound, Cp*W$(O)_2$Ph (vide supra). How the third product in this thermolysis reaction, namely Cp*W(Ph)(η^2-ONPh)(NPh), is formed remains a mystery. However, it appears that NO has inserted into one of the W–Ph bonds with the resulting PhNO ligand being attached to the tungsten center in a dihapto fashion in order to satisfy the metal's electronic requirements.

During the thermolysis of the valence-isoelectronic zirconium analogue, Cp_2ZrPh_2, the benzyne complex $Cp_2Zr(\eta^2\text{-}C_6H_4)$ is formed.[20] We have no evidence of nitrosyl benzyne complexes being formed during the thermolysis of $Cp^*W(NO)Ph_2$.

6. REDUCTION OF Cp*W(NO)(R)Cl WITH ZINC

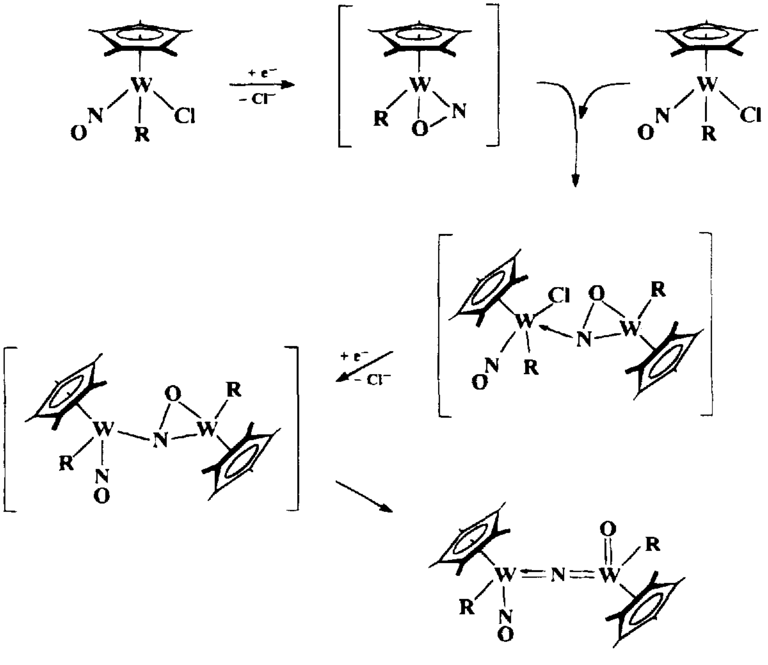
The reduction of $Cp^*W(NO)(R)Cl$ ($R = CH_2SiMe_3, CH_2CMe_3, Ph$) with an excess of zinc powder in THF results in the formation of the bimetallic oxo nitrido complexes, $[Cp^*W(NO)(R)](\mu\text{-}N)[Cp^*W(O)(R)]$, which are isolable in good yields (Eq. (7)).[21]



(7)

A plausible mechanism that accounts for the formation of this bimetallic tungsten complex is presented in Scheme 2. Initial reduction of $Cp^*W(NO)(R)Cl$ by zinc results in the formation of the corresponding anion which subsequently expels Cl^- to form the $Cp^*W(NO)(R)$ radical which may or may not have the nitrosyl ligand coordinated in a η^2-fashion to the electron-deficient metal center. This radical could then combine with another equivalent of starting material in a Lewis acid-base manner to form a bimetallic intermediate. Reduction followed by subsequent rearrangement would form the final product. The key feature of this mechanism is that it is the complex which is reduced first that undergoes subsequent nitrosyl N–O bond cleavage. Consequently, the reduction of a 2:1 mixture of

$Cp^*W(NO)(CH_2CMe_3)Cl$ and $Cp^*W(NO)Cl_2$ in THF with elemental zinc affords $[Cp^*W(NO)(CH_2CMe_3)](\mu\text{-}N)[Cp^*W(O)(Cl)]$ as brown crystals. This is as expected since it has been previously established that $Cp^*W(NO)Cl_2$ is more easily reduced than $Cp^*W(NO)(CH_2 \cdot CMe_3)Cl$.[22] Thus, the formation of $[Cp^*W(NO)(CH_2CMe_3)] \cdot (\mu\text{-}N)$ $[Cp^*W(O)(Cl)]$ proceeds via attack of the transient $Cp^*W(\eta^2\text{-}NO)Cl$ on the excess $Cp^*W(NO)(CH_2CMe_3)Cl$.

