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Coordination and Organometallic Chemistry of Metal−NO Complexes

Trevor W. Hayton, Peter Legzdins,* and W. Brett Sharp

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

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1. Introduction

The chemistry of transition-metal−NO complexes, or metal nitrosyls, has taken on added significance in recent years because of the important role that nitric oxide has been found to play as a signaling molecule in biological systems. Recent work has also established that the characteristic chemistry of nitrosyl complexes is often markedly different from that exhibited by their isoelectronic carbonyl analogues. It has been almost 10 years since these complexes were last reviewed in the book *Metal Nitrosyls*,[1] and so it seemed to us that an update of this rapidly expanding field would be appropriate at the present time. Consequently, this article picks up where *Metal Nitrosyls* left off and summarizes comprehensively the literature dealing with nitrosyl complexes from 1991 to mid-2001. Some particularly relevant work reported in late 2001 has been included where appropriate during the final stages of revising and polishing the text. As outlined in the table of contents, the pertinent information concerning the compounds themselves is first partitioned in terms of the position of the central transition metal in the periodic table and then in terms of the ligands other than NO present in the complexes. In the interests of keeping the article to a manageable size, most of the routine preparative and characterization data for individual compounds are simply referenced rather than being presented and discussed in detail. The review concludes with a general section that applies, in principle, to all classes of transition-metal−NO complexes, namely the characteristic reactivities of bound NO groups. Whenever possible, emphasis is placed on the unique physical and chemical properties imparted to nitrosyl complexes by the presence of the strongly electron-withdrawing NO ligands. If not specified otherwise, the abbreviations employed throughout are those summarized in the *ACS Style Guide*.[2]

Several general articles concerning nitrosyl complexes have appeared between 1991 and 2001. These include theoretical calculations on nitrosyl fragments[3−5] and submissions concerning electron counting in nitrosyl complexes.[6] Several review articles have also been written concerning a large array of nitrosyl-related topics, such as linkage isomerism,[7]

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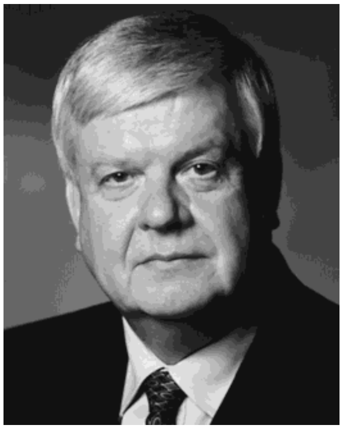
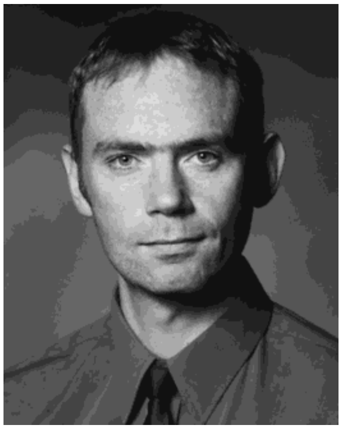
Trevor Hayton was born in Ottawa, Ontario, Canada, in 1975. He successfully completed his undergraduate studies in chemistry at the University of British Columbia in 1998 and was awarded a B.Sc. degree. He promptly started his research leading to a Ph.D. degree by working in the laboratories of Dr. Peter Legzdins. His current research interests involve establishing the chemical properties of low-valent vanadium nitrosyl and related complexes. Mr. Hayton presently holds a Natural Sciences and Engineering Research Council of Canada postgraduate scholarship. In his free time he enjoys climbing mountains.



Peter Legzdins is Professor of Chemistry at the University of British Columbia, having served as Head of the Department of Chemistry from 1990 to 2000. He received his first-class Honours B.Sc. degree from Carleton University (1964) and his Ph.D. from MIT (1968) with F. A. Cotton. After a postdoctoral year with G. Wilkinson at Imperial College in London, he joined the faculty at the University of British Columbia. In 1986 Professor Legzdins was awarded a UBC Izaak Walton Killam Memorial Fellowship. He is a Fellow of the Chemical Institute of Canada and was the recipient of the 1989 Alcan Lecture Award presented by the Canadian Society for Chemistry. He has also been awarded a 1993 UBC Killam Research Prize, a 1996 Japan Society for the Promotion of Science Fellowship, and a 2002 Canada Council Killam Research Fellowship. His principal research interests are centered on synthetic, structural, bonding, and kinetic studies of organometallic complexes that can be utilized as specific reactants or selective catalysts in organic or organometallic syntheses.

infrared spectroscopy,[8] biological aspects of nitrosyl complexes,[9] etc.[10,11]

We begin our coverage below with the group 5 metals, since no well-defined nitrosyl complexes of group 3 or 4 are currently known. This state of affairs is probably due to the following factors: (1) These metals are very oxophilic. (2) Most nitrosylating agents are potent oxidizers and potential oxygen-atom sources. (3) The low-valent chemistry of the early metals is not as well developed as it is for groups 6−9. Consequently, requisite precursor complexes are not readily available, and most attempts to make early-metal nitrosyls lead to the formation of oxo-containing products. A few reports of nitrosyls from groups 1−4 do exist, though. The interaction of NO with Na^+ and K^+ in the zeolite ETS-10 at 100 K results in the formation of the weakly bound adducts $M^+\cdots NO$ and $M^+\cdots ON$.[12] Also, the species Be(NO), Mg(NO), Sc(NO), Sc(η^2-NO), and Ti(NO) have been detected in argon matrixes as the products resulting from the reactions of laser-ablated metal atoms with nitric oxide.[13,14] The complex $Cp_2Zr(NO)(PMe_3)$ has been invoked as an intermediate during the reaction between $Cp_2Zr(PMe_3)_2$ and NO.[15]



W. Brett Sharp was born in London, England, in 1973. He studied chemistry at the University of Sussex between 1991 and 1995 while also working in the organic chemistry research laboratories of BP Chemicals during this time. After receiving a first-class Honours B.Sc. degree from the University of Sussex, he moved to Vancouver, Canada, to undertake Ph.D. studies with Dr. Peter Legzdins. His investigations into novel modes of reactivity of the nitrosyl ligand resulted in his obtaining his Ph.D. degree in early 2001. Following a brief postdoctoral appointment with Professor Legzdins, he is currently a technology transfer consultant with the UBC Industry Liason Office. During his studies, Dr. Sharp was the recipient of the Louise Gross prize from the University of Sussex and University Graduate and Gladys Estella Laird Fellowships from the University of British Columbia.

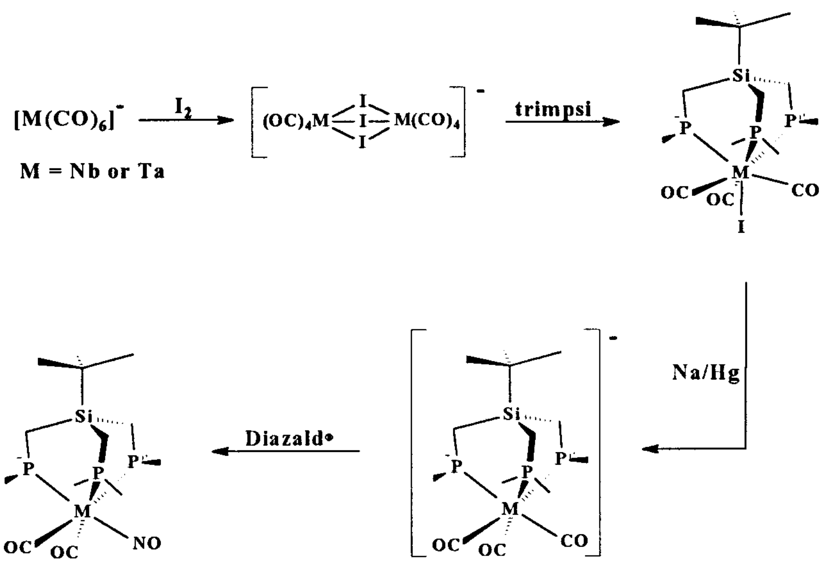
2. Group 5 Nitrosyls

2.1. Vanadium Nitrosyls

After a flurry of activity in the 1970s and 1980s, research on vanadium nitrosyls has diminished in recent years. $V(NO)_x$ ($x = 1-3$) species have been detected in an Ar matrix.[16] The complexes $[V(NO)_2(phen)_2]^+$ and $[V(NO)_2(bipy)_2]^+$ can be prepared by reacting VO_3^- with hydroxylamine and either phen or bipy in aqueous alkaline solutions and have been characterized by elemental analyses, IR spectroscopy, and cyclic voltammetry.[17] They can also be formed by treating $[V(CN)_5(NO)]^{3-}$ with excess bipy or phen in water.[18] $[V(tacn)(NO)_2(NH_3)]I$ (tacn = 1,4,7-triazacyclononane) has been formed by reacting V_2O_5, KOH, tacn, $[NH_3OH]Cl$, and NaI in water. The azide-substituted derivative, $V(tacn)(NO)_2(N_3)$, formed by metathesis of the ammine precursor with NaN_3, has been structurally characterized.[19]

The nitroxyl anion (NO^-) has been trapped in the vanadium oxide $[V_{12}O_{32}]^{4-}$ to form $[(NO)V_{12}O_{32}]^{5-}$, which has been characterized by X-ray crystallography.[20] Although not strictly a vanadium nitrosyl complex, the latter species could possibly be used as a novel nitrosylating agent.

Scheme 1



2.2. Niobium and Tantalum Nitrosyls

$M(NO)_x$ (M = Nb, Ta; $x = 2, 3$) species have been detected spectroscopically in an argon matrix.[21] Several well-defined terminal nitrosyl complexes of niobium and tantalum have also been recently synthesized. The first of these complexes to be prepared were (trimpsi)$M(CO)_2(NO)$ [M = Nb, Ta; trimpsi = $^tBuSi(CH_2PMe_2)_3$] as summarized in Scheme 1.[22]

Both of the dicarbonyl nitrosyls exhibit extremely low ν_{NO} values in their Nujol-mull IR spectra (Nb, 1518 cm^{-1}; Ta, 1515 cm^{-1}), thereby indicating the large amount of M→NO back-bonding extant in these complexes. The key steps in their syntheses involve reduction of (trimpsi)$M(CO)_3I$ with 2 equiv of Na/Hg amalgam, followed by nitrosylation with Diazald. Their thermal stability is due, most likely, to their bulky coordination environments and the presence of coligands with the right balance of π-accepting and σ-donating abilities.

cis-$[M(NO)_2(CNAr)_4]^+$ complexes (M = Nb, Ta; Ar = 2,6-$Me_2C_6H_3$)[23] are made by oxidizing $[M(CO)_6]^-$ with 2 equiv of $[NO]^+$ in the presence of excess isocyanide. The related $Ta(NO)(CNAr)_5$ (Ar = 2,6-$Me_2C_6H_3$)[24] is preparable by oxidizing $[Ta(CO)_6]^-$ with I_2 in the presence of 6 equiv of CNAr to generate $TaI(CNAr)_6$. This species is then reduced with excess KC_8 followed by reaction with Diazald to obtain $Ta(NO)(CNAr)_5$, whose IR spectrum in THF exhibits a ν_{NO} at 1542 cm^{-1}.

$$[Ta(CO)_6]^- \xrightarrow[\text{(2) 6 CNAr, −60 to 20 °C}]{\text{(1) } I_2\text{, THF, −78 °C}}$$

$$TaI(CNAr)_6 \xrightarrow[\text{(2) Diazald, 0 °C}]{\text{(1) xs } KC_8\text{, DME, −55 °C}} Ta(NO)(CNAr)_5$$

Finally, it is interesting to note that all the niobium and tantalum, and most vanadium, nitrosyls obey the 18e rule.[1] Furthermore, all known niobium and tantalum nitrosyl complexes exhibit a formal d^6 electron count at their metal centers.

3. Group 6 Nitrosyls

3.1. Chromium Nitrosyls

3.1.1. Coordination Complexes

Research with chromium nitrosyl complexes has continued apace during the past decade. Many octahedral complexes $Cr(NO)(CN)_2L_2(H_2O)$ (L = monodentate ligand or L_2 = bidentate ligand) have been isolated from the reactions of $K_3[Cr(NO)(CN)_5]\cdot H_2O$ with L or L_2. The physical properties of these complexes are consistent with their possessing octahedral structures and low-spin electron configurations designated as $\{CrNO\}^5$ according to the Enemark–Feltham notation.[1] A wide variety of Lewis bases, L or L_2, have been utilized in this manner. Representative examples include benzimidazoles,[25–28] benzothiazoles,[29] tetrahydroquinolines/isoquinolines,[30] aromatic amines,[31–33] quinolines,[34] pyrazoline-5-ones,[35,36] 8-hydroxyquinolinesulfonamides,[37] Schiff bases,[38] Mannich bases,[29] and a variety of drugs, vitamins, and other biologically important compounds.[39–41] Related 2/3-pyrazoline-5-one derivatives have also been prepared in a similar manner from the $[Cr(NO)(CN)_4]^{2-}$ anion.[42] Similar $Cr(NO)(NCS)_2L_2(H_2O)$ complexes result from the treatment of the $[Cr(NO)(NCS)_5]^{3-}$ anion with biologically active organic compounds (L).[43] Finally, mixed-ligand complexes of the type $Cr(NO)(acac)_2(L)$ (L = a substituted benzimidazole) can be obtained from the reactions of $Cr(NO)(acac)_2(H_2O)$ with L.[44]

ESR monitoring of the photosubstitution of CN^- by H_2O in $[Cr(NO)(CN)_5]^{3-}$ and $Cr(CN)_2(H_2O)_3(NO)$ reveals formation of the complexes $[Cr(CN)_{5-x}(H_2O)_x(NO)]^{x-3}$ which exhibit different stabilities in acidic and alkaline media.[45] The ESR spectra of the product complexes have also been simulated.[46]

The second-sphere coordination of protonated, branched poly(ethyleneimine) with $[Cr(NO)(CN)_5]^{3-}$ as a function of pH has been studied by ESR spectroscopy.[47] Simulation of the spectra indicated that ca. 98% of the chromium complex is bound to the polymer at pH ~ 7. New Prussian blue analogues such as $Cr[Cr(NO)(CN)_5]_{0.5}\cdot 2H_2O\cdot 1.8MeOH$ can be constructed from the $[Cr(NO)(CN)_5]^{3-}$ anion.[48] IR spectra are interpreted as being consistent with the view that the nitrosyl ligands in the anions are bridging, the ν_{NO} being some 60−110 cm^{-1} higher than that of $K_3[Cr(NO)(CN)_5]$. Overall, the $[Cr(NO)(CN)_5]^{3-}$ anion affords Prussian blue analogues with lower magnetic ordering temperatures than does the related $[Cr(CN)_6]^{3-}$ anion. Finally, the $[Cr(NO)(CN)_5]^{3-}$ anion also forms cyano-bridged complexes such as $K[L_2FCr{-}NC{-}Cr(CN)_4(NO)]$, where L = en or pn.[49]

Acid hydrolysis of $Cr(H_2O)(CN)_2(en)(NO)$ affords $[Cr(H_2O)_2(CN)(en)(NO)]^+$.[50] Linkage isomerization of bridging cyano ligands has been found to be involved in the formation of adducts between both of these chromium complexes and Hg(II) and Ag(I).[50,51] The crystal structure of $[Cr(H_2O)_5(NO)]SO_4$ supports the formulation of this complex as a Cr(III) complex of NO^-.[52] However, all electron ab initio multiconfiguration self-consistent field calculations of $Cr(NO)^{2+}$ and $[Cr(H_2O)_5(NO)]^{2+}$ reveal the net charge on chromium to be in the range +1.65e to +1.84e.[53] This indicates that the oxidation state of chromium is approximately +2 in both ions. The related $[Cr(NCMe)_5(NO)]^{2+}$ cation has also been isolated as its tetrafluoroborate salt,[54] and $[Cr(NH_3)_5(NO)][ClO_4]_2$ has recently been structurally characterized and studied by DFT methods.[55]

The chromium nitrosyls $[Cr(NO)(EHBA)]^+$ and $Cr(NO)(EHBA)_2$ (EHBA = 2-ethyl-2-hydroxybutyrate) have been characterized by continuous wave ESR and two-pulse electron spin−echo spectroscopy at X-band.[56] The g values are characteristic of a single unpaired electron in a predominantly d_{xy} orbital. The formally low-spin d^5 complexes relax ~5 orders of magnitude more slowly than low-spin Fe(III) porphyrins.

The chromium carbonyl nitrosyl $Cr_2(CO)_8(NO)_2$ has been prepared, and its crystal structure has been determined along with that of the known $[Ph_4P][Cr_2(CO)_9(NO)]$.[57] Both complexes possess metal−metal-bonded structures analogous to that of $Mn_2(CO)_{10}$, the Cr−Cr bond lengths being 3.00−3.02 Å in the neutral and 2.995 Å in the anion vs 2.904 Å for the central Mn−Mn linkage in the manganese carbonyl. $Cr_2(CO)_8(NO)_2$ is slowly formed in poor yield from $[Cr(CO)_4(NO)]^-$ and $Cr(CO)_4(NO)Br$, but it can be prepared almost quantitatively by the one-electron oxidation of $[Cr(CO)_4(NO)]^-$ by $[Ph_3C][PF_6]$.[57,58] In a related study, theoretical analysis of IR spectral evidence suggests that $Cr(CO)_3(NO)_2$ has a C_{2v} molecular structure with the NO groups occupying two equatorial positions of a trigonal bipyramid and that $Cr(CO)_4(NO)$ has a C_{4v} structure that is very similar to the isoelectronic molecule $Mn(CO)_5$.[59]

A general synthesis for *trans*,*trans*-$CrH(CO)_2(NO)(PR_3)_2$ has been developed,[60] starting from $[(\eta^6\text{-arene})Cr(CO)_2(NO)]PF_6$, $LiBH_4$, and PR_3 (R = Me, Et, Ph, OMe, OPh). The IR and NMR parameters of the chromium complexes compare well with those exhibited by their tungsten congeners, but the Cr−H linkages are less hydridic in nature and are thus less reactive with respect to addition across C≡C and C═O bonds than are the tungsten complexes. Furthermore, the specific reaction of *trans*,*trans*-$CrBr(CO)_2(NO)(PPh_3)_2$ with $LiHBEt_3$ in the presence of PPh_3 gives *trans*,*trans*-$CrH(CO)_2(NO)(PPh_3)_2$, which exhibits a distorted octahedral solid-state molecular structure.[61] Phenyldiazonium hexafluorophosphate inserts into the Cr−H bond of the hydride to produce [*trans*,*trans*-$Cr(NH{=}NPh)(CO)_2(NO)(PPh_3)_2]PF_6$, and triflic acid reacts with the hydride to afford *trans*,*trans*-$Cr(\eta^1\text{-OTf})(CO)_2(NO)(PPh_3)_2$.

Reaction of $Cr(CO)_6$ with 2 equiv of $[NO][BF_4]$ in $MeNO_2$ at 60 °C reportedly produces the unusual *trans*-dinitrosylchromium complex $[Cr(NO)_2(CO)_2(MeNO_2)_2][BF_4]_2$ from which the $MeNO_2$ ligands are very easily replaced.[62] Thus, treatment with stoichiometric amounts or excesses of Lewis bases, L, affords $[Cr(NO)_2(CO)_2L_2][BF_4]_2$ or $[Cr(NO)_2L_4][BF_4]_2$, respectively (L = $MeNO_2$, MeCN, MeOH; L_2 = bipy). Similarly, treatment of $[Cr(NO)_2(CO)_2(MeNO_2)_2][BF_4]_2$ with 2 equiv of NaOR or NaO_2CPh produces *trans*-$\{Cr(NO)_2(OR)_2\}_n$ (R = Et, ^{i}Pr) and $Cr(NO)_2(O_2CPh)_2$, respectively. The latter dinitrosyl complexes undergo trans−cis isomerization in the presence of MCl_4 (M = Ti or Sn) and then form adducts formulated as $Cr(NO)_2(OR)_2(MCl_4)_2$ and $Cr(NO)_2(O_2CPh)_2(MCl_4)$.[63] The corresponding adducts with $EtAlCl_2$ are believed to transform further into ethylidene complexes, one of which has been characterized only by IR spectroscopy.[62] Some of the dicationic dinitrosylchromium complexes catalyze the polymerization of olefins, and some of the MCl_4 adducts polymerize phenylacetylene catalytically.

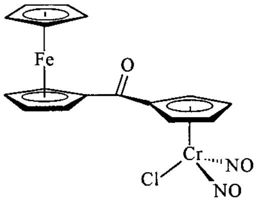
Finally, it may be noted that nitrosylation of Schiff base (SB) complexes *cis*-$(SB)Cr(CO)_4$ with NO in benzene under dry argon at room temperature affords products formulated as $(SB)Cr(NO)_2(NO_2)_2$.[64]

3.1.2. Organometallic Complexes

Microwave rotational spectra for eight isotopomers of $CpCr(CO)_2(NO)$ confirm that the complex has a piano-stool type structure with one symmetry plane and give a clear indication of different bonding and structural parameters for the NO and the CO groups.[65] The Cp−Cr−NO angle is 128°, the Cp−Cr−CO angle is 120°, the Cp−Cr bond = 1.86 Å, and two of the Cp C atoms are staggered with respect to the NO nitrogen atom. DFT has been used to calculate the equilibrium geometry and ESR hyperfine coupling constants for the 19e complex $[CpCr(CO)_2(NO)]^-$.[66] The results are in good agreement with experimental values and confirm that the unpaired electron is localized primarily on the NO ligand, which is significantly bent. However, the Cr−N−O bond angle (157°) is larger than that predicted by the analysis of the EPR data (<130°). As expected, reaction of $CpCr(CO)_2(NO)$ with LiC≡CR and subsequent addition of $[Me]^+$ leads to the carbene complexes $Cp(CO)(NO)Cr{=}C(OMe)(C{\equiv}CR)$ (R = Ph, $SiMe_3$).[67]

Chlorination/nitrosylation of $(ON)(OC)_2Cr(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ with hydrogen chloride/isoamyl nitrite affords $Cl(ON)_2Cr(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (vide infra),[68] which also results from the unexpected Friedel−Crafts acylation of the bimetallic dicarbonylnitrosyl with $(ON)(OC)_2Cr(\eta^5\text{-}$

C_5H_4)C(O)Cl.[69] The related (η^5-C_5H_4COOMe)Cr$(NO)_2$X (X = Cl) complex has been prepared similarly and has been converted to its X = I or Me derivatives by metathesis reactions.[70] In related chemistry, reaction of [(MeCp)Fe$(CO)_2$]Na with CpCr(CO)(NO)(THF) gives the heterodinuclear anion [(MeCp)(OC)Fe(μ-CO)$_2$Cr-(NO)Cp]$^-$, which has been structurally characterized as its [Ph_3PMe]$^+$ salt. It crystallizes as the trans isomer with an Fe−Cr single-bond distance of 2.611(1) Å. Alkylation of the anion with [Me]$^+$ gives the methoxycarbynes, *cis*- and *trans*-(MeCp)(OC)Fe(μ-COMe)(μ-CO)Cr(NO)Cp in low yields. Both isomers undergo slow decomposition at room temperature to produce (MeCp)Fe$(CO)_2$Me as one of the products.[71]



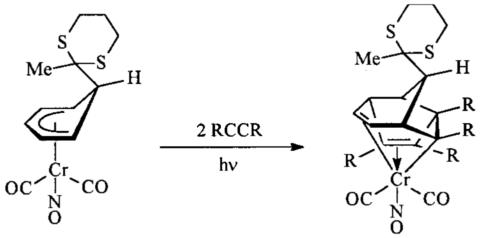
Treatment of (η^6-C_6Et_6)Cr$(CO)_2$(CE) (E = O or S) with [NO][BF_4] yields [(η^6-C_6Et_6)Cr$(CO)_2$(NO)][BF_4] and [(η^6-C_6Et_6)Cr(CO)(CS)(NO)][BF_4], respectively. The hexaethylbenzene ligand in both complexes adopts the 1,3,5-proximal-2,4,6-distal arrangement, and the tripod ligands eclipse the distal Et groups.[72] Variable-temperature NMR data exhibited by the cationic nitrosyl complexes reveal that each exists as a single conformer with the same structure as in the solid state.

The reaction between cynichrodenoic acid, (η^5-C_5H_4COOH)Cr$(CO)_2$(NO), and PCl_5 produces cynichrodenoyl chloride, (η^5-C_5H_4COCl)Cr$(CO)_2$(NO), which can be converted to functionally substituted derivatives of the parent complex.[73] Thus, reactions of the acyl chloride with amines lead to the corresponding carboxamides, with alcohols to the corresponding esters, and with pyridine to the carboxylic anhydride. Metathesis of the chloride with sodium azide affords cynichrodenoyl azide which undergoes Curtius rearrangement to form the corresponding isocyanate that can be subsequently hydrolyzed to aminocynichrodene. Interestingly, hydrolysis of the isocyanate with 20% aqueous KOH produces 30% aminocynichrodene and 40% dicynichrodenylurea, i.e., $(OC)_2(ON)$Cr[(η^5-C_5H_4)NHC(O)NH(η^5-C_5H_4)]Cr-$(CO)_2$(NO).[74] The related 1,2-dicynichrodenylethene can be prepared in 36% yield from formylcynichrodene via McMurry's low-valent titanium coupling reagent (i.e. $2TiCl_4 + LiAlH_4$), and vinylcynichrodene can be obtained by dehydration of the corresponding alcohol.[75] The NMR spectra of the various cynichrodene derivatives have been recorded, and structures of several of the complexes have been established by X-ray diffraction.

Addition of nucleophiles R$^-$ to (η^6-C_6H_6)Cr$(CO)_3$ and (η^6-C_7H_8)Cr$(CO)_3$ followed by treatment with Diazald produces (η^5-C_6H_6R)Cr$(CO)_2$(NO) and (η^5-C_7H_8R)Cr$(CO)_2$(NO), respectively. These compounds can be converted to Fischer carbene complexes, e.g. (η^5-C_6H_6R)(OC)(ON)Cr=C(OMe)Ph, by sequential treatment with nucleophiles and electrophiles. Abstraction of hydride from the dicarbonylnitrosyl species having R = H produces the corresponding air-sensitive cations, e.g. [(η^6-C_7H_8)Cr$(CO)_2$(NO)]$^+$.[76]

The photoinduced decarbonylation of Cp*Cr$(CO)_2$-(NO) in CH_3CN in the presence of excess sulfur leads to the cyclopentasulfido complex Cp*Cr(NO)(S_5), while in the case of limited sulfur supply the binuclear Cp*$_2Cr_2(NO)_2$(μ-η^1,η^2-S_2)$_2$ is formed preferentially. The corresponding reaction with elemental selenium produces Cp*$_2Cr_2(NO)_2$(μ-η^1,η^2-Se_2)$_2$ irrespective of the available amount of selenium.[77]

UV irradiation of the cyclohexadienyl complex (η^5-C_6H_6R)Cr$(CO)_2$(NO) (R = 2-methyl-1,3-dithiane-2-yl) and 2 equiv of 2-butyne or 3-hexyne in toluene or *n*-hexane produces tricyclic complexes.[78] These complexes arise from sequential [5 + 2] and homo[5 + 2] cycloadditions of two alkyne molecules to the η^5-dienyl manifold (vide infra). The tricyclic organic compound can be released from the chromium's coordination sphere by heating the complex in MeCN.



Reaction of Cp_2Cr_2(μ-$SCMe_3$)$_2$(μ-S) with ClNO results in the production of $Cp_2Cr_2(NO)_2$(μ-$SCMe_3$)(μ-$SSCMe_3$), $Cp_2Cr_2(NO)_2$(μ-$SCMe_3$)(μ-Cl), and Cp_2Cr_2-(NO)(Cl)(μ-$SCMe_3$)$_2$.[79]

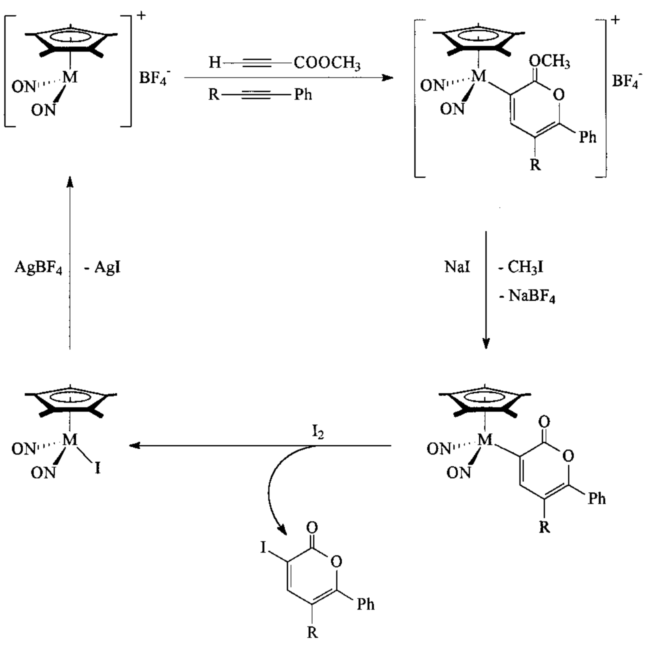
Treatment of CH_2Cl_2 solutions of [Cp′Cr(NO)X]$_2$ (Cp′ = Cp or Cp*; X = Cl or I) with various Lewis bases, L, affords good yields of Cp′Cr(NO)(L)X complexes [L = PPh_3, $P(OMe)_3$, $P(OPh)_3$, py, or $C_5H_{11}N$ (pip)].[80] In donor solvents, S, these ESR-active compounds undergo either L or X substitution to form the 17e Cp′Cr(NO)(S)X and [Cp′Cr(NO)(L)(S)]$^+$ species, respectively. Electrochemical reductions of the various CpCr(NO)(L)X compounds are irreversible and are followed by loss of [X]$^-$. Consistently, reduction of CpCr(NO)(PPh_3)I in THF by Zn in the presence of $P(OPh)_3$ produces the 18e mixed phosphine−phosphite complex CpCr(NO)(PPh_3)[$P(OPh)_3$]. Treatment of [CpCr(NO)I]$_2$ with [Ag][PF_6] in MeCN affords the paramagnetic complex [CpCr(NO)$(NCMe)_2$][PF_6], whose solid-state molecular structure has been established by an X-ray crystallographic analysis.[81] Its room-temperature ESR spectrum in DMF consists of a broad three-line pattern indicative of the unpaired electron in the 17e cation being primarily delocalized onto the nitrosyl ligand ($a(^{14}N) = 5.21$ G).

Treatment of a green suspension of CpCr(NO)-(PPh_3)I in THF with Me_3SiCH_2MgCl results in the formation of the unusual 17e monomeric organometallic radical CpCr(NO)(PPh_3)(CH_2SiMe_3).[82] Remarkably, this alkyl-for-iodide metathesis is initiated by dissociation of the phosphine ligand from the reactant, and four intermediate complexes which are formed sequentially on the reaction path from the iodide to the alkyl have been detected by IR and ESR spectroscopy.[83] This understanding of the mechanistic pathway has led to the development of a general synthetic route to other 17e CpCr(NO)(L)R complexes (L = Lewis base, R = hydrocarbyl).[84] The ESR spectra of these radicals vary greatly in appearance, ranging from featureless singlets to more complicated spectra which reveal varying degrees of delocalization of the unpaired electron. For instance, the X-band ESR spectrum of the prototypical complex, dark green CpCr(NO)(PPh$_3$)(CH$_2$SiMe$_3$), in hexanes exhibits signals which indicate that the unpaired electron density is delocalized virtually over the entire molecule. Consistently, it possesses a normal three-legged piano-stool molecular structure with no unusual bond distances or angles. The chemical properties of the CpCr(NO)(L)R complexes reveal a degree of selective substitutional lability. Thus, CpCr(NO)(PPh$_3$)(CH$_2$SiMe$_3$) is inert to CO, H$_2$, and C$_2$H$_4$ but is converted by NO to CpCr(NO)$_2$(CH$_2$SiMe$_3$), by [NO][PF$_6$] to [CpCr(NO)$_2$(PPh$_3$)][PF$_6$], and by 2 equiv of HSnPh$_3$ to CpCr(NO)(PPh$_3$)(H)(SnPh$_3$). Other less sterically congested CpCr(NO)(L)R complexes react readily with CO to form CpCr(NO)(CO)$_2$ and CpCr(NO)(L)(CO).[84]

CpCr(NO)$_2$CF$_3$ is preparable as an exceptionally thermally and oxidatively stable material by the interaction of CpCr(NO)$_2$Cl with Cd(CF$_3$)$_2$·glyme at 65 °C.[85] Treatment of Cp*Cr(NO)$_2$X (X = Cl or CH$_2$Cl) with excess NaO-^{i}Pr in 2-propanol produces Cp*Cr(NO)(O-^{i}Pr)$_2$ as a volatile, deep blue-green complex. The molecule adopts a nearly C_s piano-stool structure having a terminal NO ligand and isopropoxide ligands so oriented as to maximize Cr−O π-bonding (Cr−O(av) = 1.815(4) Å).[86] Particularly interesting is the fact that the natures of the ligands control the electronic stability of CpCr(NO)(ligand)$_2$ complexes.[87] Thus, σ-base ligands stabilize the 17e configurations of cations such as [CpCr(NO)(NH$_3$)$_2$]$^+$ whereas π-acid ligands (e.g. CO) stabilize the 18e configurations of the neutral congeners. Intermediate ligands (e.g. P(OMe)$_3$) afford complexes capable of existing in both forms.[88] The effects of π-bonding on the stability and reactivity of CpCr(NO) complexes have been recently delineated.[89]

Several anionic and paramagnetic [CpCr(NO)X$_2$]$^-$ complexes (X = halide, OTf) have been prepared, e.g. by reaction of [CpCr(NO)X]$_2$ with X$^-$, as possible precursors to neutral CpCr(NO)X$_2$ species.[90] However, 1e oxidation of these anions results in initial loss of NO from the chromium's coordination sphere, probably via a high-spin CpCr(NO)X$_2$ intermediate, and eventual formation of isolable [CpCrCl(μ-Cl)]$_2$ and CpCr(NO)$_2$Cl. The relation between spin-state and metal−ligand bonding interactions in CpCr(NO)X$_2$ complexes has been studied using DFT computational techniques, and these studies have indeed confirmed a propensity for NO-ligand dissociation from the high-spin complexes.[91] The calculated order of relative singlet vs triplet spin-state stability is CpMo(NO)Cl$_2$ $\gg$ CpCr(NO)(NH$_2$)Me > CpCr(NO)Me$_2$ > CpCr(NO)(Me)Cl $\approx$ CpCr(NO)(NH$_2$)Cl > CpCr(NO)Cl$_2$. The amide π-donation increases the HOMO−LUMO gap, thereby favoring the diamagnetic configuration, but the methyl ligand reduces electron−electron repulsion through orbital expansion, thereby lowering the relative energy of the singlet state.

Scheme 2



M = Cr, R = Et; M = Mo, W; R = Me

The formally 16e cations, [Cp*M(NO)$_2$]$^+$ (M = Cr, Mo, W) mediate the regioselective and stoichiometric assembly of iodopyrones from methyl propiolate, phenylacetylenes, and I$_2$. This process may be effected in a stoichiometric cycle, as depicted in Scheme 2.[92]

Treatment of CpCr(NO)$_2$(OTf) with σ-donor ligands (L) produces the [CpCr(NO)$_2$L][OTf] salts.[93] Potentiometric titrations and ^{1}H NMR spectroscopic studies of CpCr(NO)$_2$(OTf) in aqueous solutions provide evidence for the existence of [CpCr(NO)$_2$(H$_2$O)]$^+$ and CpCr(NO)$_2$(OH). When generated in situ by the reaction of CpCr(NO)$_2$(OTf) with an equimolar amount of CsOH in H$_2$O, the hydroxo complex reacts with a variety of acids with concomitant NO loss to form paramagnetic, mononitrosyl complexes [e.g. CpCr(NO)(acac)], some of which have been structurally characterized.[93]

Reaction of Cr(NO)(N^{i}Pr$_2$)$_3$ with PhCO$_2$H leads to Cr(NO)(N^{i}Pr$_2$)(O$_2$CPh)$_2$.[94] Treatment of the bis(benzoate) with CpNa produces CpCr(NO)(N^{i}Pr$_2$)(OC(O)Ph) which subsequently yields a series of 18e complexes CpCr(NO)(N^{i}Pr$_2$)R (R = hydrocarbyl) when treated with 1 equiv of the appropriate R$_2$Mg·x(dioxane) reagent.[95] The "strong-field" nitrosyl and amide ligands in [Cr(NO)(N^{i}Pr$_2$)]$^{2+}$ also enforce a diamagnetic configuration on the formally 14e Cr(NO)(N^{i}Pr$_2$)R$_2$ (R = CH$_2$SiMe$_3$, CH$_2$Ph) complexes which result from reaction of the bis(benzoate) with 2 equiv of the corresponding R$_2$Mg·x(dioxane) reagent. These monomeric compounds are stereochemically nonrigid in solutions and exhibit distortions in their solid-state molecular structures that reflect the existence of β-agostic C−H···Cr interactions.[95] Interestingly, attempts to prepare Cr(NO)(N^{i}Pr$_2$)(o-tolyl)$_2$ in a similar manner result in the isolation of Cr(N-o-tolyl)(O)-

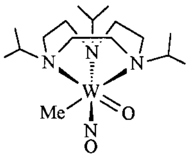
(N^iPr_2)(*o*-tolyl), a strongly bent monoimido complex evidently resulting from nitrosyl-ligand cleavage.[96]

3.2. Molybdenum and Tungsten Nitrosyls

3.2.1. Coordination Complexes

Photochemically generated $W(CO)_5$ reacts with NO in the gas phase at room temperature to form initially $W(CO)_x(NO)$ ($x = 4$ or 5) and then relatively stable $W(CO)_3(NO)_2$, which exhibits ν_{CO} at 2015 cm^{-1} and ν_{NO} at 1676 and 1712 cm^{-1}.[97] A theoretical analysis of CO-substitution reactions on *trans*-$W(CO)_4(NO)Cl$ by PMe_3 predicts an associative mechanism with a 7-coordinate intermediate in which the W−N−O angle is bent to 135.7°. For weaker donors, such as PH_3, this associative mechanism is not available since they cannot stabilize an intermediate with a bent W−N−O bond.[98]

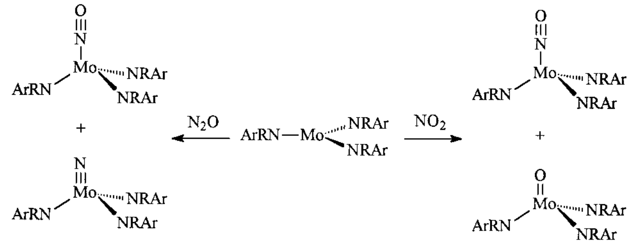
The electronic structure of $L_3W(NO)(O)Me$ (L_3 = 1,4,7-triisopropyl-1,4,7-triazacyclononane) can be described in terms of an octahedrally coordinated W(IV) center (d^2), an antiferromagnetically coupled NO ligand ($S = 1$), and one oxo and one Me anion.[99] The related molybdenum complex, $L_3Mo(NO)(O)(OH)$, is also known, and it forms the centrosymmetric dication $[\{L_3Mo(NO)(O)(OH)\}_4Na_2(H_2O)_2]^{2+}$ that has been crystallographically characterized.[100] The crystal structure exhibits two different types of nitrosyl ligand−Na interactions, either NO side-on or through the nitrosyl O atom.



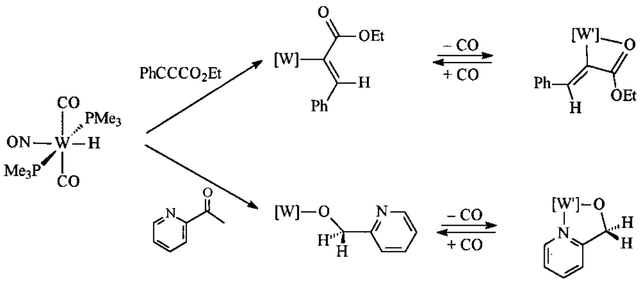
The three-coordinate complexes $Mo(NRAr)_3$ (R = *tert*-hydrocarbyl; Ar = 3,5-$C_6H_3Me_2$) or $Cr(N^iPr_2)_3$ are efficient agents for the quantitative abstraction of nitric oxide, e.g. from $Fe(NO)(L)(NRAr_F)_2$ complexes,[101] to generate $Mo(NO)(NRAr)_3$ and $Cr(NO)(N^iPr_2)_3$. The related monomeric complex $(AdS)_3Mo(NO)(py)$ (Ad = 1-adamantyl) has also recently been prepared by treatment of the thio-1-adamantyl dimer $[(ON)Mo(\mu\text{-}SAd)(SAd)_2]_2$ with pyridine.[102] Also known are the related complexes $[(ON)Mo(\mu\text{-}S^tBu)(S^tBu)_2]_2$, $[(ON)Mo(\mu\text{-}OSiMe_2{}^tBu)(OSiMe_2{}^tBu)_2]_2$, and $W(S^tBu)_3(NO)(py)$.[103,104]

$Mo(NO)(NRAr)_3$-type complexes can be formed by a number of other routes (Scheme 3). For instance, reaction of $Mo(NRAr)_3$ with N_2O results in the formation of $Mo(NO)(NRAr)_3$ and $Mo(N)(NRAr)_3$, a reaction that involves formal N−N bond cleavage.[105] This reaction in unprecedented and indeed is somewhat counterintuitive, since N_2O usually acts as a O-atom donor. The reaction has been studied in great detail by kinetics and calorimetry, and the N−N bond-cleavage step is thought to proceed through a bimetallic μ-N_2O complex.[106] The nitrosyl complex $Mo(NO)(NRAr)_3$ can also be formed by reacting $Mo(NRAr)_3$ with 0.5 equiv of NO_2, an equal amount of $Mo(O)(NRAr)_3$ also being generated during this transformation. To the best of our knowledge, this conversion is also without precedent.[107]

Scheme 3



Scheme 4



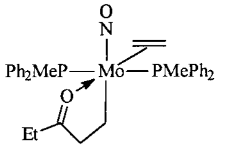
$[W] = W(NO)(CO)_2(PMe_3)_2$, $[W'] = W(NO)(CO)(PMe_3)_2$

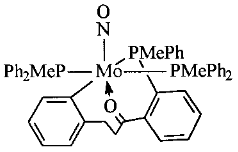
The basic hydrides, *trans,trans*-$WH(CO)_2(NO)(PR_3)_2$ (R = Me, Et, Ph, $OCMe_2$)[108] react with $BH_3{\cdot}L$ (L = THF or SMe_2) to form air-sensitive *trans*-$W(\eta^2\text{-}BH_4)(CO)(NO)(PR_3)_2$ as the main products, whereas the more acidic hydrides (i.e. R = OMe, OPh) do not. The $W(\eta^2\text{-}BH_4)(CO)(NO)(PR_3)_2$ complexes are unstable with respect to elimination of $BH_3{\cdot}PR_3$.[109]

As illustrated in Scheme 4, the reactions of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ with activated acetylenes of the type $RC{\equiv}CCO_2R'$ (R = H, Me, Ph, $R'O_2C$) initially afford tungsten vinyl compounds resulting from trans- and cis-insertion of the acetylenes into the W−H linkage of the reactant. However, some of the vinyl compounds are prone to lose CO and form four- or five-membered metallacycles in which the O atoms of the ester functionalities are coordinated to the tungsten centers.[110] In a similar manner, the W−H bond of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ adds across the C=O linkages of (pyridin-2-yl)-substituted aldehydes and ketones. This addition is followed by rapid extrusion of a coordinated CO ligand to form O,N-bidentate coordinated tungsten alkoxides.[111] Consistently, *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ behaves similarly toward simple and phenoxy-functionalized aldehydes and ketones[112] as well as β-diketones.[113] The related hydride, *mer*-$MoH(CO)(NO)(PMe_3)_3$, also undergoes facile additions of its Mo−H linkage across the C=O bonds of aldehydes or ketones, CO_2, and metal carbonyls to form isolable alkoxide, formate, or μ-formyl complexes, respectively, that exhibit no proclivity to undergo subsequent extrusion of coordinated CO.[114] Similar results have recently been reported for the tungsten analogue.[115]

The molybdenum complex *mer*-$Mo(Cl)(CO)(NO)(PMePh_2)_3$ preparable by the reaction of 4 equiv of $PMePh_2$ with *trans*-$Mo(ClAlCl_3)(NO)(CO)_4$ undergoes a metathesis reaction with $LiBH_4$ to afford the hydrido nitrosyl complex, *mer*-$MoH(CO)(NO)(PMePh_2)_3$. Reaction of this complex with ethylene (50 °C, 50 psi, 48 h) results in the loss of a $PMePh_2$ ligand

and incorporation of 3 equiv of C_2H_4 to produce complex **I** in good yield. Styrene reacts slowly (5 d, 50 °C) with benzene solutions of the hydride to give ethylbenzene and emerald-green *trans*-**II** in high yield.[116]

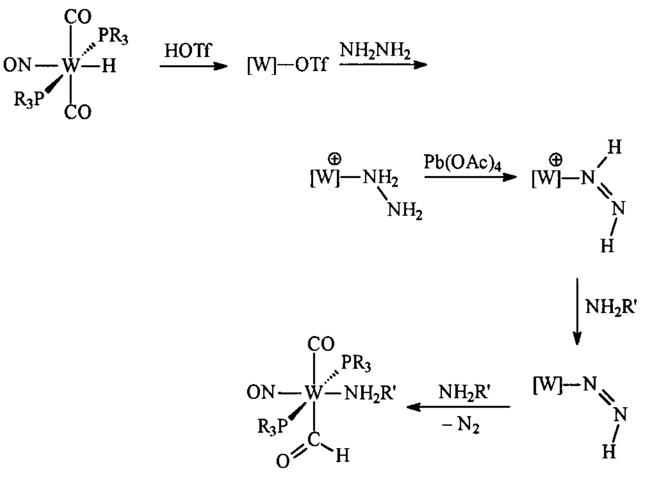

I


II

The reaction between *mer*-$MoH(CO)(NO)(PMePh_2)_3$ and propylene results in only one olefin being incorporated to form the isomeric complexes *mer*-$Mo\{\eta^2\text{-}C(O)R\}(NO)(PMePh_2)_3$ (R = ^{n}Pr, ^{i}Pr). Treatment of these latter compounds with HCl converts them to the corresponding η^1-O=CHR aldehyde complexes from which the aldehydes may be liberated by CO, the final nitrosyl product being $MoCl(CO)_2(NO)(PMePh_2)_2$ in both cases.[116]