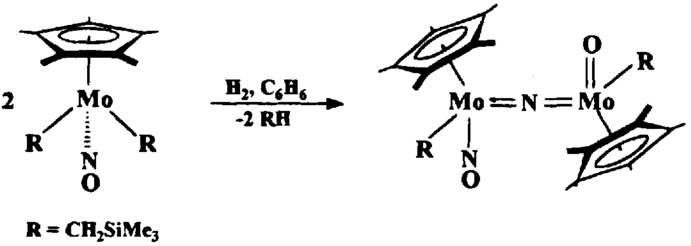


R = CH_2CMe_3, CH_2SiMe_3, Ph

SCHEME 2

7. REACTION OF $Cp^*Mo(NO)R_2$ WITH MOLECULAR HYDROGEN

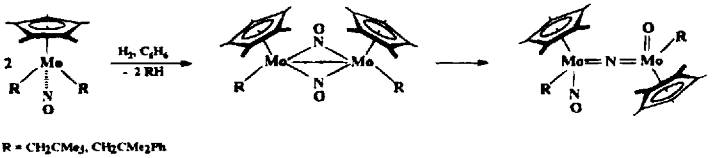
When a benzene solution of $Cp^*Mo(NO)(CH_2SiMe_3)_2$ is reacted with 1 atm of molecular hydrogen for 20 min, the oxo nitrido bimetallic species, [Cp*Mo(NO)(CH_2CMe_3)](μ-N)[Cp*Mo(O)(CH_2CMe_3)] can be isolated from the final reaction mixture (Eq. (8)).[28] This bimetallic complex is analogous to the tungsten congeners prepared from the zinc reduction of the alkyl chloride precursors (vide supra).



(8)

When the alkyl group of the starting dialkyl precusor is changed to either the neopentyl or neophyl group, an intermediate bridging nitrosyl complex, [Cp*Mo(R)$]_2$(μ-NO$)_2$, can be isolated.[23] The solid-state structure of [Cp*Mo(CH_2CMe_3)$]_2$(μ-NO$)_2$ has been established by X-ray crystallography. The most chemically interesting features of the molecular structure are its cis geometry and its symmetrical Mo(μ-NO$)_2$Mo bridging system whose intramolecular dimensions resemble those extant in [CpCr(NO)$]_2$(μ-NO$)_2$,[24] (CpFe$)_2$(μ-NO$)_2$,[25] and (CpCo$)_2$(μ-NO$)_2$.[26] In particular, the Mo–Mo separation of 2.5930 (7) Å is indicative of the existence of a relatively short single metal–metal bond.[27] Each metal center may thus be viewed as having a formal 16-valence-electron configuration. Interestingly, [Cp*Mo (CH_2CMe_3)$]_2$(μ-NO$)_2$ does not form adducts with simple Lewis bases such as phosphines or pyridine.

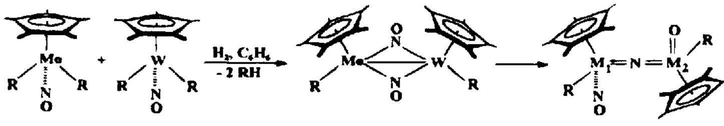
Solutions of this bimetallic bridging nitrosyl complex then isomerize over the course of two hours at room temperature to the bimetallic bridging oxo nitrido complexes, [Cp*Mo(NO)(R)](μ-N) [Cp*Mo(O)(R)] as shown in Eq. (9).