IR and NMR spectroscopic evidence has also been presented for the existence of intermolecular M−H···H−OR′ hydrogen bonding between the hydride ligand of $WH(CO)_2(NO)(PR_3)_2$ complexes and acidic alcohols.[117] The IR and NMR data suggest C_{2v} symmetry around tungsten in the adducts, and an H···H distance of 1.77 Å has been estimated for one of the adducts [R = Me, R′ = $(CF_3)_2CH$] from the hydride $T_{1\min}$ relaxation time. As illustrated in Scheme 5, reactions of *trans,trans*-$WH(CO)_2(NO)(PR_3)_2$ (R = Ph, cyclohexyl) with HOTf give *trans,trans*-$W(\eta^1\text{-}OTf)(CO)_2(NO)(PR_3)_2$ and H_2. The weakly coordinated triflate ligands are cleanly displaced by N_2H_4 to form *trans,trans*-$[W(NH_2NH_2)(CO)_2(NO)(PR_3)_2][OTf]$, and selective oxidation of the N_2H_4 ligands in the latter complexes with $Pb(OAc)_4$ at −78 °C provides *trans,trans*-$[W(NH{=}NH)(CO)_2(NO)(PR_3)_2][OTf]$. The spectroscopic properties of the diazene complexes suggest that NH=NH is coordinated to W via a single N atom and with *trans*-NH=NH geometry.[118] It has also been shown that deprotonation of the ligated NH=NH by bases and subsequent hydrogen migration to carbonyl ligands affords metal formyl complexes.[119]

Scheme 5



$[W] = W(CO)_2(NO)(PR_3)_2$

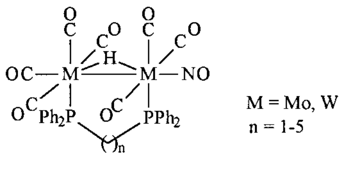
Interestingly, the phenyldiazene complex *trans,trans*-$[W(NH{=}NPh)(CO)_2(NO)(PPh_3)_2][PF_6]$ reacts with $[Br]^-$ by displacement of the NH=NPh ligand but with azide and amines by displacement of the CO ligand.[120] The congeneric molybdenum hydride, *trans,trans*-$MoH(CO)_2(NO)(PR_3)_2$, undergoes many of the same transformations outlined above for its tungsten analogue.[121]

There are many examples of CO ligand substitution by the isoelectronic $[NO]^+$. For example, nitrosylation of $M(N{-}N)(CO)_4$ with $[NO][BF_4]$ in MeOH readily affords $[M(N{-}N)(CO)_2(NO)(MeOH)][BF_4]$ [M = Mo, W; N−N = a bis(pyrazolyl)methane-*N,N′* ligand].[122] The labile MeOH ligands in the cationic molybdenum complex containing the bis(3,5-dimethylpyrazol-1-yl)methane-*N,N* ligand are readily displaced by anionic, $[X]^-$, or neutral, L, Lewis bases to form the corresponding $Mo(N{-}N)(CO)_2(NO)X$ or $[Mo(N{-}N)(CO)(NO)L_2][BF_4]$ complexes, respectively. The N−N ligand in this cationic reactant is also replaced when treated with an excess of a variety of bidentate ligands (L−L) which form $[Mo(L{-}L)_2(CO)(NO)][BF_4]$ products. Interestingly, dithiocarbamate anions, $[S{-}S]^-$, react with this cation in MeCN to form the orange-red dimeric products, $[Mo(\mu\text{-}\{S{-}S\})(CO)_2(NO)]_2$, in which there are no formal Mo−Mo bonds.[122] In related chemistry, treatment of $M(CO)_4(L{-}L')$ [L−L′ = a chelating 2-(diphenylphosphinyl)aniline ligand] with $[NO][BF_4]$ affords $[M(CO)_3(NO)(L{-}L')][BF_4]$ for M = W but $M(CO)_2(NO)(L{-}L')FBF_3$ for M = Mo.[123] When L−L′ is a bidentate N_4-annulene ligand, only the cationic tricarbonyl products are formed for both metals.[124] The related *mer*-$[M(CO)_3(dppe)(NO)][BF_4]$ salts (M = Mo, W) undergo CO-displacement reactions in the presence of MeCN and phosphines, and they afford the σ-alkynyl complexes $M(C{\equiv}CR)(CO)_2(dppe)(NO)$ when reacted with an equimolar amount of the acetylide salts $M'C{\equiv}CR$ (M′ = Li, Na).[125]

Interestingly, no well-defined nitrosyl products are accessible from reactions of $W(CO)_4(PR_3)(Ph_2PC_6H_4X\text{-}2)$ (X = NH_2 or CO_2H) complexes with $[NO]^+$ salts. Thermally unstable $[W(CO)_3(NO)(PR_3)(Ph_2PC_6H_4X\text{-}2)]^+$ derivatives can be synthesized via displacement reactions of weakly coordinated ligands ($[FPF_5]^-$ and MeCN) by $Ph_2PC_6H_4X$-2 from preformed nitrosyl species such as $W(CO)_3(NO)(PR_3)(FPF_5)$ and $[W(CO)_2(NO)(MeCN)_3]^+$.[126] However, they are prone to lose CO and readily transform to more stable species such as $[W(CO)_2(NO)(PR_3)(\eta^2\text{-}Ph_2PC_6H_4X\text{-}2)]^+$.[127] The 2-(diphenylphosphino)aniline cationic complexes having X = NH_2 can be deprotonated with hydride transfer reagents (e.g. $LiAlH_4$, $LiHBEt_3$, etc.) to obtain $W(CO)_2(NO)(PR_3)(\eta^2\text{-}Ph_2PC_6H_4NH\text{-}2)$ and $W(CO)_2(NO)(\eta^2\text{-}Ph_2PC_6H_4NH_2\text{-}2)(\eta^2\text{-}Ph_2PC_6H_4NH\text{-}2)$.[127] This chemistry has recently been extended to encompass pyridyl-functionalized phosphine ligands. Thus, substitution of CO ligands occurs when $P(2\text{-}py)_3M(CO)_3$ [$P(2\text{-}py)_3$ = tris(2-pyridyl)phosphine coordinated facially to the metal centers through three pyridyl N atoms] is treated with 1 or 2 equiv of $[NO][BF_4]$ in CH_3NO_2 to afford $[P(2\text{-}py)_3M(CO)_2(NO)][BF_4]$ and $[P(2\text{-}py)_3M(CO)(NO)_2][BF_4]_2$, respectively. Dissociation of the CO ligands from the dications generates the 16e species

$[P(2\text{-py})_3M(NO)_2]^{2+}$ that bind most Lewis bases, L, to give $[P(2\text{-py})_3M(L)(NO)_2]^{2+}$. The Lewis acidity of $[P(2\text{-py})_3M(NO)_2]^{2+}$ is estimated to be comparable to that of $TiCl_4$ when M = Mo and to BF_3 and $AlCl_3$ when M = W.[128] Furthermore, several cationic nitrosyl compounds incorporating mono- and bidentate coordinated pyridylphosphine ligands have also been isolated [e.g. *cis,cis*-$[W(CO)_2(NO)(Ph_2PR)(\eta^2\text{-}Ph_2PR][BF_4]$ (R = 2-pyridyl)], and some of these have been converted to neutral hydrido complexes [e.g. *trans, trans*-$HW(CO)_2(NO)(Ph_2PR)_2]$ by treatment with hydride transfer reagents.[129] Reaction of *N*,*N*′-bis(diphenylphosphino)-*N*,*N*′-bis(*p*-tolylsulfonyl)-1,2-ethanediamine (L−L) with *trans*-$W(CO)_4(NO)Br$ affords the corresponding *cis,cis,trans*-(L−L)$W(CO)_2(NO)Br$ complex, whose IR data suggest that the chelating ligand is about as electron-withdrawing as diphos-F_{20}.[130]

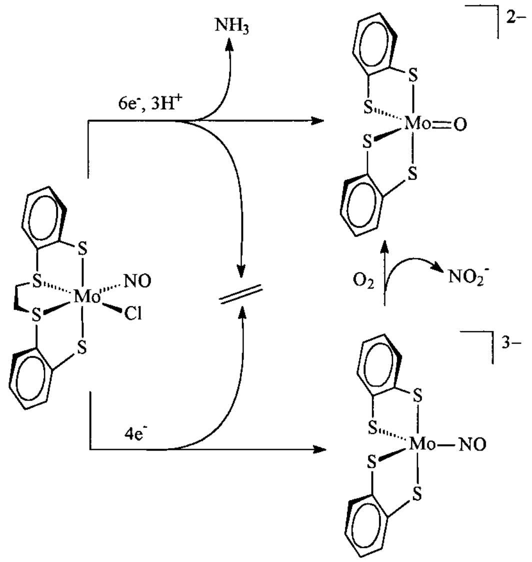
Binuclear molybdenum and tungsten carbonylnitrosyls bridged both by hydride and by bidentate phosphine ligands, e.g. $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)M_2(CO)_7(NO)$ (M = Mo, W; *n* = 1−5; shown below) and $(\mu\text{-H})(\mu\text{-}(Ph_2PCH_2)_3CMe)W_2(CO)_7(NO)$, have been prepared by nitrosylation of their anionic octacarbonyl precursors with 1 equiv of $[NO][BF_4]$ in CH_2Cl_2 at −60 °C.[131,132] Carbonyl ligand-substitution reactions of these bimetallic complexes[133] and the related $HW_2(CO)_9(NO)$ species[134−136] have been reported. The congeneric molybdenum complex, $(\mu\text{-H})Mo_2(CO)_9(NO)$, is preparable in 32% yield by treatment of $Na[HMo_2(CO)_{10}]$ with acidic $NaNO_2$, and it undergoes similar CO-substitution reactions with a variety of Lewis bases.[137]



It has been reported that $MoOCl_3(PPh_3)_2$ reacts with NO to give $Mo_2(\mu\text{-O})_2(\mu\text{-NO})_2(PPh_3)_4$[138] and that NO-bridged $Cs_2[Mo_2Cl_5H(\mu\text{-NO})_2]$ may be employed in the oxygenation of NO with insufficient oxygen.[139] It has also been reported that treatment of *cis*-(Ald)$Mo(CO)_4$ (Ald = aldimines) with NO affords mixtures of unusual (NO)(Ald)$Mo(CO)_2(NO_2)$ and $(NO)_2$(Ald)$Mo(NO_2)_2$ complexes, whereas ClNO yields only (Ald)$Mo(CO)_2(NO)Cl$.[140]

Numerous nitrosyl complexes of the group 6 metals with sulfur-dominated coordination spheres have been synthesized and characterized by Sellmann and co-workers, often in the quest for complexes modeling functional characteristics of metal sulfur oxidoreductases. Examples of such complexes include $Cr(NO)_x(\text{'}S_4\text{'})_y$ (*x* = 2, *y* = 1; x =1, *y* = 2), $[W(NO)_2(\text{'}S_2\text{'})_2]^{2-}$, W(L)(NO)('$S_4$') (L = NO, $NPMe_3$, $NPEt_3$), $(\mu\text{-O})[W(NO)(\text{'}S_4\text{'})]_2$, and MX(NO)('$S_4$') (M = Mo, W; X = Cl, SR, $NHNR_2$) in which 'S_2'$^{2-}$ = 1,2-benzenedithiolate(2−) and 'S_4'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2−).[141−143] Hydrolysis of MoX(NO)('S_4') complexes (X = Cl, Br, NMe_2, $NPMe_3$) affords $(\mu\text{-O})[Mo(NO)(\text{'}S_4\text{'})]_2$ in which the μ-oxo ligand acts as a σ,π donor to each metal center.[144] Redox-substitution reactions of Mo^{III}(SPh)(NO)('S_4') with phosphines yield the 17e complexes, $Mo^{II}(PR_3)$(NO)('S_4'), which can be oxidized or reduced electrochemically.[145] Alkylation of Mo(NO)(Cl)('S_4') by $[R_3O]^+$ (R = Me, Et) yields the monoalkyl derivatives, [Mo(NO)(Cl)(R-'S_4')]$^+$, and the chloro ligand in the neutral complex may be metathesized by thiolates.[146] Other Mo(L)(NO)('S_4') (L = SPh, PMe_3, or NO) complexes also undergo attack at one thiolate atom of the S_4 ligand when treated with electrophiles.[147] Molybdenum complexes of the type $[Mo(NO)(\mu\text{-'}S_4\text{'})]_2$, [Mo(NO)('$S_5$')]$^+$, and $Mo(NO)_2$('S_5'), where 'S_4' is a tetrathiadecane ligand and 'S_5' is a thioether thiolate ligand, are formed by treatment of their carbonyl precursors with $[NO]^+$ or NO, and the 'S_5' complexes form 1:1 adducts with PMe_3 and $[N_3]^-$.[148,149]

Scheme 6



A particularly interesting transformation involving a sulfur ligand on a nitrosyl complex is ethylene extrusion from the backbone of 1,2-bis(2-mercaptophenylthio)ethane (dttd) in Mo(NO)Cl(dttd) by electroreduction.[150] The nitrosyl dithiolene product, $[Mo(NO)(1,2\text{-}C_6H_4S_2)_2]^{3-}$, reacts with dioxygen to give free nitrite and the oxide, $[Mo(O)(1,2\text{-}C_6H_4S_2)_2]^{2-}$, in the presence of phenol. As illustrated in Scheme 6, multielectron reduction of Mo(NO)Cl(dttd) also releases ethylene and incurs the cleavage of the NO bond to give ammonia and the same oxide. More recently it has been shown that a mononuclear nitrosyl complex containing the S_2CPCy_3 ligand, $MoBr(NO)(CO)_2(S_2CPCy_3)$, can be prepared from $Mo(CO)_3(NCMe)_3$ in three steps: (1) nitrosylation with an excess of $[NO][BF_4]$; (2) addition of bromide with $[Ph_4P][Br]$ or $[Et_4N][Br]$; (3) ligand substitution by S_2CPCy_3.[151] The nitrosyl complex readily reacts with $M(CO)_3(NCR)_3$ (M = Mo, W) to give binuclear nitrosyl complexes, $(OC)_2(ON)Mo(\mu\text{-Br})(\mu\text{-}S_2CPCy_3)M(CO)_3$, which undergo CO-substitution reactions with phosphines and phosphites. Complexes with μ-PPh_2 ligands in place of μ-Br atoms are also known.[152]

Diethyldithiocarbamate complexes of the types $[Mo(Et_2NCS_2)(CO)_2(NO)X]^-$ and $Mo(Et_2NCS_2)(CO)(NO)L_2$ (X = halide or pseudohalide, L = Lewis base) exhibit solid-state molecular structures in which the stronger electron-withdrawing NO ligand prefers to be trans to the better electron donors such as $[NCS]^-$, $[N_3]^-$, or $[Br]^-$.[153] Reactions of NO with $W(phen)(CO)_2(SPh)_2$, $W(phen)(CO)_2(1,2\text{-}S_2\text{-arene})$, and $W(phen)(CO)_3(RSH)$ result in clean conversions to $W(phen)(CO)_2(NO)(SPh)$, $W(phen)(NO)_2(1,2\text{-}S_2\text{-arene})$, and $W(phen)(CO)_2(NO)(SR)$, respectively. The conversions are accompanied by the simultaneous eliminations of PhSNO, CO, and HNO from the respective reactants.[154]

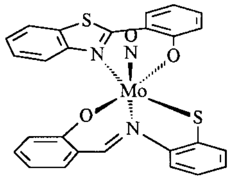
A new Prussian blue analogue composed of $K_{0.9}Mn^{II}_{1.05}[Mo^{I}(CN)_5(NO)]\cdot 5H_2O\cdot 1.9MeOH$ has been prepared.[155] It has a fcc structure, and it exhibits spontaneous magnetization with a Curie temperature of 39 K. Octahedral mixed-ligand cyanonitrosyl complexes of molybdenum, $Mo(NO)(CN)_3(L)_2$, are preparable by the interaction of the pentacyanonitrosylmolybdate(II) anion with various pyridine derivatives.[156] The reaction of $MoO_2(dedtc)_2$ (dedtc = *N,N*-diethyldithiocarbamate) with hydroxylamine in MeOH produces $Mo(NO)(dedtc)_3$.[157] The related $Mo(NO)(NS_3)$ ($NS_3 = N(CH_2CH_2S)_3{}^{3-}$) is obtained as a yellow, diamagnetic solid from the reaction of the diazenide $Mo(NS_3)(N_2Me)$ with NO.[158]

3.2.1.1. Dinitrosyl Complexes. The conversion of surface nitrosyl species to dinitrosyls at higher coverages has been observed by vibrational spectroscopy during the adsorption of NO on an oxygen-modified Mo(110) surface. The conversion of $NO_{(a)}$ to $(NO)_{2(a)}$ probably occurs via addition of a second NO molecule to terminally bound $NO_{(a)}$.[159]

It is well-known that $[NO][BF_4]$ reacts with $M(CO)_6$ (M = Mo, W) in MeCN to give $[M(NO)_2(MeCN)_4][BF_4]_2$.[160] An improved preparation of $Mo(NO)_2(S_2CNEt_2)$ involves treatment of its di- and tricarbonyl precursors with NO, a process that affords the desired compound in 75% yield.[161] Reaction of $Mo(CO)_2(NO)Br(\kappa^2\text{-}S_2CPCy_3)$ with an equimolar amount of $LiBHEt_3$ in THF or with excess $NaBH_4$ in THF/2-propanol provides the dinuclear complex $Mo_2(CO)_4(NO)_2(\mu\text{-}\kappa^2;\kappa^1\text{-}S_2C(H)PCy_3)_2$.[162] The solid-state molecular structure of this complex contains a cisoid disposition of two $[S_2C(H)PCy_3]^-$ ligands and a central quasicubane cage formed by two Mo, four S, and two C atoms.

The ethylidene complex $(AlCl_2)_2(\mu\text{-}OCHMe_2)_2Mo(NO)_2({=}CHMe)$ has been spectroscopically characterized and is reported to be an active catalyst for olefin metathesis. It is formed by the reaction of $[Mo(NO)_2(OCHMe_2)_2]_n$[163] with $EtAlCl_2$ in hexane−toluene, putatively via the 1:1 adduct $(EtAlCl_2)_2(\mu\text{-}OCHMe_2)_2Mo(NO)_2$.[164] Analogous complexes having μ-OR groups (R = Me, Et) can be prepared similarly.[165] In a similar manner, various dinitrosylmolybdenum complexes with Et_4Sn (alkylating agent) and $AlCl_3$ (Lewis acid) form catalytically active systems for olefin metathesis.[166,167] Related $Mo(NO)_2(OAc)_2\cdot MeOH$, $Na_2[Mo(NO)_2(OAc)_4]$, and $Mo(NO)_2(OBz)_2$ precursors have been prepared and examined similarly for such catalytic activity.[168] Finally, it may be noted that $Mo(NO)_2(O_2CR)_2$/Lewis acid catalysts (Lewis acid = $TiCl_4$, $SnCl_4$, $EtAlCl_2$) polymerize monosubstituted acetylenes. However, the catalytic ability of the catalyst and the nature of the products obtained (e.g. polymer or cyclotrimer) depend strongly on the Lewis acid and the solvent.[169]

A variety of $Mo(NO)_2(HL)_2$ complexes (H_2L = a Schiff base) are preparable by the metathesis reactions of $Mo(NO)_2(acac)_2$ with H_2L. The Schiff bases behave as monobasic bidentate ligands, coordinating to the metal center through the azomethine N and enolic O of the hydrazide moiety after deprotonation.[170,171] Tetradentate Schiff bases form the mononuclear complexes *trans*-$Mo(NO)_2(L')$ or ligand-bridged dinuclear complexes, *trans*-$[Mo(NO)_2(L')]_2$.[172] Similar synthetic methodology affords dinitrosylmolybdenum complexes of heterocyclic acids.[173] The ligand exchange reaction of $Mo(NO)_2(acac)_2$ with salicylaldehyde-2-mercaptoanil affords a product that simultaneously contains an azomethine ligand and its cyclic oxidation product (vide infra).[174] In related chemistry, octahedral $Mo(NO)_2(CN)_2L_2\cdot 2H_2O$ complexes can be obtained from the interaction of $[Mo(NO)_2(CN)_4]^{2-}$ with Lewis bases, L.[175−177]



Polymeric $[M(NO)_2Cl_2]_n$ (M = Mo, W) reacts with excess NaF in MeCN at room temperature and in the presence of 15-crown-5 to produce crystalline mixtures of $[Na_2(15\text{-crown-}5)_2(MeCN)][Mo(NO)_2Cl_4]$, $[Na(15\text{-crown-}5)]_2[Mo(NO)F_4Cl]$, $[Na(15\text{-crown-}5)]_2[W(NO)_2Cl_4]$, and $[Na(15\text{-crown-}5)]_2[W(NO)F_4Cl]$, respectively. The crystals can be separated by selection, and the complexes have been characterized by IR spectroscopy and X-ray crystallography.[178] Furthermore, reactions of $[Mo(NO)_2Cl_2]_n$ with PPh_3, $OPPh_3$, or Me_3SiNPR_3 (R = Et, Ph) in CH_2Cl_2 or MeCN suspension produce $[MoCl(\mu\text{-}Cl)(NO)_2(OPEt_3)]_2$, $[MoCl_3(NO)(OPPh_3)_2][MoCl_4(OPPh_3)_2]$, and $MoCl_2(NO)(PPh_3)_2(MeCN)$ as the nitrosyl-containing products, and these have been characterized by IR spectroscopy and X-ray crystallography.[179] The reactions of $[M(NO)_2Cl_2]_n$ (M = Mo, W) with unidentate (L) and bidentate (L_2) Lewis bases afford a variety of monomeric *cis*-$M(NO)_2Cl_2L_2$ complexes in 70−90% yields.[180−182] Similar $M(NO)_2X_2(HA)_2$ complexes (M = Mo, W; X = Cl, Br; HA = heterocarboxylic acid) have also been isolated from the reactions of $[M(NO)_2X_2]_n$ with HA.[183]

Reductive nitrosylation of molybdate(VI) by $NH_2OH\cdot HCl$ in ${}^{i}PrOH$ solutions gives dinitrosyl complexes, whereas only mononitrosyl complexes are formed in MeOH. These transformations permit complexes such as $Mo(NO)_2L_2Cl_2$, $[Mo(NO)_2(O^iPr)_2]_n$, and $Mo(NO)Cl(OMe)_2L_2$ (L = ROH, py; L_2 = phen) to be isolated from the final reaction mixtures.[163] The reaction of Na_2MoO_4 and $NH_2OH\cdot HCl$ with 8-quinolinol (QOH) gives an orange yellow solid from which $Mo(NO)_2(QO)_2$, $MoO_2(QO)_2$, $Mo(NO)(QO)_2$, and $Mo(NO)(NH_2O)(QO)_2$ can reportedly be obtained by repeated solvent extraction followed by column chromatography.[184] Related $Mo(NO)_2(HA)_2$ complexes (H_2A = benzohydroxamic acid, salicylhydroxamic acid) have been prepared by the reductive nitrosylation of $[NH_4]_6[Mo_7O_{24}]$ by $NH_2OH{\cdot}HCl$ in the presence of H_2A in aqueous aerobic conditions.[185] Chloride abstraction from the 1,10-phenanthroline complexes $M(NO)_2Cl_2(phen)$ by $AgClO_4$ in acetone produces $[M(NO)_2(phen)(acetone)Cl][ClO_4]$, and combination of these species with the related $[M(NO)_2(phen)(pyrazine)Cl][ClO_4]$ produces homo- and heterodinuclear complexes of the type $[Cl(phen)(NO)_2M(pyrazine)M(NO)_2(phen)Cl][ClO_4]_2$ (M = Mo or W) which have molecular structures of C_{2v} symmetry.[186,187] Oxo–nitrosyl polymetalates containing $[M(NO)_2]^{2+}$ units (M = Mo, W) of the type $[M_4O_{12}M(NO)_2\{RC(NH)NO\}_2\{RC(NH_2)NHO\}_2]^{2-}$ (R = hydrocarbyl or 2-thienylmethyl) have been prepared from monomeric precursors reacting with polyoxometalates, and they have been characterized by various techniques.[188,189] Reductive nitrosylation of $MoO_2(acac)_2$, $[Bu_4N]_2[Mo_6O_{19}]$, and $[Bu_4N]_2[Mo_4O_{12}(Me_2CNO)_2]$ by acetone oxime in MeOH or EtOH under reflux produces $Mo(NO)(acac)_2(Me_2CNO)$, $[Mo(NO)(OR)(Me_2CNO)_2]_2$, and $Mo_2(NO)_2(OR)_2Cl(Me_2CNO)_3(Me_2CNHO)$ (R = Me or Et), respectively.[190] The thus-formed $[Mo(NO)(OMe)(Me_2CNO)_2]_2$ reacts with $[Bu_4N]_2[Mo_2O_7]$ to yield $[Bu_4N]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$, thereby suggesting that reactions of Mo(II) nitrosyl complexes with polyoxomolybdates could well be a general route to a variety of oxo–nitrosyl species. Consistently, pentanuclear complexes $[Bu_4N]_2[M_4O_{12}M(NO)_2(H_2L)_2L_2]$ (M = Mo, W) have been obtained by the reactions of M(VI) polynuclear complexes with mononuclear M(0) dinitrosyls and methylthioamidoxime (H_2L), and they have also been structurally characterized.[191]

The doubly charged Lewis acid precursors $[HC(py)_3M(NO)_2(CO)][SbF_6]_2$ [M = Mo, W; $HC(py)_3$ = tris(2-pyridyl)methane] are conveniently synthesized by reaction of $HC(py)_3M(CO)_3$ with 2 equiv of $[NO][SbF_6]$.[192] Facile loss of CO from the precursors generates $[HC(py)_3M(NO)_2][SbF_6]_2$ in which the Lewis acidity of the tungsten complex is greater than that of the molybdenum complex. With the ^1H NMR chemical shifts of bound crotonaldehyde as a qualitative assessment of relative acidity, the acidity of the tungsten species is comparable to that of BF_3 and $AlCl_3$, while that of the molybdenum species is similar to that of $TiCl_4$. Analysis of the NMR spectra of Lewis acid–organic carbonyl base adducts show that η^1-M(O=C) interactions dominate the chemistry.[192]

Diastereospecific alkylation of $[Mo(NO)_2(\text{'}S_2\text{'})_2]^{2-}$ ('S_2' = 1,2-benzenedithiolate) by racemic 1,2-dibromopropane and 1,2-dibromobutane affords chiral $Mo(NO)_2(\text{'}RS_4\text{'})$ [R = Me, Et; 'RS_4'H_2 = 1,2-bis(2-mercaptophenylthio)alkane].[193] Finally, the complex $W(\eta^2\text{-mp})_2(CO)_3$ (mp = 2-S-C_5H_5N) reacts with gaseous NO to give $W(\eta^2\text{-mp})_2(NO)_2$ in quantitative yield.[194]

3.2.1.2. Clusters. The predominant product from the reaction between the complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ and $W(CO)_4(NO)I$ at 40–50 °C is the antiferromagnetic adduct $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(\mu\text{-}I)_2(CO)_4(NO)_2$, in which a sulfur atom bridges all four metal atoms. Further heating in the presence of an excess of the chromium reactant affords the trinuclear antiferromagnetic cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)W(SCMe_3)(NO)$, in which W–Cr = 3.090(1) Å and Cr–Cr = 3.027(1) Å.[195] In a related reaction, polymeric $[W(NO)_2Cl_2]_n$ reacts with $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ in benzene at 40 °C to form $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$. Thermolysis of this latter trimetallic cluster initiates both cluster formation and nitrosylation of the binuclear dichromium unit and results in the production of a plethora of products.[79] Of these, the triangular clusters $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)(X)$ (X = NO, Cl, and $SCMe_3$) merit particular mention.

The 12e alkoxide-supported tungsten clusters, $W_4(OR)_{12}$, react with NO in hydrocarbon solutions at 22 °C to produce $[W(OR)_3(NO)(py)]_2$ in the presence of pyridine.[196] The solid-state molecular structure of the complex having R = CH_2CHMe_2 is centrosymmetric, each W is in an octahedral coordination environment, and a pair of μ-OR bridges span a nonbonding W–W distance of 3.406(1) Å.[196]

An octahedral cluster, $Mo_6S_8(NO)(PEt_3)_5$, and a dodecahedral cluster, $Mo_{12}S_{16}(PEt_3)_{10}$, are obtained from the reaction of $Mo_6S_8(PEt_3)_6$ with $[NO][BF_4]$. The nitrosyl cluster exhibits a tetragonal distortion of its core such that the molybdenum atom bearing the NO ligand projects outward so as to enhance π-back-donation to the NO ligand.[197]

The CO ligands in $HW_2(CO)_9(NO)$ can be substituted by a range of phosphines and isonitriles.[198,199] Treatment of $HW_2(CO)_9(NO)$ with $[HW(CO)_5]^-$ results in the formation of $[(\mu\text{-}H)_2W_3(CO)_{13}(NO)]^-$ from which a carbonyl ligand can be displaced by a variety of Lewis bases, L, to form the corresponding $[(\mu\text{-}H)_2W_3(CO)_{12}(L)(NO)]^-$ anions.[200] Tetrameric clusters of Mo and W containing triply bridging hydroxide groups, i.e., $[M(CO)_2(NO)(\mu_3\text{-}OH)]_4$, result from reaction of the monoanionic tricarbonyl precursor with $[NO][BF_4]$.[201]

Nitrosyl derivatives of polyoxomolybdates and tungstates have been prepared with a view to studying (a) the change in electronic structure of the clusters arising from the replacement of a terminal π-donor oxo ligand by the very strong π-acceptor nitrosyl ligand, (b) the chemistry of the resulting M–N (M = Mo, W) multiple bonds, and (c) the clusters as possible models for pollution control.[202] Common sources of the nitrosyl ligand for the synthesis of these derivatives are NO itself, $[NO]^+$, nitrosyl halides, and hydroxylamine. The synthesis and X-ray diffraction characterization of nitrosyl derivatives of polyoxomolybdates have been recently reviewed.[202] Most of these derivatives contain the $Mo^{II}(NO)$ unit, and their structures are related to the following structural types: Lindqvist; Keggin; decatungstate $[W_{10}O_{32}]^{4-}$.

In a similar manner, the reactions of amidoximes with $MoO_2(acac)_2$ or α-$[Bu_4N]_4[Mo_8O_{26}]$ in alcohols or MeCN afford compounds with different nuclearities and various molybdenum cores. Addition of NH_2OH to the reaction mixtures gives nitrosyl complexes containing either the $Mo(NO)^{3+}$ or the $Mo(NO)_2^{2+}$ units.[203]

Reactions of NH_2OH with isopolyoxomolybdates in ROH afford nitrosylpolyoxomolybdates $[Mo_5O_{13}(OR)_4(NO)]^{3-}$ (R = Me or Et).[204] The $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ has approximately C_{4v} symmetry (i.e. a square pyramid of Mo atoms), contains an apical and linear Mo−NO unit, and may be viewed as deriving from the hitherto unknown lacunar $[Mo_5O_{18}]^{6-}$ Lindqvist anion. The sixth (octahedral) site is occupied by a $[Na]^+$ cation which interacts with the four terminal axial O atoms of the anion. The $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion is a convenient precursor for the synthesis of new nitrosyl polyoxomolybdates.[205] Thus, treatment with acetylacetone and tris(hydroxymethyl)ethane respectively produces the anions $[Mo_8O_{22}(NO)_2(acac)_2]^{4-}$ and $[Mo_6O_{10}(NO)_2\{MeC(CH_2O)_3\}_4]^{2-}$. The framework of the former anion is related to those of other derivatized octamolybdates of the $[Mo_8O_{26}X_2]^{2n-4}$ type, whereas the latter is made up of two $[Mo_3O_5(NO)\{MeC(CH_2O)_3\}_2]^-$ units connected by nearly linear Mo−O−Mo bridges, a relatively rare feature in polyoxometalates.[205]

In MeOH, the sodium salt of the monovacant Lindqvist-type nitrosyl polyoxomethoxomolybdate, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$, reacts with a number of divalent or trivalent cations, X, to yield 2:1 adducts $[X\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{n-}$ which are isolable as $[Bu_4N]^+$ salts. In these compounds the two $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anions provide an eight-coordinate (either cubic or square-antiprismatic) environment for the central cation, X. Some of the similar species containing the related $[W_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ anion have also been prepared.[206] The defect Lindqvist-type species, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$, can act both as a ligand and as a source of the $Mo(NO)^{3+}$ unit. This is illustrated by its reaction with various Ni(II) salts in MeOH to give $(Bu_4N)_2[\{Ni(MeOH)_2\}_2\{Mo(NO)\}_2(\mu_3\text{-}OH)_2(\mu\text{-}OMe)_4\{Mo_5O_{13}(OMe)_4(NO)\}_2]$. The product polyoxomolybdate is made of a central rhomblike $\{Ni_2Mo_2\}$ cluster linked to two terminal $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ units, each terminal cluster being linked to a molybdenum center of the central unit through two oxo ligands.[207]

Reaction of $[Bu_4N]_3[Mo_6O_{18}(NO)]$ with Me_2SO_4 in MeOH produces $[Bu_4N]_2[SMo_{12}O_{40}]$ and $(Bu_4N)_2[Mo_6O_{17}(OMe)(NO)]$.[208] X-ray diffraction has established that the $[Mo_6O_{17}(OMe)(NO)]^{2-}$ anion is structurally related to $[Mo_6O_{18}(NO)]^{3-}$ and $[Mo_6O_{19}]^{2-}$, but due to its location on an inversion center, only structural parameters for the disorder-averaged anion were obtained. The ^{95}Mo NMR spectra of the nitrosyl anions exhibit the expected numbers of Mo signals, although much effort was required to detect the $Mo^{II}(NO)$ signal. The diamagnetic Keggin derivatives $(Bu_4N)_4[PM_{11}O_{39}\{Mo(NO)\}]$ (M = Mo, W) can be synthesized in MeCN by reaction of the lacunary $[PM_{11}O_{39}]^{7-}$ species with either $(Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ or $[Mo(NO)(OMe)(Me_2CNO)_2]_2$ acting as the source of the $Mo^{II}(NO)$ unit.[209] The monosubstituted Keggin compounds $K_5[SiW_{11}O_{39}Ru^{III}(NO)]$[210] and $Cs_5[PW_{11}O_{39}Fe^{III}(NO)]$ are also known.[211] Reactions of $[Cp^*RhCl_2]_2$ with the abovementioned polyoxomolybdates in the presence of $AgNO_3$ afford Cp*Rh fragments bound to lacunar polyanions of the Lindqvist type via the four terminal oxygen atoms around the vacant site. Typical examples include $[Bu_4N][Mo_5O_{13}(OMe)_4(NO)\{RhCp^*(solv)\}]$ (solv = H_2O, MeOH) and $Mo_5O_{13}(OMe)_4(NO)\{(RhCp^*)_2(\mu\text{-}Cl)\}$.[212] The whole series of Lindqvist-type nitrosyl derivatives $[Bu_4N]_3[M_5O_{18}\{M'(NO)\}]$ (M, M′ = Mo, W) can be synthesized by the reaction of $Mo(NO)\{MeC(NH_2)NO\}(acac)_2$ or $W(NO)Cl_3(MeCN)_2$ with $[Bu_4N]_2[Mo_2O_7]$ or $[Bu_4N]_2[WO_4]$ in MeCN.[213] All four species are essentially localized mixed-valence complexes, with five d^0-M(VI) centers and one d^4-M′(II) center, with some electronic delocalization being indicated by NMR and electrochemical data.

Reduction of either $[Bu_4N]_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot x MeOH$ or $[Bu_4N]_3[Mo_6O_{18}(NO)]$ with various reducing agents, including $N_2H_4\cdot HCl$, in MeOH/MeCN yields nitrosyl decamolybdates, among which $[Bu_4N][Mo_{10}O_{25}(OMe)_6(NO)]$ and two forms of $[Bu_4N]_2[Mo_{10}O_{24}(OMe)_7(NO)]$ have been crystallographically characterized. Their molecular structures are closely related to that of $[W_{10}O_{32}]^{4-}$ and consist of two halves of five edge-sharing octahedra connected through four quasi-linear Mo−O−Mo bridges.[214] Both anions contain molybdenum atoms in three different formal oxidation states, namely Mo(II), Mo(V), and Mo(VI), with considerable electron delocalization among the eight equatorial Mo sites. This electron delocalization has been studied in great detail by DFT methods.[215]

In MeOH, the defect nitrosyl polyoxomolybdate, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$, reacts with $[Ag]^+$ to give $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$, which exhibits attractive Ag···Ag interactions between the two square-planar closed-shell Ag(I) cations.[216]

The tungsten oxo nitrosyl complexes $(Bu_4N)_2[W_5O_{12}(NO)_2\{RC(NH_2)NHO\}_2\{RC(NH)NO\}_2]$ (R = Me_2CH, $CH_3CH_2CH_2$, CH_3SCH_2) can be synthesized by the reactions of $[Bu_4N]_2[W_6O_{19}]$ and $[W(NO)_2(acac)(MeCN)_2][BF_4]$ with butylamidoxime derivatives.[217] The pentanuclear species is formed by the interaction of the electron-withdrawing $W(NO)_2^{2+}$ unit between the two dinuclear $W_2O_5^{2+}$ cores.

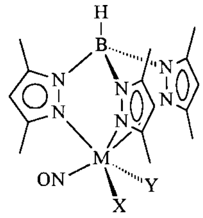
In recent years, giant clusters have received much attention because of their novel optical, electric, and magnetic properties. However, in most of these clusters, the NO groups merely function as spectator ligands. By utilization of reduction−oxidation−reconstitution, polymerization−reduction−polymerization, or stepwise substitution of magnetic centers methodologies, a series of nanoscale polyoxomolybdates such as $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$ ($\{Mo_{36}(NO)_4\}$), $[Mo_{57}V_6O_{180}(NO)_6(OH)_3(H_2O)_{18}]^{21-}$ ($\{Mo_{57}(NO)_6V_6\}$), $[Mo_{57}Fe^{III}6O_{174}(NO)_6(OH)_3(H_2O)_{24}]^{15-}$ ($\{Mo_{57}(NO)_6Fe^{III}6\}$),[218−222] $[Mo_{57}Fe^{II}6O_{177}(NO)_6(OH)_2(H_2O)_{22}(MoO)_2]^{18-}$ ($\{Mo_{57}(NO)_6Fe^{II}6\}$), and $[Mo_{154}O_{420}(NO)_{14}(OH)_{28}(H_2O)_{70}]^{(25\pm5)-}$ ($\{Mo_{154}(NO)_{14}\}$)[223] have been obtained.[224,225] Of these, $\{Mo_{154}(NO)_{14}\}$ is particularly interesting since it is the most spectacular giant polymolybdate structure that is still a discrete anion. It is preparable from $Na_2[MoO_4]$, NH_4VO_3, and $NH_2OH\cdot HCl$, and it is a water-soluble big wheel with more than 700 atoms whose cavity is broader at the equator (d = 20 Å at the narrowest point).[226]

Other recent developments in this area of chemistry include the following reports. Ultrathin multilayer films of the ammonium salt of $\{Mo_{57}(NO)_6V_6\}$ and poly(allylamine hydrochloride) (PAH) have been prepared by the consecutive stepwise adsorption of Mo_{57} and PAH from dilute aqueous solution.[227] The Mo_{57} density in the film can be readily controlled by varying the polyelectrolyte interlayer separation between each Mo_{57} layer, and the total film thickness can be controlled by altering the number of adsorption cycles. In addition, reaction of $\{Mo_{36}(NO)_4\}$ with $LaCl_3$ in the presence of $NH_4OH{\cdot}HCl$ gives a novel chainlike polymer, $[Mo_{36}O_{108}(NO)_4(MoO)_2La_2(H_2O)_{28}]_n{\cdot}56nH_2O$ in which the $\{Mo_{36}(NO)_4\}$ units are linked to each other by two parallel La atoms.[224] In a related transformation, reaction of $[H_3O]^+\{Mo_{36}(NO)_4\}$ with $NH_2OH{\cdot}HCl$ in refluxing water for ≤30 min affords a novel nanopolymer, $\{[H_3O]^+12\{(H_2O)MoO_{2.5}\{Mo_{36}(NO)_4\}O_{2.5}Mo(H_2O)\}^{12-}\}_n{\cdot}44nH_2O$, as red-brown monoclinic block crystals in ca. 80% yield. The structure of the polymer consists of one-dimensional covalently bonded chains of polyoxometalate clusters containing 38 Mo atoms.[228]

Finally, the new nanocompound $(NH_4)_{15}[H_3Mo_{57}V_6(NO)_6O_{189}(H_2O)_{12}(VO)_6]{\cdot}{\sim}60H_2O$ has recently been obtained by the introduction of six VO^{3+} units into the cavities of $\{Mo_{57}(NO)_6V_6\}$.[229]

3.2.1.3. Pyrazolylborate Complexes. There are several similarities between the physical and chemical properties of the poly(pyrazolyl)borate complexes described in this section and the related cyclopentadienyl systems that are considered in later sections of this review. In addition to forming many similar complexes, both ligands are uninegative, occupy three coordination sites, and formally donate six electrons to the central metals. Throughout this section the standard abbreviation system for poly(pyrazolyl)borate ligands is employed.[230] Thus, by convention, Tp* is used as the abbreviation for the frequently used tris(3,5-dimethylpyrazol-1-yl)hydroborato ligand, $HB(3,5\text{-}Me_2C_3N_2H)_3$. Otherwise, the basic $[HB(pz)_3]^-$ structure is denoted by Tp, and any non-hydrogen substituent in the 3-position is denoted by a superscript. Any non-hydrogen substituent in the 5-position follows the 3-substituent as a superscript separated by a comma. Thus, $[HB(3\text{-isopropyl-}5\text{-methylpz})_3]^-$ is denoted as $Tp^{iPr,Me}$, and $[HB(3,5\text{-diphenylpz})_3]^-$ is Tp^{Ph_2}. Since Tp* uniquely defines the position of the two methyl substituents, a substituent in the 4-position follows the asterisk; thus, $[HB(3,5\text{-dimethyl-}4\text{-benzylpz})_3]^-$ is simply Tp^{*Bz}.

By far, the largest amount of work with the Tp and Tp* ligands has been done with molybdenum and tungsten, usually starting with the easily prepared and versatile $[Tp'M(CO)_3]^-$ anions (Tp′ = Tp or Tp*). As with their Cp′ analogues, treatment of these anions with Diazald affords $Tp'M(CO)_2(NO)$ complexes which in turn are readily converted to $Tp'M(NO)X_2$ (X = F, Cl, Br, I) and $Tp'M(NO)_2Cl$ by reactions with halogen sources or ClNO, respectively. The halide ligands in the mononitrosyl dihalides may be exchanged by metathesis reactions with a wide variety of Lewis-basic reagents, Y, or anionic reagents, $[Y]^-$, to obtain $Tp'M(NO)(X)(Y)$ or $Tp'M(NO)Y_2$ mono- and polynuclear complexes that now constitute a large subarea of poly(pyrazolyl)borate chemistry. Recent examples of such metathesis reactions and the resulting products formed are presented in the following paragraphs. The bulk of this work has been performed by McCleverty and co-workers.

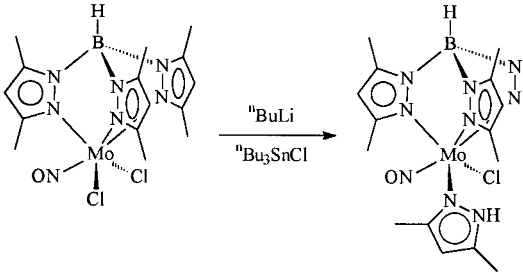


$Tp^*Mo(NO)I_2$ and its congeners react with cyclic ethers such as oxacyclobutane, THF, or oxacycloheptane in the presence of traces of moisture to produce diamagnetic alkoxide complexes, e.g. $Tp^*Mo(NO)I\{O(CH_2)_nI\}$ (n = 3, 4, 6, respectively).[231,232] The related alkoxide compounds $Tp^*Mo(NO)X(OR)$ and $Tp^*Mo(NO)(OR)_2$ (X = I, Cl; R = substituent containing a long alkyl chain) and their amide (NHR) analogues have been prepared, and all undergo 1-electron reduction processes.[233,234] The related $Tp^*Mo(NO)X(Q)$ (X = Cl, I, OR; HQ = cholesterol) compounds exhibit similar behavior.[235] The trends in reduction potentials of a number of similar complexes have also been determined.[236] These include complexes containing $Tp^*Mo(NO)Cl$ groups linked by saturated-α,ω-diamido bridging ligands[237,238] for some of which the first reductions occur at increasingly anodic potentials as the size of the bridging ligand is decreased. They also include $Tp^*M(NO)Cl(NHC_6H_4\text{-}3\text{-}Z)$ (M = Mo, W) systems whose first reduction potentials correlate linearly with the Hammett *meta* substituent parameters for Z.[239] $Tp^*Mo(NO)(O{-}O)$ compounds in which O−O represents a large (e.g. 14-member) chelate ring which forms a cyclic polyether structure are also known.[240]

By utilization of metathesis reactions of its dihalo precursors, the redox-active $Tp^*M(NO)X$ moiety (M = Mo or W; X = Cl, Br, or I) has been appended in monometallic $[Tp^*M(NO)(X)(Y)]$ or bimetallic $[Tp^*M(NO)(X)(\mu\text{-}Y)(X)(ON)MTp^*]$ complexes to entities Y such as an arylamino derivative of retinal,[241] protected and unprotected monosaccharides,[242] various alkoxides, amides, and β-diketonates,[243−248,249] bipyridine and bipyridylpolyene bridges,[250−253] extended polypyridyl-type bridging ligands,[254] extended diphenol bridging ligands,[255] glucofuranoside and galactopyranoside derivatives,[256] asymmetric bridging ligands containing a pyridyl and a phenolate donor,[257−259] a bridging S−S group,[260] a bridging O atom,[261−263] stilbenamide ligands carrying long-chain alkoxy substitutents,[264] stilbazoles,[265] ligands based on 4-hydroxyphenylalkanols,[266] a variety of mono- and bifunctional O- and N-donor ligands,[267−270] thiolates,[271] redox-active fluorenone-based ligands,[272] Schiff bases,[273] diolates,[274] and pyrazine.[275,276] On occasion, the related $Tp^*M(NO)(Y)$ derivatives of the systems listed in this paragraph have also been prepared and characterized during the above-cited studies.