(9)

These isomerizations involve the conversion of bridging nitrosyl ligands to their oxo and nitrido constituents. The isomerization depicted in Eq. (9) is an intramolecular process since an equimolar mixture of [Cp*Mo(CH$_2$CMe$_3$)]$_2$(μ-NO)$_2$ and [Cp*Mo(CH$_2$CMe$_2$Ph)]$_2$(μ-NO)$_2$ converts cleanly to an equimolar mixture of [Cp*Mo(NO)(CH$_2$CMe$_3$)](μ-N)[Cp*Mo(O)(CH$_2$CMe$_3$)] and [Cp*Mo(NO)(CH$_2$CMe$_2$Ph)](μ-N)[Cp*Mo(O)(CH$_2$CMe$_2$Ph)]. Consistently, a kinetic analysis of the isomerization of the neophyl system in toluene by UV-Vis spectroscopy has established that the isomerization is first order over the temperature range 23–50°C with k_{obs} (23°C) $= 3.7 \pm 0.8 \times 10^{-5}$ s^{-1}, $\Delta H\ddagger = 61 \pm 12$ kJ/mol and $\Delta S\ddagger = -124 \pm 38$ J/mol (-29 ± 8 cal/mol K). A related fragmentation of a CO ligand occurs during thermolysis of [(silox)$_2$WCl(CO)$_2$]$_2$ which affords the oxo-μ-carbido complex, (silox)$_2$(O)W = C = WCl$_2$(silox)$_2$.[28]

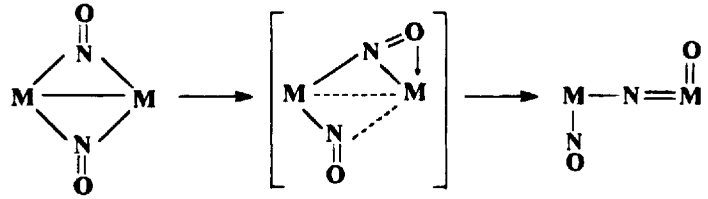
Hydrogenation of a mixture of Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$ and Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ results in the formation of a heterobimetallic species, [Cp*Mo(CH$_2$SiMe$_3$)](μ-NO)$_2$[Cp*W(CH$_2$SiMe$_3$)], which similary isomerizes in solution to a 60:40 mixture of [Cp*M$_1$(NO)(CH$_2$SiMe$_3$)](μ-N)[Cp*M$_2$(O)(CH$_2$SiMe$_3$)] (60% M$_1$ = W, 40% M$_1$ = Mo) (Eq. (10)). An X-ray analysis has confirmed that both structural isomers are present in the unit cell.



(10)

A plausible mechanism for the first steps in the conversions shown in Eqs. (9) and (10) involves initial formation of Cp*Mo(NO)(R)H which could then combine with the original Cp*M(NO)R$_2$ reactants with concomitant loss of RH to afford the bimetallic bridging products. The M(μ-NO)$_2$M bridging systems in these products could then cleave in the manner depicted below to form the final nitrido-bridged complexes, the thermodynamic driving force of the isomerization being the formation of a strong M = O bond as well as a strong M = N–M linkage.[15] The greater oxophilicity of Mo results in the Mo

= O-containing isomer of $[Cp^*M_1(NO)(CH_2SiMe_3)](\mu\text{-}N)[Cp^*M_2(O)(CH_2SiMe_3)]$ being formed preferentially.