The majority of these bimetallic complexes was prepared to examine their electrochemistry and to

Scheme 7



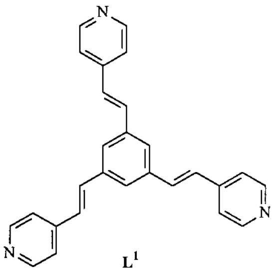
ascertain the extent of the electron−electron exchange interactions across the bridging ligands. For instance, the EPR spectra of the binuclear molybdenum complexes having bipyridine and bipyridylpolyene bridges all show that the two unpaired electrons (one at each 17e molybdenum center) are in rapid exchange across the bridging ligand at room temperature.[251] In a related study of Mo−Mo interactions through chains of four carbon atoms, it has been shown that the interactions are greatest for an alkene bridge and least for an alkane bridge.[277] Bimetallic complexes having dipyridyl and diphenol bridging ligands containing oligothienyl spacers show strong electrochemical interactions between the termini.[278] Similarly, bimetallic complexes which contain electron-donating ferrocenyl groups attached via conjugated bridges to electron-deficient Tp*Mo(NO)Cl fragments exhibit significant intercomponent interactions.[279] For the mixed-valence complexes Tp*Mo(NO)Cl-{O(C_6H_4)$_n$O}Mo(O)ClTp* (n = 1 or 2) and related species bridged by {OC_6H_4py} groups, spectroscopic data indicate that the nitrosylmolybdenum and oxomolybdenum centers are weakly interacting.[280]

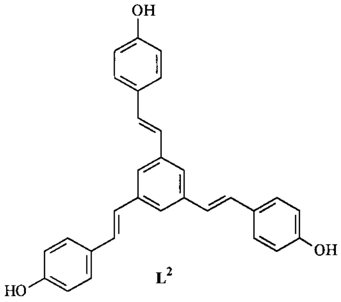
Tp*M(NO)X_2 complexes (M = Mo or W; X = Cl or I) react with (+)- and (−)-1-phenylethylamine to afford diastereomeric mixtures of TpM(NO)X-(NHCHMePh). These can be separated by chromatography, and the solid-state molecular structure of Tp*Mo(NO)I{(+)-NHCHMePh} reveals the absolute configuration at the metal center to be *S*.[281] The corresponding Tp*Mo(NO)Cl{(−)-Q} complex (HQ = menthol) exhibits an *R* absolute configuration at the metal.[282] Tp*Mo(NO)Cl_2 reacts with various reducing agents in the presence of $[Et_3NH]^+$ to afford $[Et_3NH]$-[Tp*Mo(NO)Cl_2], a 17e species that reacts with pyridine to form Tp*Mo(NO)Cl(py).[283] Spectroelectrochemical studies and molecular orbital calculations on the mononuclear, 17e Tp*Mo(NO)Cl(py) (py = a substituted pyridine derivative) complexes permit a rationale of the electrochromism exhibited by these species in the near-IR region of the electronic spectrum.[284] Furthermore, as illustrated in Scheme 7, reduction of Tp*Mo(NO)Cl_2 with ^{n}BuLi in the presence of ^{n}Bu$_3$SnCl affords paramagnetic, 17e Tp*Mo(NO)Cl(3,5-$Me_2C_3HN_2H$). Related Tp*Mo(NO)-(X)Q (Q = a pyrazole) can be prepared by the reduction of Tp*Mo(NO)X_2 by Q (X = I) or by ^{n}BuLi in the presence of Q (X = Cl).[285] In another study, He(I) gas-phase photoelectron spectroscopy of Tp*Mo(E)$(OR)_2$ (E = O, NO; R = Et, ^{i}Pr) reveals that the NO complexes (formally Mo(II)) are 0.8 eV more difficult to ionize than the O analogues (formally Mo(V)). This counterintuitive result has been ascribed to the differing π interactions of the NO and O ligands with the metal centers.[286]

The reaction of Tp*Mo(NO)Cl_2 with Cu(II), Ni(II), or Pd(II) Schiff-base complexes can afford bimetallic or trimetallic species containing two or three potential redox centers.[287,288] However, cyclic and differential pulse voltammetry measurements indicate that the trimetallic species primarily undergo two accessible sequential 1-electron reductions associated with the Tp*Mo(NO)Cl centers.[289,290] In related work, mononuclear Tp*Mo(NO)Cl(L) groups [L = a potentially bridging ligand of which one terminus (pyridyl or phenolate) is attached to the molybdenum and the second terminus (pyridyl) is pendant] have been attached to the axial positions of a Ru(tpp) core (tpp = *meso*-5,10,15,20-tetraphenylporphyrinate). By using Ru(tpp)(CO)(EtOH), of which only the axial EtOH ligand is substitutionally labile, binuclear complexes with Ru(μ-L)Mo linkages have been obtained. With Ru(tpp)$(THF)_2$, in which both THF ligands are labile, trinuclear Mo(μ-L)Ru(μ-L)Mo species result. The complexes exhibit weak electrochemical interactions between the molybdenum groups and the Ru(tpp) core.[291] In related work, the $[Ru(bipy)_3]^{2+}$ chromophore has been linked at the periphery to the electron-accepting Tp*M(NO)Cl fragments, and this results in complete quenching of the of the $d\pi$(Ru)−π^*(bipy) metal-to-ligand charge-transfer excited state at room temperature.[292]

Various Tp′Mo$(CO)_2$(NO) and Tp′Mo(NO)X_2 (Tp′ = $Tp^{p\text{-}MeOPh}$, $Tp^{iPr,Me}$, or Tp^{*R}; X = Cl, I, OMe, or OEt) complexes and related species having even bulkier Tp′ ligands[293] have been prepared and structurally characterized.[294−296] In addition, the solid-state molecular structures of $L_3Mo(CO)_2(NO)$ compounds in which L_3 is a uninegative nitrogen-tripod ligand derived from heterocyclic compounds including 1-*H*-pyrazole and 1-*H*-1,2,4-triazole have been determined.[297] The molybdenum atom remains in an octahedral coordination environment in all these complexes. However, an attempt to prepare $Tp^{iPr,Me}$Mo-$(CO)_2$(NO) produced instead {HB(O-^{i}Pr)R_2}Mo$(CO)_2$-(NO) (R = 3-isopropyl-5-methylpz) in which the alkoxy O atom of the isopropoxide group is bound to the boron and molybdenum atoms.[298] Interestingly, the spectral and electrochemical properties of Tp^{*Bz} nitrosyl complexes of Mo and W are virtually identical to their Tp* analogues, thereby indicating that the addition of a benzyl group has no significant electronic effect. Nevertheless, $Tp^{*Bz}Mo(CO)_2(NO)$ exhibits an unusual inverted bowllike structure.[299] The reduction potentials of $Tp^{p\text{-}MeOPh}$Mo(NO)Cl(ER) (E = O or NH; R = hydrocarbyl) complexes are similar to those of their counterparts containing the Tp* ligand. Furthermore, a comparison of the structures of 24 Tp^xMo(NO) complexes containing various substituents, x, in the 3-position of the Tp ligand indicates that variations in the steric demands of the ligand set are primarily accommodated by changes in the angles made at the molybdenum atom by the coligands rather than those made by the Tp ligand.[300] Recently, some B−B-linked “back-to-back” bis[tris-(pyrazolyl)borate] bridging ligands have been synthesized and used to prepare a variety of molybdenum complexes.[301]

More complex assemblies involving the Tp*M(NO)(X) fragments are also known. For instance, the trinuclear complexes of L^1 and L^2 (shown) with a paramagnetic Tp*Mo(NO)Cl at each binding site exhibit EPR spectra that demonstrate that all three electrons are in fast exchange between all three metal centers.[302]


L^1


L^2

This work has been subsequently extended to encompass other di-, tri-, and tetranucleating pyridyl ligands which facilitate multicenter magnetic exchange between paramagnetic Mo centers.[303] Metal-directed reactions involving the octahedral precursor complexes $Tp^*M(NO)I_2$ (M = Mo, W) and 1,4-dihydroxybenzene result in the formation of metallocyclophanes, $[Tp^*M(NO)(O_2C_6H_4)]_3$, containing triangular arrays of interacting redox-active octahedral metal centers.[304] The corresponding reaction with 2,7-dihydroxynaphthalene affords binuclear $[Tp^*Mo(NO)(2,7\text{-}O_2C_{10}H_6)]_2$ as its major product,[305] but with xylenedithiols and related species, mono-, bi-, tri-, and tetranuclear metallocyclophanes can be formed.[306−308] The reaction between $TpMo(NO)I_2$ and tetrahexylcalix[4]resorcinarene affords contained molecules in which two, three, or four TpMo(NO) units are incorporated into the rim to produce a host site. An X-ray crystallographic analysis of the tetrametalated derivative reveals that one nitrosyl ligand forms a hydrogen bond with a CH_2Cl_2 guest molecule included in the host site.[309,310] Similar Tp*Mo(NO)Cl complexes of new pyridyl-based tetranucleating bridging ligands have been described. One of these has a tetrahedral donor set, whereas the other contains two orthogonal noninteracting components.[311] More recently, trinuclear molybdenum nitrosyl complexes containing Tp*Mo(NO) groups have been synthesized by using various di- and trinucleating ligands.[312]

Nonlinear and potential nonlinear optical materials containing the molybdenum and tungsten mononitrosyl redox centers in Tp′M(NO)(X)(L)-type complexes have been synthesized. These include stilbene derivatives containing ferrocenyl, methoxy, or dimethylamino donor groups[313] and diaromatic azo derivatives.[314] The ferrocenyl derivatives frequently exhibit second harmonic generation upon irradiation at 1907 nm, whereas the other derivatives containing NMe_2 or OR groups (R = Me or Et) are generally inactive. The monomolybdated metalloligand $Tp^*Mo(NO)(Cl)(OC_6H_4PPh_2\text{-}p)$ can be viewed as a modified triphenylphosphine ligand and can be used to generate novel transition-metal complexes in which electron transfer and magnetism are embedded within a stable ligand framework.[315]

$Tp^*Mo(NO)I_2$ reacts with the oligochalcogenides $[NH_4]_2S_{10}$ and $[Et_4N]_2Se_6$ in THF to produce the mononuclear cyclopentachalcogenido complexes $Tp^*Mo(NO)(E_5)$ (E = S, Se) and with H_2E to form the binuclear chalcogenido-bridged products $Tp^*{}_2Mo_2(NO)_2(\mu\text{-}E)_2$.[316] The solid-state molecular structure of $Tp^*Mo(NO)(Se_5)$ exhibits a six-membered $MoSe_5$ metallacycle in the chair conformation and a linear Mo−N−O linkage.

Symmetrically substituted $[TpMo(CO)(NO)(\pi\text{-allyl})]^+$ complexes are preparable from the corresponding $TpMo(CO)_2(\pi\text{-allyl})$ precursors by treatment with $[NO][BF_4]$ in MeCN at 0 °C. The $[BF_4]^-$ salts are unstable in solution but can be stabilized by the noncoordinating counterion $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$ (BAr^f4^-).[317] The solid-state molecular structure of $[TpMo(CO)(NO)(\eta^3\text{-}C_3H_5)][BAr^f4]$ exhibits a significant $\eta^3 \rightarrow \eta^2$ distortion of the allyl moiety that persists in solutions.

Finally, in related chemistry, $[L_3Mo(NO)Cl_2][PF_6]$ ($L_3 = N,N',N''$-trimethyl-1,4,7-triazacyclononane) reacts with MeOH to give $[L_3Mo(NO)(Cl)(OMe)][PF_6]$, but the reaction with 4-ferrocenylphenol results in reduction rather than phenoxide formation. On the other hand, $[L_3Mo(NO)Br_2][PF_6]$ reacts with 4-amino-2-methyl-4′-ferrocenylazobenzene (Q) to give a bimetallic complex, $L_3Mo(NO)Br_2Q$, that contains a 7-coordinate paramagnetic molybdenum center ($\mu_{eff} = 3.13$).[318]

3.2.2. Organometallic Complexes

Treatment of $Cp'M(CO)_3Cl$ (Cp′ = Cp, MeCp; M = Mo, W) with equimolar amounts of $Na[Fe(CO)_3(NO)]$ at ambient temperatures yields the following complexes which are separable by column chromatography: orange $Cp'M(CO)_2(NO)$; violet $[Cp'M(CO)_3]_2$; black $Cp'M(\mu_3\text{-}NH)(\mu_2\text{-}NO)(\mu_2\text{-}CO)Fe_2(CO)_6$.[319−321] The addition of $[NO][BF_4]$ to solutions of $Cp_2Mo_2(CO)_4(\mu\text{-}RCCR')$ effects substitution of one of the carbonyl ligands and produces $[Cp_2Mo_2(CO)_3(NO)(\mu\text{-}RCCR')][BF_4]$ (R, R′ = CO_2Me, Me, or H).[322] Similarly, the bimetallic complexes $[Cp'_2Mo_2(\mu\text{-}PPh_2)_2(O)(NO)][BF_4]$ (Cp′ = Cp or $\eta^5\text{-}C_5H_4CO_2Me$) result from treatment of their neutral carbonyl precursors with $[NO][BF_4]$.[323]

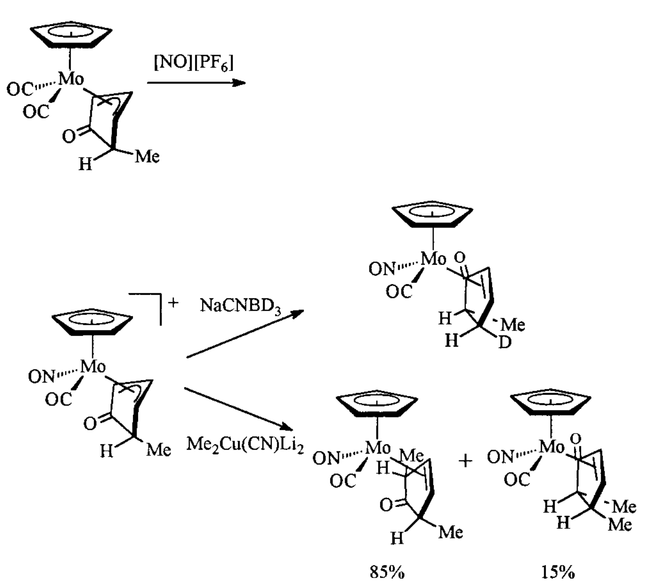
The most convenient synthetic route to the $CpM(CO)_2(NO)$ complexes (M = Mo, W) involves treating $M(CO)_6$ with NaCp in $THF-{}^nBu_2O$ to obtain the salts $Na[CpM(CO)_3]$, which when treated with Diazald $[4\text{-}MeC_6H_4SO_2N(NO)Me]$ in THF give good yields of the dicarbonyl nitrosyls.[324] Similar synthetic methodology may be employed to prepare the analogous *cis*- and *trans*-dimolybdenum complexes, $\{Mo(CO)_2(NO)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}$, which contain the bridging bis(dimethylsilanediyl)bis(η^5-cyclopentadienyl) ligand.[325] Analysis of the microwave spectrum of $CpW(CO)_2(NO)$ affords the following structural parameters for this “piano-stool” molecule: Cp−W = 2.06(3) Å; Cp−W−N = 122.7(10)°; Cp−W−CO = 123.2(10)°. The difference between the nitrosyl and carbonyl angles with respect to the Cp symmetry axis is much smaller for this complex than for its chromium congener.[326] The electron impact (EI) and multiphoton ionization (MPI) mass spectra of CpMo(CO)$_2$(NO) have been recorded, and they reveal that primary loss of CO ligands from molecular ions is favored over NO or Cp elimination.[327]

Photodecarbonylation of Cp*Mo(CO)$_2$(NO) in CH$_3$CN in the presence of sulfur or selenium gives the binuclear derivatives Cp*$_2$Mo$_2$(NO)$_2$(μ-η^1,η^2-E$_2$)$_2$ (E = S, Se) which are also obtained by treating Cp*Mo(NO)I$_2$ with H$_2$S or H$_2$Se, respectively.[77] The analogous reactions of Cp*W(NO)I$_2$ with H$_2$S and H$_2$Se afford the cyclopentasulfido and -selenido complexes, Cp*W(NO)(E$_5$) (E = S, Se), as well as some non-nitrosyl products.

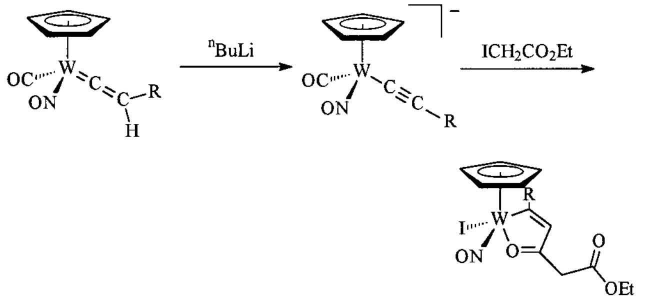
In contrast to suggestions in the literature that ether solvents are incompatible with nitrosonium salts, treatment of CpM(CO)$_2$(η^3-allyl) complexes with solid [NO][PF$_6$] in 1,2-dimethoxyethane at -10 °C produces analytically pure [CpMo(CO)(NO)(η^3-allyl)][PF$_6$] as yellow solids.[328] The related allyl(carborane)nitrosyl complex, *closo*-3-(η^3-C$_3$H$_5$)-3-(CO)-3-(NO)-3,1,2-MoC$_2$B$_9$H$_{11}$, is also obtained by treatment of its dicarbonyl precursor with [NO][BF$_4$] in CH$_2$Cl$_2$ at room temperature. Attack of nucleophiles at the allyl ligand of the carborane complex affords the corresponding η^2-alkene derivatives, e.g. the [*closo*-3-(η^2-CH$_2$=CHEt)-3-(CO)-3-(NO)-3,1,2-MoC$_2$B$_9$H$_{11}$]$^-$ anion from the reaction with [Me]$^-$.[329]

It is well-known that the CO and NO ligands in a [CpMo(CO)(NO)(η^3-allyl)]$^+$ complex exert differential electronic effects on the allyl ligand and thereby control the regiochemistry of nucleophilic attack. Hence, the synthetic challenge is to arrange the appropriate terminus of the allyl to have the relationship to the nitrosyl group that will result in attack at the desired location. Thus, for [CpMo(CO)(NO)(η^3-allyl)]$^+$ cations, nucleophilic addition occurs at the unsubstituted end of the allyl, and an *E*-olefin with no newly created chiral centers is formed. Sequential addition of two different nucleophiles to these cations, however, creates these chiral centers in alkyl ligands.[330] Finally, addition of nucleophiles to homochiral [(neomenthyl-Cp)Mo(NO)(CO)(phenylallyl)]$^+$ complexes yields chiral olefins in high enantiomeric purity. These principles have also been applied to the stereospecific functionalization of (π-allyl)Mo complexes derived from cyclopentenone (vide infra).[331] Thus, electrophilic [CpMo(NO)(CO)(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]$^+$ reacts with nucleophiles (e.g. higher order cuprates, malonates, enolates, and cyanoborodeuteride) to form CpMo(NO)(CO)(η^2-alkene) complexes of 4-substituted 2-cyclopentenones in good to excellent yields and with high regioselectivity (Scheme 8). High yield oxidative demetalation with ceric ammonium nitrate provides the 4-substituted cyclopentenones. This chemistry has been extended to encompass the synthesis of disubstituted cyclopentenones,[331] and similar transformations have recently been utilized as a new synthetic approach to *C*-glycosides.[332]

Scheme 8



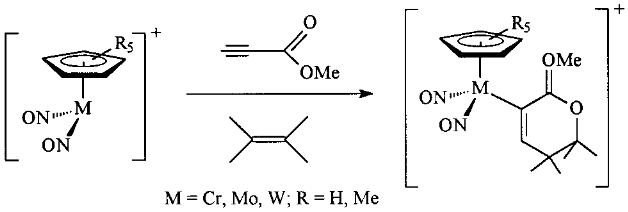
Reaction of CpM(CO)$_2$(NO) with LiC≡CR and subsequent addition of an electrophile leads either to a (vinylidene)- or an (η^2-alkyne)metal complex.[67] Cp(CO)(NO)M=C=C(R)(R′) derivatives are formed when alkyl or aryl acetylides (R = alkyl or Ph) and either a C-electrophile or dilute acid (R′ = Me or H) are used. The acetylene complexes Cp(CO)(NO)M(RC≡CR′) (R = SiMe$_3$, Me, allyl, Ph; R′ = SiMe$_3$) are formed either when LiC≡CSiMe$_3$ is used and the addition product is trapped by allyl bromide, triflate, or Me$_3$SiCl or when the addition product of LiC≡CPh with the dicarbonyl nitrosyl is trapped by Me$_3$SiCl.[67] Furthermore, treatment of the η^1-acetylide anionic complexes [Cp(CO)(NO)WC≡CR]$^-$ with ethyl iodoacetate in THF at -78 °C affords, after protonation with dilute acids, the corresponding oxametallacyclopentadienyl complexes, CpW(I)(NO)[η^2-O=C(CH$_2$COOEt)CH=CR], i.e.[333]



Reactions of Cp(NO)(CO)W=C=CH(R) (R = H, Me, Ph) with Ph$_2$PCl produce the metallacycles Cp(NO)(CO)W(*C*=CH(R)*P*Ph$_2$),[334] while treatment of Cp(NO)(CO)W=C=CH(^{t}Bu) with excess NH$_2$(^{i}Pr) yields Cp(NO)(CO)W=C(CH$_2$(^{t}Bu))(NH(^{i}Pr)).[335]

Chiral-at-metal carbene complexes Cp(CO)(NO)Mo=(C(CMe=CH$_2$)(NRCH$_2$(2-furyl)) can be synthesized from CpMo(CO)$_2$(NO) via the familiar nucleophilic addition/alkylation/aminolysis sequence. The N-alkylated analogues (i.e. R = Me, CH$_2$Ph) undergo intramolecular Diels–Alder reactions upon warming to give isoindole derivatives.[336] These molybdenum carbenes are less reactive than their analogues containing a (MeCp)Mn(CO)$_2$ or a W(CO)$_5$ fragment.

Reaction of the Cp′M(CO)$_2$(NO) precursors with 1 equiv of ClNO affords the corresponding dinitrosyl chlorides, Cp′M(NO)$_2$Cl. Chloride abstraction from Cp′M(NO)$_2$Cl (Cp′ = Cp, Cp*; M = Cr, Mo, W) with an equimolar amount of AgBF$_4$ in CH$_2$Cl$_2$ generates reactive solutions of Cp′M(NO)$_2$BF$_4$ which behave as though they contain the formally 16e [Cp′M(NO)$_2$]$^+$ cations.[337] Thus, all the CpM(NO)$_2$BF$_4$ complexes abstract a Ph group from the [BPh$_4$]$^-$ anion to form the known CpM(NO)$_2$Ph compounds, and CpW(NO)$_2$BF$_4$ catalyzes the oligomerization of α-methylpropene. Furthermore, methyl propiolate and 2,3-dimethyl-2-butene condense regiospecifically in the coordination spheres of all the [Cp′M(NO)$_2$]$^+$ cations to produce the cationic lactone complexes shown as follows:



M = Cr, Mo, W; R = H, Me

These cations undergo facile O-demethylation reactions upon exposure to an acetone solution of NaI. The resulting η^1-lactone-containing organometallic compounds have all been fully characterized by conventional spectrosopic techniques, and the neutral CpMo lactone complex liberates the iodolactone from the molybdenum's coodination sphere upon treatment with iodine.[337] In a similar manner, the 16e [Cp*M(NO)$_2$]$^+$ cations mediate the regioselective and stoichiometric assembly of iodopyrones from HC≡CCO$_2$Me, RC≡CPh (R = Me, Et), and I$_2$.[92]

Cp′Mo(NO)$_2$(CH$_2$X) complexes (Cp′ = Cp, Cp*; X = Cl, Br) are isolated in 80−90% yield after the treatment of the Cp′Mo(NO)$_2$X complexes in THF with ethereal CH$_2$N$_2$ in the presence of copper powder.[338] The analogous CH$_2$I complexes are obtained in >90% yield by treating the CH$_2$Cl derivatives with NaI in THF. The structural and IR data indicate the donor properties of the halomethyl ligands to be intermediate between halide and alkyl ligands. The Cp′Mo(NO)$_2$(CH$_2$X) complexes react initially with O$_2$ to give CH$_2$O and regenerate the parent Cp′Mo(NO)$_2$X compounds, whereas the Cp′Mo(NO)$_2$Cl complexes react with O$_2$ after an induction period to give the well-known Cp′Mo(O)$_2$Cl complexes as well as NO$_2$, ClNO, and N$_2$O.[338] Some molybdenum and tungsten complexes containing the *cis*-[M(NO)(N$_2$Ar)]$^{2+}$ structural unit which are the formal analogues of the M(NO)$_2$ systems considered above have been reported.[339]

CpMo(NO)$_2$CF$_3$ is obtainable by the interaction of Cd(CF$_3$)$_2$·glyme with CpMo(NO)$_2$Cl at 65 °C. However, the congeneric tungsten complex is not afforded by the analogous reaction with CpW(NO)$_2$Cl.[85] CpMo(NO)$_2$CF$_3$ reacts immediately upon exposure to air, and under an inert atmosphere it begins to decompose noticeably within 10 h at ambient temperatures.

3.2.2.1. Cp′M(NO)X$_2$ Complexes. These systems and their organic derivatives have been studied extensively in recent years. The mononitrosyl Cp′M(NO)X$_2$ compounds (X = Cl, Br, I) of molybdenum and tungsten are obtainable by the reaction of their dicarbonyl precursors with the appropriate halogenating agent, PCl$_5$ being a particularly useful chlorinating agent.[340] These compounds are monomeric in solution, but in the solid state may exist as monomers or dimers depending on the nature of Cp′, M, and X.[1,341] In a similar manner, the hydroxo derivative [CpMo(NO)I]$_2$(μ-OH)$_2$ is a dimer in the solid state.[342] The Cp′M(NO)X$_2$ compounds are precursors to a host of other compounds containing the Cp′M(NO) fragments. Thus, treatment with [NO]$^+$ or [Ag]$^+$ salts in MeCN affords a series of diamagnetic cationic nitrosyl complexes, [Cp*Mo(NO)(NCMe)$_3$]$^{2+}$ and [Cp′M(NO)Cl(NCMe)$_2$]$^+$, which can be isolated as their [PF$_6$]$^-$ or [BF$_4$]$^-$ salts. The physical and spectroscopic properties of these organometallic cations are consistent with their possessing four-legged piano-stool molecular structures.[81]

Treatment of Cp*M(NO)Cl$_2$ with arylamines, ArNH$_2$ (Ar = Ph, *o*-tolyl, *p*-tolyl), affords the 18e adducts Cp*M(NO)Cl$_2$(NH$_2$Ar), which can be dehydrohalogenated with a strong base to produce the amido chloro complexes Cp*M(NO)(NHAr)Cl (M = Mo, W) in good yields. Interestingly, treatment of Cp*M(NO)Cl$_2$ with excess primary alkylamines produces directly the amido chloro complexes Cp*M(NO)(NHR)Cl (R = alkyl). Mixed alkyl amido and alkoxo amido complexes are preparable by sequential treatment of Cp*M(NO)Cl$_2$ with 1 equiv of an alkylating reagent or lithium alkoxide followed by treatment with excess alkylamine.[343] Similarly, stepwise treatment of Cp*M(NO)Cl$_2$ in THF at low temperatures with 2 equiv of alkoxide anion affords first Cp*M(NO)(OR)Cl and then Cp*M(NO)(OR)$_2$ in reasonable yields. Alkoxo alkyl complexes are preparable from the corresponding alkyl chloro precursors by similar metatheses.[344] Finally, treatment of Cp*M(NO)(X)Cl complexes (X = CH$_2$SiMe$_3$, CH$_2$CMe$_3$, NHCMe$_3$, OCMe$_3$, Cl) with lithium phosphides results in either chloride metathesis, reduction of the starting material, or scrambling of the ligands of the starting complex.[345]

The three related complexes Cp*W(NO)(CH$_2$CMe$_3$)(NHCMe$_3$), Cp*W(NO)(OCMe$_3$)(NHCMe$_3$), and Cp*W(NO)(OCMe$_3$)(CH$_2$CMe$_3$), which differ only in the nature of the pair of groups α to the metal center, have been treated with ^{t}BuNC, *p*-tolylNCO, and CS$_2$ to establish the relative tendencies of the W−C, W−N, and W−O linkages to undergo insertions of these reagents.[346] The only site of insertion for ^{t}BuNC is the W−C bond, the W−N and W−O bonds being unreactive toward this substrate. In contrast, the preferential site of insertion for *p*-tolylNCO and CS$_2$ is W−N > W−O > W−C and W−N ≈ W−C > W−O, respectively. These observations can be rationalized in terms of two different mechanisms being operative, one involving initial adduct formation at the metal center and the other involving direct attack at the tungsten−element bond undergoing the insertion.

The reaction of CpMo(NO)I$_2$ with the mercury derivatives of substituted *N*,*N*-dimethylbenzylamines [Hg(Qdmba)$_2$] affords the complexes CpMo(NO)(I)(Qdmba) in nearly quantitative yield as a racemic mixture of both enantiomers. When the reaction is carried out with Hg{SC$_6$H$_4$C(H)(Me)NMe$_2$}$_2$, a 1:1

mixture of both diastereoisomers is obtained, and the resolution of this mixture can be accomplished by fractional crystallization from CH_2Cl_2/hexane.[347] In a related study, the resolution of the chiral metal center in CpMo(NO)(*syn*-crotyl)((1*S*)-10-camphorsulfonate) was also effected by fractional crystallization. An X-ray crystallographic analysis of the (−)-diastereomer revealed an *S* configuration at the metal.[342] The chiral chelate complexes Cp′Mo(NO)I(α-aminocarboxylate) have also been obtained as mixtures of isomers by metathesis reactions of their diiodo precursors.[348]

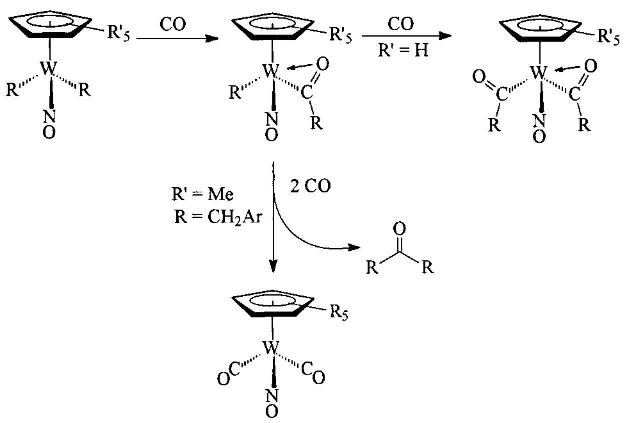
The Cp*M(NO)I_2 complexes react with dithiocarbamates, Na[S_2CNR_2] (R = Me, Et), in THF to form the corresponding Cp*M(NO)I(S_2CNR_2) complexes in high yields.[349] Similar treatments with phosphinodithioate (Na[S_2PMe_2]) and phosphorodithioate ([NH_4][$S_2P(OMe)_2$]) effect metathesis of one or both iodo groups in the diiodo reactants.

The ortho-metalated phosphine complex Cp*W(NO)(H)(η^2-$PPh_2C_6H_4$) undergoes reductive elimination of the aryl and hydride ligands in the presence of two-electron donors, L, to give compounds Cp*W(NO)(PPh_3)(L) (L = isocyanides, ketones, EtOAc, or PMe_3) in excellent yields. Spectroscopic data for the product complexes reveal that the 16e Cp*W(NO)(PPh_3) fragment is an exceptionally strong π-donor, coordinating the C=O linkages of the ketone and ester ligands in an η^2-fashion. Interestingly, the PMe_3 reaction also affords the phosphine substitution product Cp*W(NO)(H)(PMe_3)(η^1-$C_6H_4PPh_2$).[350]

The halide ligands in the Cp′M(NO)X_2 complexes may be replaced sequentially by various hydrocarbyl groups, R, to obtain a wide range of Cp′M(NO)(R)X and Cp′M(NO)R_2 complexes.[351,352] Cp*W(NO)(CH_2SiMe_3)$_2$ may also be utilized as a precursor for the synthesis of asymmetric Cp*W(NO)(CH_2SiMe_3)R (R = alkyl, aryl) complexes via Cp*W(NO)(CH_2SiMe_3)Cl.[353] In general, these hydrocarbyl complexes are monomeric, 16e species that react with a number of small molecules. For instance, hydrolyses of Cp′Mo(NO)R_2 complexes generally afford bimetallic [Cp′Mo(NO)R]$_2$(μ-O) compounds which possess linear Mo−O−Mo linkages.[354] Similar hydrolyses occur for the tungsten analogues. The initial investigations of the characteristic chemistry of the Cp′M(NO)R_2 complexes have been previously summarized.[355,356] More recent results are presented below. Under certain conditions these complexes undergo nitrosyl N−O bond cleavage during their chemical transformations,[357] and these processes are considered in a subsequent section of this review.

The 16e Cp′M(NO)R_2 complexes react with CO in a stepwise fashion as illustrated in Scheme 9.[358] The first step involves the formation of 18e monoacyl species Cp′M(NO)(η^2-C{O}R)R, via initially formed Cp′M(NO)(CO)R_2 adducts. The η^2-acyl complexes may be isolable as such or may undergo spontaneous reductive elimination of the symmetrical ketone. The second step involves the uptake of a second 1 equiv of CO and the formation of the 18e bis(acyl) complex, Cp′M(NO)(η^2-C{O}R)(COR), again via an initially formed carbonyl adduct. The outcomes of the reactions are dependent on both the natures of Cp′, R, and M and the experimental conditions employed. Thus, various acyl complexes of tungsten can be obtained in this manner, but all molybdenum systems investigated convert to Cp′Mo$(CO)_2$(NO) and R_2CO when exposed to CO.[358] Consistently, the asymmetric complexes Cp*W(NO)(R)(R′) (R, R′ = alkyl, aryl) insert 1 equiv of CO regioselectively into their W−C σ bonds to produce the corresponding η^2-acyl complexes. All complexes containing a Me_3SiCH_2 ligand form enolate species Cp*W(NO)(R)(OC{=CH_2}$SiMe_3$), probably via formation of an intermediate acyl complex and subsequent rearrangement via a 1,2-silyl shift. The relative migratory aptitudes of the various ligands (i.e. CH_2CMe_3 > CH_2SiMe_3 > *o*-tolyl > Ph > Me) appear to be primarily a function of the steric bulk of the ligand, the most sterically demanding ligands migrating to CO preferentially.[359]

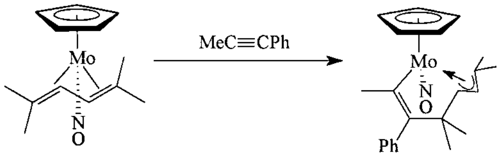
Scheme 9



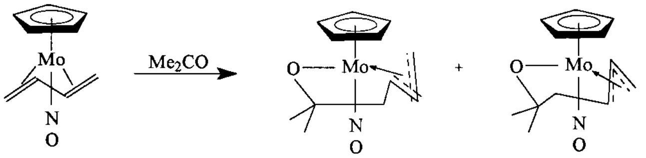
In the three series of complexes Cp*M(NO)Cl_2, Cp*M(NO)(R)Cl, and Cp*M(NO)R_2 (M = Mo, W; R = CH_2CMe_3) the molybdenum complexes are the stronger Lewis acids, and the mononeopentyl derivatives for both metals are more reactive toward a variety of substrates (e.g. CO, $CNCMe_3$) than are their bis(neopentyl) analogues.[360] Interestingly, the phosphine complexes Cp*M(NO)(CH_2CMe_3)(Cl)(PMe_3) are readily dehydrohalogenated by lithium diisopropylamide in THF to afford the cyclometalated complexes (η^5,η^1-$C_5H_4CH_2$)M(NO)(CH_2CMe_3)(PMe_3). In related chemistry, it has been shown that treatment of solutions of Cp*M(NO)(η^2-CH_2Ph)Cl (M = Mo, W) with an equimolar amount of solid $AgBF_4$ in MeCN affords the orange complexes [Cp*M(NO)(η^2-CH_2Ph)(NCMe)][BF_4] in good yields. Similar treatment with silver carboxylates produces Cp′M(NO)(η^1-CH_2Ph)(η^2-O_2CR) compounds for both Cp and Cp* systems.[361]

The heterocumulenes carbon disulfide, *p*-tolyl isocyanate, and carbon dioxide insert into one of the M−C σ-bonds of Cp*M(NO)$(aryl)_2$ complexes to produce η^2-thiocarboxylate-, η^2-amide-, and η^2-carboxylate-containing complexes, respectively.[362] Furthermore, Cp*W(NO)(η^2-S_2CPh)(Ph) reacts with PMe_3 to form Cp*W(NO)[η^2-$S_2C(PMe_3)Ph$](Ph), which contains a zwitterionic phosphonium betaine ligand.

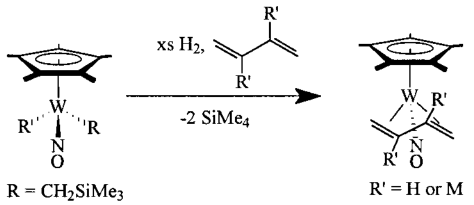
Reduction of [Cp*Mo(NO)I_2]$_2$ by Na/Hg in THF at −30 °C in the presence of an isomeric mixture of (*E*)- and (*Z*)-1,3- pentadiene affords two isolable isomers of Cp*Mo(NO)(η^4-*trans*-1,3-pentadiene) resulting from the coordination of the (*E*)- and (*Z*)-diene to the metal center in a twisted, transoidal fashion.[363] When treated with acetylenes, CpMo(NO)(η^4-*trans*-diene) complexes effect a coupling between the diene ligand and the alkyne to produce an η^4 (η^3, η^1) ligand in which the η^3-allyl portion of the ligand is oriented *endo* with respect to the Cp ring. Thus, the reaction of CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) with 1-phenylpropyne gives the complex shown as follows:



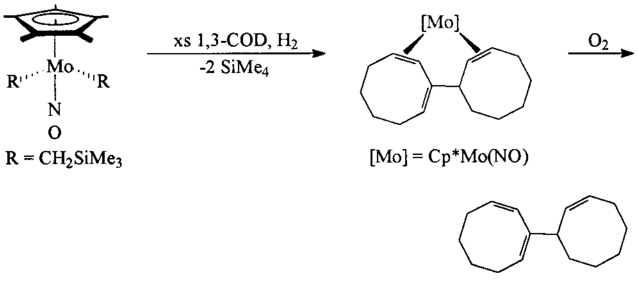
The reactions between CpMo(NO)(η^4-*trans*-diene) complexes and protonic acids, HX, afford the η^3-allyl complexes CpMo(NO)(η^3-allyl)(X), in which the allyl linkage is asymmetrically bound to the metal.[363] In related chemistry, CpMo(NO)(η^4-*trans*-diene) compounds undergo coupling reactions with acetone to form *endo*- and *exo*-allyl complexes. Thus, CpMo(NO)(η^4-*trans*-C_4H_6) forms two complexes of composition CpMo(NO)(η^4-$CH_2CH{=}CHCH_2COMe_2$) when combined with Me_2CO, i.e.[364]



In related chemistry, treatment of Cp*M(NO)(CH_2SiMe_3)$_2$ (M = Mo, W) with H_2 in the presence of acyclic, conjugated dienes affords Cp*M(NO)(η^4-*trans*-diene) complexes,[365] the tungsten species being inaccessible by other synthetic routes (vide supra):

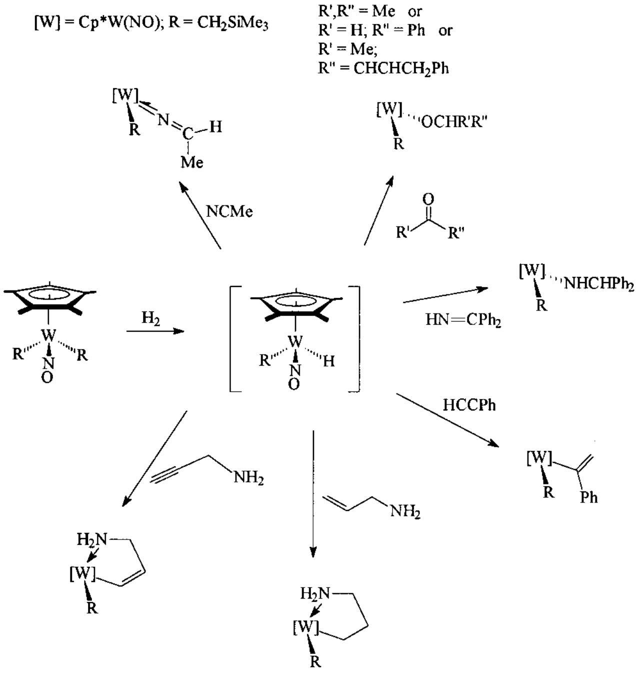


When 1,3-cyclooctadiene is employed as the trapping agent under identical experimental conditions, it undergoes a coupling in the metals' coordination spheres and forms the following complexes illustrated for molybdenum:



The 2-(2-cyclooctenyl)-1,3-cyclooctadiene thus formed may be conveniently liberated by exposing the product complexes to O_2 under ambient conditions.[365] In general, treatment of solutions of Cp*W(NO)(CH_2SiMe_3)$_2$ with H_2 generates in situ the reactive 16e alkyl hydride Cp*W(NO)(CH_2SiMe_3)H, whose existence can be inferred on the basis of the varied chemical reactions that it undergoes when generated in the presence of reactive substrates.[366] For instance, PPh_3 affords the orthometalated complex Cp*W(NO)(H)[η^2-$PPh_2C_6H_4$] (vide supra), probably via the 18e adduct Cp*W(NO)(CH_2SiMe_3)(H)(PPh_3). The characteristic chemistry of the hydride is, however, dominated by the ability of its W–H link to insert unsaturated linkages, the regioselectivity of the insertions indicating that the hydride ligand is hydridic in nature. Thus, it adds across N≡CR, O=CR_2, HN=CR_2, and unsymmetrical RC≡CR′ functional groups to form W–N=CHR, W–O–CHR_2, W–NH-CHR_2, and W–CR=CR′H linkages. Insertions of other olefinic substrates into the W–H bond are successful only if the unsaturated hydrocarbon also contains a Lewis-base functional group. Thus, propargylamine and allylamine produce the related metallacyclic complexes shown at the bottom of Scheme 10.[366]

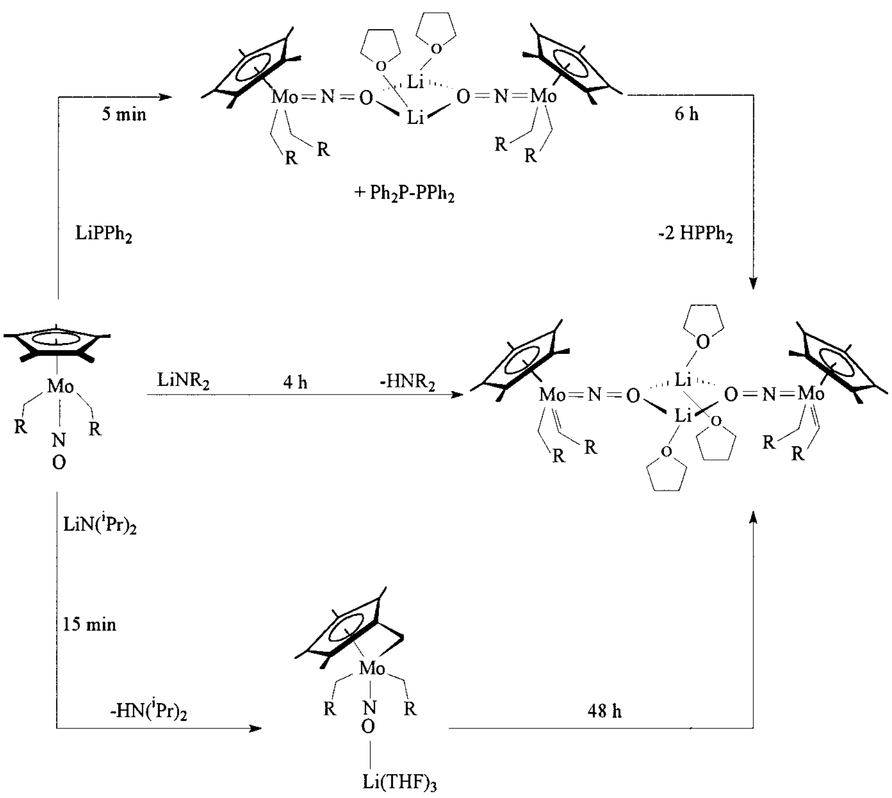
Scheme 10



Exposure of C_6H_6 solutions of Cp*Mo(NO)R_2 complexes (R = CH_2CMe_3, CH_2CMe_2Ph) to H_2 at 5 °C results in the formation of bimetallic (Cp*MoR)$_2$(μ-NO)$_2$ products. Similar treatment of an equimolar mixture of the two Cp*M(NO)R_2 (M = Mo, W; R = CH_2SiMe_3) complexes affords the heterobimetallic species (Cp*MoR)(μ-NO)$_2$(Cp*WR). The bimetallic complexes are thermally unstable, and the bridging M(μ-NO)$_2$M linkages spontaneously isomerize to (ON)M=N=M=O groupings in solutions at ambient temperatures (see section 9.3 later in this review).[367]

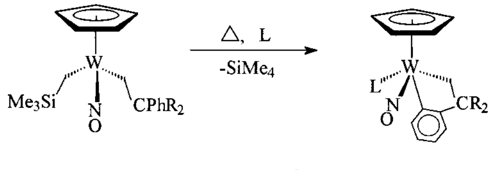
As illustrated in Scheme 11, conversion of Cp*Mo(NO)(CH_2SiMe_3)$_2$ to the lithium salt of the anionic alkylidene complex [Cp*Mo(NO)(CH_2SiMe_3)(=$CHSiMe_3$)]$_2$[$Li_2(THF)_3$] may be effected with various lithium

Scheme 11



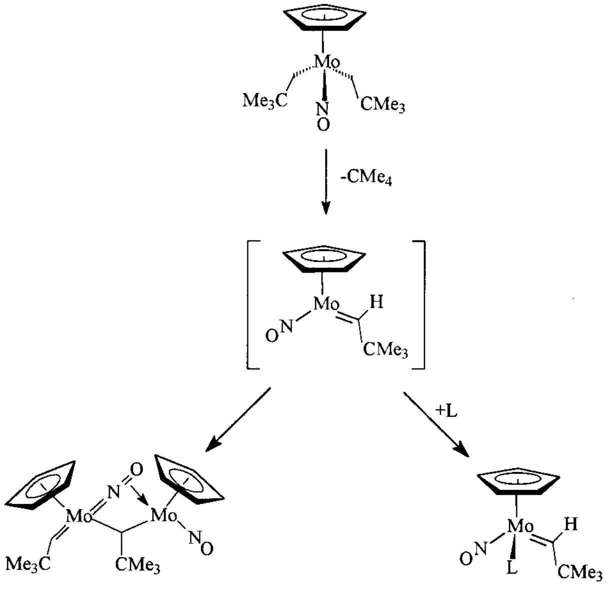
reagents, each of which follows a different mechanistic pathway.[368,369] Thus, $LiNR_2$ ($R = SiMe_3$) effects this conversion directly with no detectable intermediates. However, LDA deprotonates the Cp* ligand to form the lithium salt of the isolable "tucked-in" ate complex that slowly converts to the final complex when left in THF or C_6D_6 solution at ambient temperatures for 48 h. On the other hand, $LiPPh_2$ in THF results in a one-electron reduction that produces the dialkyl anion shown. This 17e anion is converted to the 18e alkylidene anion by the $Ph_2P{-}PPh_2$ coproduct which effects the requisite hydrogen-atom abstraction. Finally, addition of a sterically undemanding alkyllithium reagent such as MeLi to the 16e dialkyl reactant leads to the formation of the 18e trialkyl anionic complex $[Cp^*Mo(NO)(CH_2SiMe_3)_2(Me)][Li(THF)_3]$, which upon warming loses methane and forms $[Cp^*Mo(NO)(CH_2SiMe_3)({=}CHSiMe_3)]_2[Li_2(THF)_3]$. In most cases, this chemistry exhibited by the molybdenum system is duplicated by $Cp^*W(NO)(CH_2SiMe_3)_2$.[369]

The unsymmetrical dialkyl complex $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ is thermally unstable and converts to a metallacyclic complex when exposed to acetonitrile or PPh_3 in CH_2Cl_2, e.g.