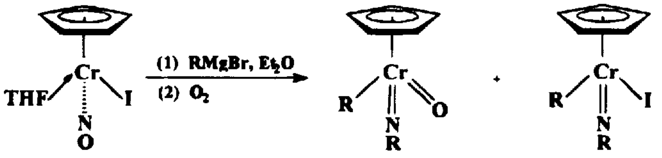


M = Cp*M'R (M' = Mo, W; R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph)

It is interesting that these particular $M(\mu\text{-}NO)_2M$ groupings are prone to undergo this isomerization when other such linkages (e.g., those in $[CpCr(NO)]_2(\mu\text{-}NO)_2$, $(CpFe)_2(\mu\text{-}NO)_2$, and $(CpCo)_2(\mu\text{-}NO)_2$ cited earlier as well as those in $[Cp^*Ru(Cl)]_2(\mu\text{-}NO)_2$,[29] $[Cp^*Ru(\mu\text{-}NO)]_2$,[30] $[Cp^*Ru(Ph)]_2(\mu\text{-}NO)_2$,[30] and $[Cp^*Fe(\mu\text{-}NO)]_2$[31]) show no such proclivity.

8. TREATMENT OF CpCr(NO)(THF)I WITH (MESITYL)MgBr AND MOLECULAR OXYGEN

The reaction of the chromium nitrosyl complex, CpCr(NO)(THF)I, with the sterically demanding Grignard reagent, (mes)MgBr, and trace amounts of molecular oxygen produces two products, CpCr(N-mes)(mes)(O) and CpCr(N-mes)(mes)I (Eq. (11)).[32]



(11)

R = mes (2,4,6-$C_6H_2Me_3$)

This represents the first and only example of nitrosyl N–O bond cleavage that we have encountered to date while working with our organometallic chromium nitrosyl systems. ESR evidence suggests that this reaction apparently proceeds via the 17-electron anion, $[CpCr(NO)(mes)_2]^-$. [Chromium nitrosyl complexes in this class preferentially form 17-valence-electron species of the type, $[CpCr(NO)X_2]^-$ (X = halide or alkyl), a feature which differs from the molybdenum and tungsten systems which form stable 16-valence-electron dialkyl and diaryl complexes.[33]] Molecular oxygen may then function as an oxidant to form the unstable 16-valence-electron species, $CpCr(NO)(mes)_2$, which then undergoes an intramolecular rearrangement similar to that shown for the reaction of CpW(NO)(*o*-tolyl)$_2$ with water (vide supra). This reaction is, however, difficult to study since the exposure of CpCr(NO)(THF)I and (mes)MgBr to large amounts of molecular oxygen results in CpCr(N-mes)(mes)I being the only isolable product from the final reaction mixture.

CONCLUSIONS

As summarized in this article, the reactions which yield nitrosyl N–O bond cleaved products are varied both with respect to the nature of the organometallic products that are produced as well as to the conditions that are needed to induce the cleavages. The reaction conditions are generally mild and involve either thermolysis, reduction (zinc or molecular hydrogen), reactions with water or molecular oxygen, or the use of potassium salts. It appears that when coordinatively and electronically unsaturated intermediates are produced in a reaction, the nitrosyl ligand either adopts an η^2-linkage to the metal center or forms dimeric species with bridging nitrosyl ligands in order to satisfy the metals' electronic requirements. Since Group 6 metals are relatively oxophilic, the thermodynamic driving force of these N–O bond dissociation reactions is probably the formation of strong metal-oxo bonds. We are continuing to investigate these and related reactions, since ultimately we would like to be able to induce nitrosyl N–O bond cleavage under well-defined experimental conditions. Furthermore, a better understanding of such nitrosyl N–O bond-dissociation processes in monomeric organometallic systems should shed more light on the mechanisms of catalytic decomposition or reduction of NO on metal surfaces or in cluster complexes.

Acknowledgments

We are grateful to the Natural Sciences and Engineering Research Council of Canada for generously supporting our research efforts over the years in the form of grants and postgraduate scholarships. We are also grateful to the University of British Columbia for the award of University Graduate Fellowships to several members of the Legzdins research group. This article was made possible by the hard work and insight of all past and present Legzdins group members. Finally, we gratefully acknowledge our fruitful collaborations with Drs. Jim Trotter (UBC), Steve Rettig (UBC), Fred Einstein (SFU), Ray Batchelor (SFU), and their co-workers.

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