R = Me, L = NCMe;
R = Ph, L = PPh_3

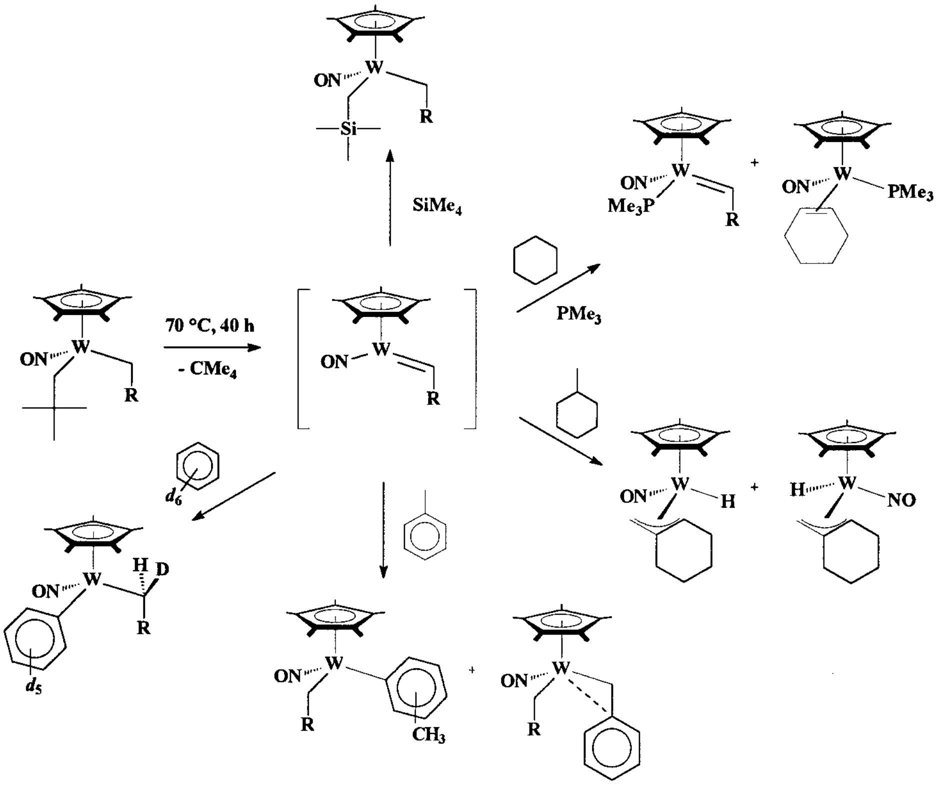
Scheme 12



The related complex $CpW(NO)(CH_2SiMe_3)(CH_2CMe_2Ph)$ behaves similarly.[370]

Thermolysis of $CpMo(NO)(CH_2CMe_3)_2$ in CH_2Cl_2 at ambient temperatures affords the bimetallic complex shown below on the left of Scheme 12.[371] Its most interesting structural feature is the μ-η^1-η^2-NO group which functions as a formal 5-electron donor to the two metal centers. This bimetallic complex probably arises via the initial formation of $CpMo(NO)({=}CHCMe_3)$, a species that may be trapped as the 18e adduct $CpMo(NO)({=}CHCMe_3)(L)$ when the thermolysis of the bis(neopentyl) complex is effected in the presence of phosphines or pyridine (L). Ther-

Scheme 13



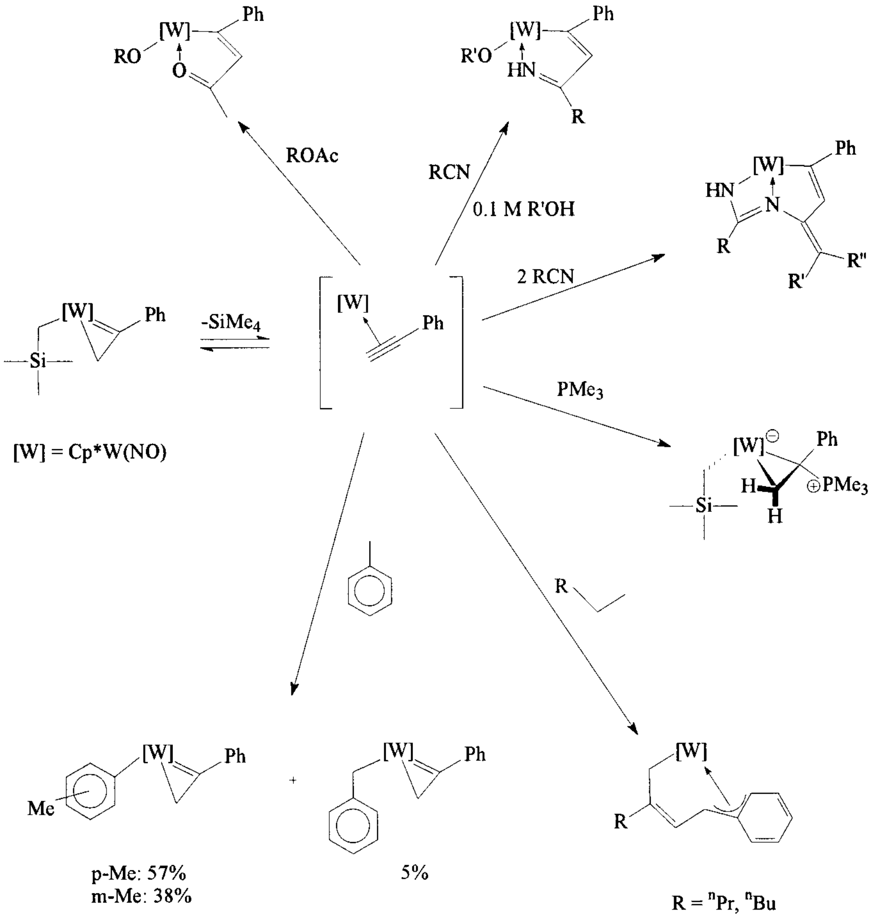
molysis of CpMo(NO)(CH$_2$CMe$_3$)$_2$ in the presence of excess PMe$_3$ in CH$_2$Cl$_2$ produces [(Me$_3$P)$_4$Mo(NO)Cl]$_2$.[372] The transient 16e neopentylidene complex or its labile pyridine adduct reacts with the heteroatom-H bonds of amines, alcohols, thiols, or carboxylic acids (EHR) to form the neopentyl complexes CpMo(NO)(CH$_2$CMe$_3$)(ER) that result from *syn* addition of the E−H bond across the Mo═C link. Similar reactions with bifunctional reagents produce bimetallic complexes, e.g. diols OH−X−OH produce Mo−O−X−O−Mo-linked products.[373]

The highly reactive alkylidene complex Cp*W(NO)(═CHCMe$_3$) is generated by thermolysis of its bis(neopentyl) precursor at 70 °C, and it is capable of effecting single, double, and triple C−H bond activations of various organic substrates (R = CMe$_3$ in Scheme 13).[374,375] Interestingly, these activations can occur in the presence of excess PMe$_3$, as exemplified by the formation of the Cp*W(NO)(η^2-cyclohexene)(PMe$_3$) complex shown in Scheme 13. In contrast to cyclohexane, methylcyclohexane and ethylcyclohexane afford principally the allyl hydride complexes Cp*W(NO)(η^3-C$_7$H$_{11}$)(H) and Cp*W(NO)(η^3-C$_8$H$_{13}$)(H), respectively, under identical experimental conditions. Kinetic and mechanistic studies indicate that the C−H activation chemistry derived from the bis(neopentyl) complex proceeds through two distinct steps, namely (1) rate-determining intramolecular α-H elimination of neopentane to form the alkylidene complex and (2) 1,2-cis-addition of a substrate C−H bond across the W═C linkage in the intermediate.

The thermolysis of Cp*W(NO)(CH$_2$CMe$_3$)$_2$ in toluene affords a surprisingly complex mixture of six products. The two major products are the neopentyl aryl complexes Cp*W(NO)(CH$_2$CMe$_3$)(C$_6$H$_4$-3-Me) and Cp*W(NO)(CH$_2$CMe$_3$)(C$_6$H$_4$-4-Me) in approximately 47% and 33% yields. Of the other four products, one is the aryl isomer of these complexes, namely Cp*W(NO)(CH$_2$CMe$_3$)(C$_6$H$_4$-2-Me) (~1%). The remaining three products all arise from the incorporation of *two* molecules of toluene, namely, Cp*W(NO)(CH$_2$C$_6$H$_5$)(C$_6$H$_4$-3-Me) (~12%), Cp*W(NO)(CH$_2$C$_6$H$_5$)(C$_6$H$_4$-4-Me) (~6%), and Cp*W(NO)(CH$_2$C$_6$H$_5$)$_2$ (~1%). It has been demonstrated that the formation of these latter complexes involves the transient formation of Cp*W(NO)(CH$_2$CMe$_3$)(CH$_2$C$_6$H$_5$), the product of toluene activation at the methyl position, which reductively eliminates neopentane to generate the C−H-activating benzylidene complex Cp*W(NO)(═CHC$_6$H$_5$). This intermediate can also be trapped by PMe$_3$ to obtain the adducts Cp*W(NO)(═CHC$_6$H$_5$)(PMe$_3$) in two rotameric forms. From their reactions with toluene, it can be deduced that both alkylidene intermediates exhibit a preference for activating the stronger aryl sp^2 C−H bonds. The C−H-activating ability of the benzylidene complex encompasses aliphatic substrates as well, as it reacts with tetramethylsilane and cyclohexanes in a manner similar to that summarized above for the neopentylidene intermediate.[375]

The reactivity differences observed experimentally for Cp*W(NO)(CH$_2$CMe$_3$)$_2$ and CpMo(NO)(CH$_2$CMe$_3$)$_2$ have been investigated using density functional theory.[376] The reactions of the CpW(NO)(CH$_2$) model complex with NH$_3$ and CH$_4$ are more exothermic and have lower activation barriers than the corresponding processes for CpMo(NO)(CH$_2$). The η^2(C,H) methane complexes CpM(NO)(CH$_2$)(CH$_4$) (M = Mo, W) can undergo two competitive processes: C−H activation to afford CpM(NO)Me$_2$ or loss of methane. The relative barrier heights are almost identical for M = W, whereas the formation of CpM(NO)Me$_2$ is signifi-

Scheme 14



cantly disfavored for M = Mo. The activation of C−H and N−H bonds proceeds via a direct, metal-assisted 1,2-addition across the M=CH$_2$ bond without a distinct carbene−hydride intermediate. The relative orbital energies, which are consistently lower for Mo than for W, can be used to rationalize various reactivity differences observed experimentally for the CpM(NO)(alkyl)$_2$ species, including the selective coordination of small molecules.[376] In related chemistry, it has been demonstrated that electrophilic addition of [SMe]$^+$ to the Mo=C linkage in CpMo(NO)(PMe$_3$)[=CMe(OEt)] results in the formation of the cationic molybdathiacyclopropane complex.[377]

Thermal activation of Cp*W(NO)(η^2-CPh=CH$_2$)(CH$_2$SiMe$_3$) in neat hydrocarbon solutions transiently generates Cp*W(NO)(η^2-PhC≡CH), which subsequently activates solvent C−H bonds.[378,379] Representative examples of the C−H activation processes that have been effected by this complex are summarized in Scheme 14. As expected, intra- and intermolecular selectivity studies reveal that the strongest C−H bond (yielding the stronger M−C bond) is the preferred site of reactivity. The dual C−H bond activations of aliphatic hydrocarbons depicted in Scheme 14 are particularly interesting since these processes exhibit a selectivity for substrates that contain an ethyl substituent. Attempts to trap the intermediate acetylene complex with PMe$_3$ result in the formation of the metallacyclopropane complex Cp*W(NO)(CH$_2$SiMe$_3$)(η^2-CH$_2$CPh(PMe$_3$)).[379]

In general, thermolysis of Cp*W(NO)(η^2-CPh=CH$_2$)(CH$_2$SiMe$_3$) in the presence of unsaturated, heteroatom-containing compounds such as esters and nitriles quantitatively affords metallacyclic products of reductive coupling. These products are trapped as 18e complexes via either intramolecular rearrangement or intermolecular reaction with added trapping agents. The nature of these products (see Scheme 14) is again consistent with the intermediacy of the acetylene complex, Cp*W(NO)(η^2-CPh≡CH).[380] As illustrated, with esters, reductive coupling and C−O bond cleavage yield alkoxide-containing oxametallacyclopentadiene complexes. With nitriles under differing experimental conditions, a variety of azametallacycles are formed. A qualitative orbital-overlap rationale has been proposed to account for the observed chemistry.[381]

The solid-state molecular structure of Cp*W(NO)(CH$_2$SiMe$_3$)(CPh=CH$_2$) reveals that its vinyl ligand exists in a distorted form that cannot readily be described by either of the classic η^1-vinyl- or 1-metallacyclopropene limiting structures. However, the NMR parameters for the CPhCH$_2$ fragment in this complex in solutions are characteristic of those of a 1-metallacyclopropene unit.[382] Related vinyl-containing complexes of tungsten, Cp*W(NO)(η^2-CPhCH$_2$)X and Cp*W(NO)(η^1-CPh=CH$_2$)(LX) [X = Cl, OTf; LX = O$_2$CPh, NHCMe$_3$, (PPh$_3$)(H)], have been examined similarly, and it has been shown that the nature of the tungsten−vinyl interaction in these compounds is dependent upon the donor strength of the 1e X or

3e LX donor ligands that are also present in the tungsten's coordination sphere. Reaction of Cp*W(NO)(η^2-CPhCH$_2$)Cl with diallylamine results in coupling of the amine-N with the vinyl group to give Cp*W(NO)(η^2-CHPhCH$_2$N(C$_3$H$_5$)$_2$)Cl.[382]

As summarized in the preceding sections, electronically and coordinatively unsaturated Cp*W(NO)(L) complexes have been postulated as intermediates in several related systems. Consequently, model CpW(NO)(L) compounds (L = PH$_3$, CO, CH$_2$, H$_2$CCH$_2$, HCCH) have been investigated theoretically by DFT computational techniques.[383] The structural parameters calculated for saturated CpW(NO)(PH$_3$)(L) complexes are in good agreement with the solid-state molecular structures determined crystallographically for the corresponding Cp*W(NO)(PMe$_3$)(L) compounds. The 16e, singlet CpW(NO)(L) species have geometries comparable to those of the same fragment in the phosphine adducts and include a high pyramidal conformation at W. The energy of the triplet spin state is calculated to be close to, or even lower than, that of the singlet state for these unsaturated compounds, and it depends largely on the π-bonding capabilities of L. The preferred alkyne conformation, the unusually stable triplet states, and the strong W-to-Lπ-donation observed in these systems may all be rationalized by the relatively high energies of the occupied orbitals of the formally W(0) compounds.[383]

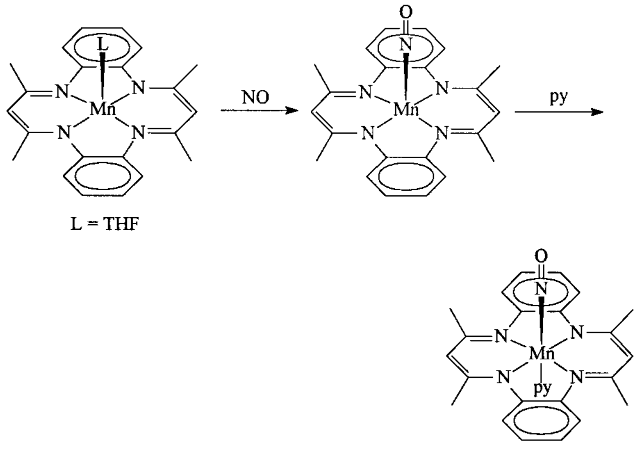
4. Group 7 Nitrosyls

4.1. Manganese and Technetium Nitrosyls

4.1.1. Coordination Complexes

[Mn(NO)(CN)$_5$]$^{3-}$, the manganese analogue of nitroprusside, has been structurally characterized with a variety of counterions,[384−386] and its formation by NO transfer to Mn(II) from nitroprusside has also been reported.[387] Many {MnNO}^{6} manganese nitrosyl complexes of composition Mn(NO)(CN)$_2$(L)$_2$(H$_2$O) have been synthesized by the treatment of [Mn(NO)(CN)$_5$]$^{3-}$ with a variety of monodentate and bidentate Lewis bases.[388−391]

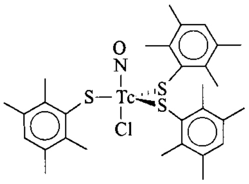
The manganese complex Mn(tmtaa)(thf) (tmtaa = dibenzotetramethyltetraaza[14]annulene) reacts with gaseous NO to form the paramagnetic nitrosyl complex Mn(tmtaa)(NO). This compound then reacts with pyridine to form the diamagnetic adduct, i.e.[392]



At first glance, the paramagnetism of Mn(tmtaa)(NO) is rather surprising given the strong π-acceptor nature of NO and the formal d^6 electron count, but it is attributed to the excitation of two electrons into a low-lying LUMO. This excitation is inhibited by the binding of a strong σ-donor trans to the NO ligand, an action that raises the energy of the LUMO and leads to a diamagnetic species.

[Mn(CO)$_3$(NO)]$^{2-}$, formally a d^{10} nitrosyl, has been synthesized by Ellis and co-workers via the two-electron reduction of Mn(PPh$_3$)(CO)$_3$(NO).[393] This anion reacts with Ph$_3$SnCl to form [Mn(CO)$_3$(NO)(SnPh$_3$)]$^-$. The infrared multiphoton dissociation spectrum of the related nitrosyl anion [Mn(CO)$_3$(NO)(CF$_3$)]$^-$ has also been recorded.[394] The neutral complex Mn(NO)(CO)$_2$(PPh$_2$H)$_2$ can be prepared by the straightforward thermal substitution of the carbonyl ligands in Mn(CO)$_4$(NO).[395]

Several technetium nitrosyls have also been synthesized in recent years. These include the d^4 nitrosyl Tc(NO)(Cl)(tmbt)$_3$ (tmbt = 2,3,5,6-tetramethylbenzenethiol)[396] (vide infra) and several d^6 nitrosyls having the general formula Tc(NO)X$_2$(L)$_3$ in which X is a pseudohalide and L is usually a phosphine.[397−403] The precursor to these types of compounds is the interesting and synthetically important complex [Bu$_4$N][Tc(NO)(Cl)$_4$].[404] In addition, it has been established that the ESR parameters $A_{||}$ and $g_{||}$ of technetium nitrosyls are different for Tc(II) and Tc(VI) complexes.[405] Finally, the cationic [Tc(NO)(NH$_3$)(phen)$_2$]$^+$ has been prepared by reacting [NH$_4$]$_2$[TcCl$_6$] or [NH$_4$]$_2$[TcO$_4$] with hydroxylamine and 1,10-phenanthroline.[406]

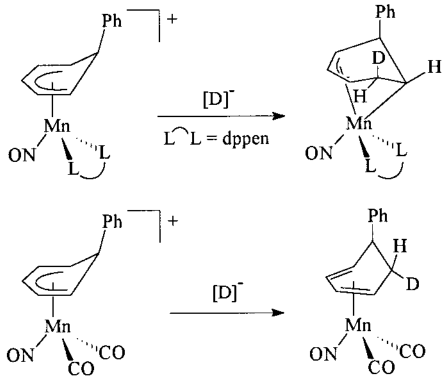


Several dinitrosyl complexes having the composition Mn(NO)$_2$(CN)$_2$(L)$_2$ have been synthesized by reacting the dianion [Mn(NO)$_2$(CN)$_4$]$^{2-}$ with various donor ligands.[407,408] The hydrido dinitrosyl complexes Mn(NO)$_2$(PR$_3$)$_2$H (R = Me, Et), which can be made by reacting the bromo precursors with NaBH$_4$,[409] react with CO$_2$ to form η^1-formato complexes. These complexes have been studied by a variety of NMR techniques to characterize the metal−hydride interactions which appear to be normal.[410,411] The isoelectronic Mn(NO)$_2$(PPh$_3$)$_2$(X) (X = BF$_4^-$, OTf$^-$, OSO$_2$F$^-$, etc.) species have been prepared by adding HX to the hydride precursor.[412]

4.1.2. Organometallic Complexes

Several complexes of the type [Cp′Mn(CO)(NO)(L)]$^+$ (L = phosphine) are now known.[413,414] They can be made by the electron-transfer-catalyzed substitution of a carbonyl ligand in [Cp′Mn(CO)$_2$(NO)]$^+$ by a phosphine via a 19e intermediate.[415] Interestingly, the photolysis of [Cp′Mn(CO)$_2$(NO)]$^+$ at low temperature affords predominantly [Cp′Mn(CO)-

Scheme 15



(NO)]$^+$.[416] Finally, the complex [(1-Ph-η^4-SC$_4$H$_4$)Mn(CO)$_2$(NO)]$^+$ has also been prepared by treating the neutral tricarbonyl precursor with [NO][BF$_4$].[417]

The addition of [D]$^-$ to [(η^5-cyclohexadienyl)Mn(CO)$_2$(NO)]$^+$ affords only the *endo* product (Scheme 15) and is believed to proceed via a formyl intermediate. The same reaction with [(η^5-cyclohexadienyl)Mn(dppen)(NO)]$^+$ [dppen = *cis*-1,2-bis(diphenylphosphino)ethylene] affords exclusively the *exo* product, (6-*exo*-Ph,1-σ,3−5-η-C$_6$H$_7$)Mn(dppen)(NO), thereby giving credence to the proposed mechanism for the carbonyl species. Furthermore, the investigators suggest that the nitrosyl ligand may well bend during the reaction pathway.[418]

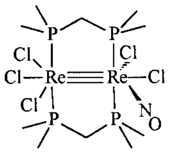
The reaction between Rh$_2$(CO)$_4$(μ-RNNNR)$_2$ (R = *p*-tolyl) and Cp′Mn(NO)(CN)(PPh$_3$) yields a heteropolynuclear cluster,[419] while CpMn(NO)(CN)(P(OMe)$_3$) reacts with BPh$_3$ to form a cyano−borane adduct.[420]

4.2. Rhenium Nitrosyls

4.2.1. Coordination Complexes

Several d^5 nitrosyl complexes of rhenium having the general form Re(X)$_3$(NO)(L)$_2$ are known, and some have been structurally characterized.[421−428] They usually result from the reaction between NO and Re(O)(X)$_3$(L)$_2$. Also isolated from a reaction of this type is the d^4 nitrosyl Re(NO)(Ph)Br$_3$(PPh$_3$).[429] The cationic d^5 and d^6 nitrosyl complexes [ReCl(NO)(dppe)$_2$]$^{2+/+}$ and [ReF(NO)(dppe)$_2$]$^+$ are also known.[430,431] [Na(15-crown-5)][ReFCl$_3$(NO)(MeCN)] has been prepared by reacting NaF and 15-crown-5 with ReCl$_3$(NO)$_2$(MeCN).[432] The substitution kinetics of the aquo ligand in the [Re(NO)(H$_2$O)(CN)$_4$]$^{2-}$ anion have been studied, but no definitive mechanistic conclusions could be drawn about this conversion.[433,434]

The complex Re$_2$Cl$_4$(μ-dmpm)$_3$ contains a central Re≡Re bond and reacts with 2 equiv of [NO][PF$_6$] to afford Cl$_3$Re(μ-dmpm)$_2$ReCl$_2$(NO) in 41% yield. This complex possesses a solid-state molecular structure in which the nitrosyl ligand is cis to the Re≡Re bond (vide infra).[435,436] The related complex [Re$_2$(μ-H)(μ-Br)(P(O)Ph$_2$)Br$_2$(NO)(μ-dppm)$_2$]$^+$ has also been reported.[437,438]



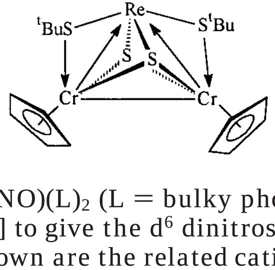
Several thiolate-bridged dimers and trimers of rhenium nitrosyls have been formed by the reaction between Re$_2$(CO)$_4$(NO)$_2$Cl$_4$ and Na[SCMe$_3$]. Several of these have been structurally characterized, including Re$_3$(CO)$_3$(NO)$_3$(μ-SCMe$_3$)$_3$(μ_3-SCMe$_3$)(μ-O) and Re$_3$(CO)$_3$(NO)$_3$(μ-SCMe$_3$)$_3$(μ_3-S)(μ_3-Cl).[439]

Several d^6 nitrosyls of the type Re(NO)X$_2$(L)$_3$ (X = halide; L = nitrile, phosphine, or phosphite) have been recently reported.[427,440−443] In one instance the halides have been metathesized with MeLi.[444] Also stable are cationic complexes having the general formulas [Re(NO)(X)(L)$_3$(CO)]$^+$ and [Re(NO)(L)$_4$(CO)]$^{2+}$.[441,443,445] The anionic complex [Re(NO)(CO)$_2$(I)$_3$]$^-$, which exhibits a ν_{NO} at 1771 cm^{-1} (KBr), can be made by adding excess NaI to acetone solutions of [CpRe(NO)(CO)$_2$]$^+$.[446] If only 1.5 equiv of NaI is added, then CpRe(NO)(CO)(I) is the isolated product. The cationic complex [(bdmpza)Re(CO)$_2$(NO)]$^+$ [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], isoelectronic to [CpRe(NO)(CO)$_2$]$^+$, is also known.[447]

Much research has been devoted to the synthesis and spectroscopic characterization of ReH$_2$(CO)(NO)(PR$_3$)$_2$ and related dihydrides.[410,411,448−455] It has been demonstrated that perfluoro-*tert*-butanol can hydrogen bond to the oxygen atom of the NO ligand in such species. Furthermore, it has been reported that mixtures of ReH$_2$(NO)(CO)(PR$_3$)$_2$ (R = ^{i}Pr, Me, O^{i}Pr) and CF$_3$COOH can hydrogenate benzaldehyde in CD$_2$Cl$_2$.[456]

The dihydrogen complexes Re(NO)(H$_2$)Br$_2$(PR$_3$)$_2$ (R = Cy, ^{i}Pr) have been prepared from [Et$_4$N][Re(NO)Br$_5$] and excess PR$_3$ in ethanol.[457] They are very rare examples of nitrosyl−dihydrogen complexes, and they react with BH$_3$ to form the [BH$_4$]$^-$ adducts or with H$_2$ to form the tetrahydrides ReH$_4$(NO)(PR$_3$)$_2$. They also form the anions [ReH$_3$(NO)(PR$_3$)$_2$]$^-$ when treated with KH in the presence of 18-crown-6.[458] When [ReH$_3$(NO)(P^{i}Pr$_3$)$_2$]$^-$ is reacted with phenylacetylene, the anionic vinyl complex [ReH$_2$(CPh=CH$_2$)(NO)(P^{i}Pr$_3$)$_2$]$^-$ is formed in 75% yield.[459]

The reaction between Cp$_2$Cr$_2$(SCMe$_3$)$_2$S and Re$_2$(NO)$_2$(CO)$_4$Cl$_4$ leads to a number of Cr$_x$Re$_y$ clusters such as Cp$_2$Cr$_2$(μ_3-S)$_2$(μ-SCMe$_3$)$_2$Re(CO)(NO) (vide infra).[460,461] However, no reaction occurs when Re(NO)(CO)(PR$_3$)$_2$Cl$_2$ is used in place of Re$_2$(NO)$_2$(CO)$_4$Cl$_4$.[461] Denitrosylation of [CpCr(μ-SCMe$_3$)$_2$(μ_3-S)Re(CO)(NO)]$_2$ by Co$_2$(CO)$_8$ has been observed.[462]



Re(H)(BH$_4$)(NO)(L)$_2$ (L = bulky phosphine) reacts with [NO][BF$_4$] to give the d^6 dinitrosyl Re(NO)$_2$(H)(L)$_2$.[457] Also known are the related cationic complexes

$[Re(NO)_2(PR_3)_2]^+$ and $[Re(NO)_2(PR_3)_2(L)]^+$ (L = CO, PhCHO).[463] For the L = PhCHO derivative, one ReNO linkage is bent, thereby making the complex a formally 16e species. This bending has been attributed to the steric effects of the phosphine coligands. The complex $Re(NO)_2(X)_2(PR_3)_2$ has been claimed,[464] and it has been partially characterized by ESR, ^{31}P NMR, and magnetic susceptibility measurements. Also known is *trans*-$[Re(NO)_2(dppe)_2]^+$, which has been prepared in 70% yield by the action of NO(g) and $TlBF_4$ on *trans*-$ReCl(N_2)(dppe)_2$. It exhibits a single ν_{NO} stretching frequency at 1650 cm^{-1} and is one of the very few *trans*-dinitrosyl complexes to be isolated.[431] Unfortunately, an X-ray crystallographic analysis of this important complex has not yet been performed, but the *trans*-dinitrosyl $[Mn(NO)_2pc]^-$ (H_2pc = phthalocyanine) has been structurally characterized.[465]

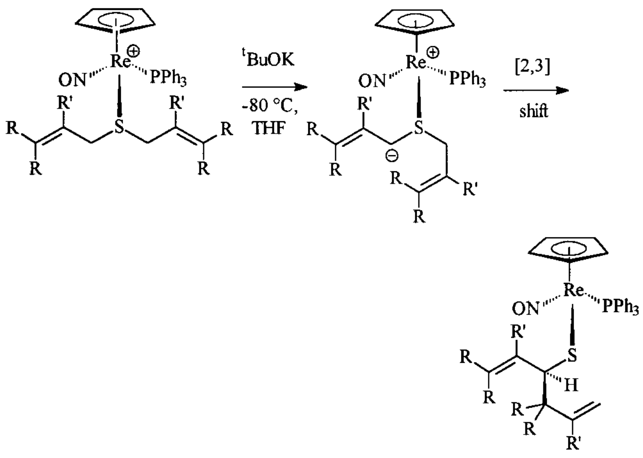
4.2.2. Organometallic Complexes

A great deal of research has been done by the Gladysz group on complexes containing the chiral Cp′Re(NO)(PPh_3) fragments.[466] Generally, the nitrosyl ligand is not involved in the chemistry. The parent compounds of this series, $[Cp'Re(NO)(PPh_3)(CO)]^+$, have been studied in great detail,[467,468] and the electronic structures of $CpRe(NO)(PPh_3)(X)$ (X = Cl, Br, I) have also been investigated by valence photoelectron spectroscopy.[469] When X = I in the latter complexes, CuR reagents can effect the metathesis to generate the corresponding rhenium organometallic derivatives such as $CpRe(NO)(PPh_3)Me$.[470] The related methyl complexes $CpRe(NO)(PR_3)Me$ (R = C_6H_4-4-Me, C_6H_4-4-^tBu, C_6H_4-4-Ph, C_6H_4-4-OMe) can be oxidized to their 17e cations with ferrocenium salts.[471,472]

Both Cp and Cp* versions of $Cp'Re(NO)(PPh_3)(L)$ (L = CH_2Cl_2, C_6H_5Cl) are known,[473,474] as are the haloalkane complexes having L = $ICH_2CH_2CMe_3$, ICy, I^{i}Pr, and $I(CH_2)_4Re(CO)_5$.[475−477] These complexes are usually generated by treating $Cp'Re(NO)(PPh_3)Me$ with $HBF_4{\cdot}OEt_2$ in the presence of an alkyl halide. The Cp*-containing fragment displays higher thermodynamic binding selectivity but, curiously, is more thermally sensitive.[473] The haloalkane ligand can be easily displaced by a large number of unsaturated substrates and Lewis bases such as alkenes,[478−485] alkynes,[486] ketones,[487−492] aldehydes,[491,493−499] imines,[500−502] allenes,[503] ethers,[504−506] sulfides,[507] sulfoxides (both *S* and *O* bound),[508] amines,[509−513] nitriles,[514] and esters.[515] The familiar PPh_3 ligand has also been replaced with the perfluorinated analogue, $P(C_6F_5)_3$.[516]

If the rhenium fragment has been resolved and the unsaturated substrate has enantiotopic faces, then two diastereomers are generated. The interconversion of these π diastereomers has been studied in detail. The suggested mechanism is a nondissociative one in which a C−H σ-bond to the metal center is formed as the alkene rotates from face to face.[481,517] The use of HPLC to resolve enantiomers has been described,[518] and procedures for measuring the optical rotations of organometallic compounds have been outlined.[519]

Scheme 16



Much research has been done on functionalizing the unsaturated substrates once they are bound to the rhenium fragment. This functionalization usually consists of deprotonation by a strong base or the addition of a nucleophile. The deprotonation reactions are summarized first. The cationic DMSO complex $[CpRe(NO)(PPh_3)(S\text{-}DMSO)]^+$, undergoes a [1,2] H migration when treated with base and forms $CpRe(NO)(PPh_3)(CH_2S(O)Me)$.[520] Deprotonation followed by protonation converts the alkene complex $[CpRe(NO)(PPh_3)(\eta^2\text{-}CH_2{=}CHR)]^+$ to the alkylidene complex $[CpRe(NO)(PPh_3)({=}CHCH_2R)]^+$.[521] However, some alkene complexes readily isomerize to vinyl-containing species upon deprotonation.[521,522]

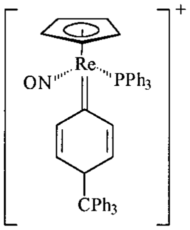
Also well studied are amide and phosphide complexes of the type $CpRe(NO)(PPh_3)(ER'R)$ (E = N, P; R = alkyl, aryl; R′ = H, alkyl, aryl),[523−527] which are formed by deprotonation of the parent amine or phosphine complex. One such complex, $(\eta^5\text{-}C_5H_4PPh_2)Re(NO)(PPh_3)(PPh_2)$, reacts with $[Rh(NBD)Cl]_2$ and $[Ag][PF_6]$ to give $[(NBD)Rh(\kappa^2\text{-}(\eta^5\text{-}C_5H_4\mathit{P}Ph_2)Re(NO)(PPh_3)(\mathit{P}Ph_2))]^+$, which is effective as a enantioselective hydrogenation catalyst.[528] $CpRe(NO)(PPh_3)(CH_2CN)$ can also be deprotonated and then reacted with MeOTf to obtain $CpRe(NO)(PPh_3)(CHMeCN)$.[529]

Gladysz and co-workers have also studied the [2,3] sigmatropic rearrangement at the $CpRe(NO)(PPh_3)$ center illustrated in Scheme 16 which proceeds by deprotonation of a σ-bound sulfide.[530−533] It was found that the chirality of the rhenium fragment was transferred to the new carbon stereocenter during the reaction. Also, the alkene substituents in $[CpRe(NO)(PPh_3)(S(CH_2CH{=}CH_2)_2)]^+$ can undergo olefin metathesis reactions.[534]

The additions of nucleophiles to unsaturated substrates at these rhenium centers are well documented. For example, the cations $[CpRe(NO)(PPh_3)(\eta^2\text{-}O{=}CHR)]^+$ (R = Me, Et, CH_2Ph, Ph) react with $[Et_4N][CN]$ to afford $CpRe(NO)(PPh_3)(OCH(CN)R)$.[535,536] In a similar manner, treatment of $[CpRe(NO)(PPh_3)(\eta^2\text{-alkene})]^+$ cations with R_2CuLi reagents gives the neutral alkyl species.[537,538] Addition of R_2CuLi to an η^1-cycloalkenone complex, followed by workup in aqueous HI, generates $CpRe(NO)(PPh_3)I$ and the 3-substituted cyclopentenone in good enantiomeric excess.[539] Similarly, the addition of RLi to cationic [CpRe(NO)(PPh$_3$)(η^1-N(Me)=CHPh)]$^+$ complexes forms amido complexes of the type CpRe(NO)(PPh$_3$)(N(Me)CH(R)Ph).[540] Nucleophilic addition to quinoline complexes is also possible,[541–544] and treatment of η^2-aldehyde complexes with [H]$^-$ generates rhenium alkoxides of the type CpRe(NO)(PPh$_3$)(OCH$_2$R).[545,546] Both silyl and germyl complexes of the type CpRe(NO)(PPh$_3$)(MR$_3$) (M = Si, Ge; R = alkyl, halide) are known.[547–549]

The Gladysz group has also expended considerable effort in synthesizing $-(C{\equiv}C)_n-$ chains capped by the Cp′Re(NO)(PPh$_3$) fragments.[550–557] Chain lengths as great as $n = 10$ have been obtained.[558,559] In general, the alkylidyne moiety is introduced into the metal's coordination sphere as an η^2-acetylene complex (e.g. [Cp′Re(NO)(PPh$_3$)(η^2-acetylene)]$^+$). This cation can then be deprotonated to obtain the neutral alkylidyne.[470,560,561] These carbon-chain materials are redox active,[562–566] and many are heterometallic.[561,567–574] For these complexes ν_{NO} steadily increases as the chain gets longer and reaches a maximum at ~1660 cm^{-1}, thereby indicating a decrease in back-bonding to the nitrosyl ligand with increased chain length.[558]

The phenyl complex CpRe(NO)(PPh$_3$)Ph reacts with [Ph$_3$C][PF$_6$] to give the following thermally unstable bis(vinyl)alkylidene complex decomposing above −40 °C:[575]



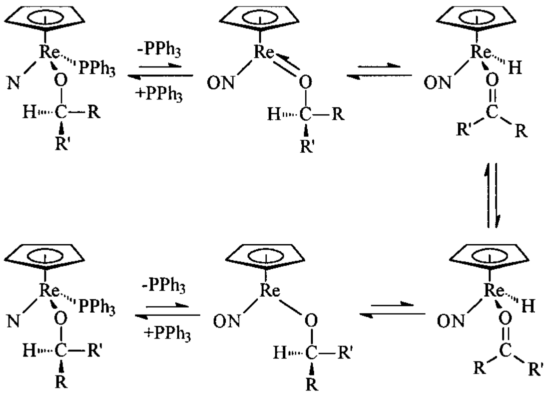
Several related alkylidene complexes are known.[576,577] These can be converted into alkene complexes by treatment with diazoalkanes. In contrast, the cationic propylidene complex [CpRe(NO)(PPh$_3$)(=CHEt)]$^+$ cleanly converts to the η^2-propene complex [CpRe(NO)(PPh$_3$)(η^2-CH$_2$=CHMe)]$^+$ via an intramolecular hydrogen shift usually termed a Wagner–Meerwein-type rearrangement.[578]

The *N*-pyrrole complex CpRe(NO)(PPh$_3$)(*N*-NC$_4$H$_4$) isomerizes to the *C*-pyrrole complex CpRe(NO)(PPh$_3$)(*C*-NC$_4$H$_4$) upon addition of HOTf or HBF$_4$·OEt$_2$ followed by 1 equiv of KH.[579,580]

As illustrated in Scheme 17, the CpRe(NO)(PPh$_3$)(OMe) complex catalyzes the epimerization of secondary alcohols via a ketone hydride intermediate.[581,582]

Other studies that have been effected with complexes containing the chiral Cp′Re(NO)(PPh$_3$) fragments include the following. Allyl alcohol bound to the [CpRe(NO)(PPh$_3$)]$^+$ fragment can undergo nucleophilic substitution at the hydroxyl group without affecting the alkene portion.[583–585] CpRe(NO)(CO)H inserts alkenes into its Re–H linkage to form the corresponding alkyl complexes.[586] [Cp′Re(NO)(PPh$_3$)(CO)]$^+$ can also be made with a chiral-substituted Cp ring.[587–589] Furthermore, (η^5,η^1-C$_5$H$_4$CH$_2$CH$_2$*N*Me$_2$)Re(NO)(CO)Br has been prepared, and its chemistry is similar to that of CpRe(NO)(PPh$_3$)X.[590]

Scheme 17



Positional disorder between the nitrosyl and carbonyl ligands in [Cp′Re(NO)(CO)$_2$]$^+$ has been found for Cp′ = C$_5$Me$_4$H and C$_5$H$_4$SiMe$_3$. The authors suggest that this type of disorder is fairly common among carbonyl nitrosyl complexes on the basis of their analyses of the structural reports of similar compounds extant in the literature.[591]

To close this section, it may be noted that the Fischer carbene complex (η^5-7,8-C$_2$B$_9$H$_{11}$)Re(NO)(CO)(=C(OMe)R) (R = Ph, C$_6$H$_4$Me-4) has been prepared,[592] and many complexes of the type Cp*Re(NO)(CO)(η^1-*C*OOH) and Cp*Re(NO)(CO)(μ-η^x-CO$_2$)-MR$_n$ ($x = 1$, MR$_n$ = SnMe$_3$; $x = 2$, MR$_n$ = ZrCp$_2$, Mo(CO)$_2$Cp) are known.[593–598] Finally, the cationic thiophene complex [CpRe(NO)(PPh$_3$)(*S*-SC$_4$H$_4$)]$^+$ reacts with strong bases to form CpRe(NO)(PPh$_3$)(*C*-SC$_4$H$_3$). This complex then reacts with strong acids to give the carbene species [CpRe(NO)(PPh$_3$)(*C*-SC$_4$H$_4$)]$^+$ at low temperature, but upon warming, it reconverts to [CpRe(NO)(PPh$_3$)(*S*-SC$_4$H$_4$)]$^+$.[599,600]

5. Group 8 Nitrosyls

5.1. Iron Nitrosyls

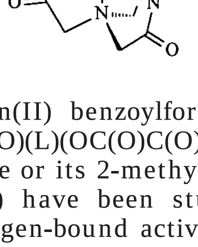
5.1.1. Coordination Complexes

The [Fe(CN)$_5$(NO)]$^{2-}$ nitroprusside anion is perhaps the earliest discovered nitrosyl complex, and it remains the subject of intense research efforts.[601–604] Numerous single-crystal[384,605–615] and powder[616–619] X-ray/neutron diffraction studies continue to be carried out on nitroprusside with various counterions. The bonding in these cation–anion pairs is not always straightforward since there is the possibility of bridging interactions via the cyanide ligands.[620] So-called "double complexes", such as the copper nitroprusside species [(en)$_2$Cu(–NC–)Fe(CN)$_4$(NO)] have received considerable attention due to the weak antiferromagnetic coupling exhibited between the two metal centers of the cation and anion.[621–631]

Irradiation of ground-state [Fe(CN)$_5$(NO)]$^{2-}$ with 400–540 nm light produces two exceptionally long-lived ($\tau > 10^7$ s) metastable states. It has long been proposed that these metastable states are formed via charge transfer from the iron d$_{xy}$ orbital to the antibonding π^* NO orbital and that they may thus involve bending of the nitrosyl ligand. Recently, Coppens and co-workers have utilized low-temperature X-ray diffraction studies to confirm that these states are comprised of an isonitrosyl (M—O—N) form and a less prevalent side-on η^2-bound NO form.[632−635] This work is presented in more detail in another review in this special issue of *Chemical Reviews*.

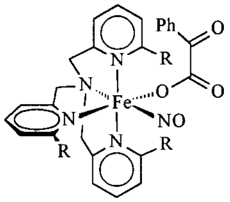
Iron-based enzymes play a prominent role in physiological systems, and this fact has led to the development of a number of model complexes with which to study the active sites of these proteins. In this regard, nitric oxide has been shown to interact with many enzymatic sites to reversibly form stable Fe—NO complexes.[636] The binding in these complexes is similar to the coordination of dioxygen to such metal centers, although the nitrosyl products are far more stable and easy to characterize than are their superoxo analogues. Many non-heme iron proteins are activated by O_2 binding to the metal core,[637] and transition-metal nitrosyl complexes have therefore been extensively investigated with a view to modeling the interactions of O_2 with metal centers.

$\{Fe-NO\}^7$ coordination complexes such as Fe(NO)(edta) and $(L_3)Fe(NO)(N_3)_2$ (L_3 = triazacyclononane and derivatives) have been studied in great detail by Solomon and co-workers using diverse techniques including ESR, EXAFS, resonance Raman, magnetic circular dichroism, and magnetic susceptibility measurements. These studies have shown the $\{Fe-NO\}^7$ complexes to be best described as a high-spin ferric ion ($S = 5/2$) antiferromagnetically coupled to NO^- ($S = 1$).[638−642] Mössbauer spectroscopic studies by the research groups of Wieghardt and Bill on these complexes and also $(L_3)Fe(NO)(ONO)(NO_2)$ and the series $[(L_4)Fe(NO)Cl]^{0,+,2+}$ (L_4 = tetraazacyclotetradecane) are in agreement with this description.[643,644] A series of trigonal bipyramidal $\{Fe-NO\}^7$ complexes has been reported by Borovik and co-workers. These complexes were synthesized with tripodal ligands derived from tris(carbamoylmethyl)amine (vide infra) by reaction of $Fe(OAc)_2$ with the tripotassium salt of the ligand. The R groups in these complexes form cavities around the metal ion which can influence the properties of the molecule. For instance, while the solid-state molecular structures of these species are similar, the Fe—N—O angle is related to the size of the cavity. A smaller cavity (R = ^{i}Pr) results in a more linear metal—nitrosyl linkage and hence a less rhombic ESR spectrum. Magnetic moment, Mössbauer, and ESR data are all consistent with an electronic configuration of $[Fe^{III}-NO^-]$.[645,646]



R = N-(*S*)-(-)-(α)-methylbenzyl
= isopropyl
= cyclopentyl
= 3,5-dimethyl phenyl

Iron(II) benzoylformate complexes of the type Fe(NO)(L)(OC(O)C(O)Ph) (L = tris(2-pyridylmethyl)amine or its 2-methyl-substituted equivalent) (vide infra) have been studied to model the putative dioxygen-bound active-site structure of α-keto acid dependent non-heme Fe^{II} enzymes.[647]



R = H, Me

Lippard and co-workers have described the diiron dinitrosyl complex $[Fe_2(\mu\text{-Et-HPTB})(\mu\text{-}O_2CPh)(NO)_2][BF_4]_2\cdot3MeCN$ (Et-HPTB = *N,N,N′,N′*-tetrakis(*N*-ethyl-2-benzimidazolylmethyl)-2-hydroxy-1,3,diaminopropane) as a model for the binding of O_2 to non-heme iron proteins.[648] The iron nitrosyl complexes $E(CH_2CH_2SC_6H_4\text{-}o\text{-}S)_2Fe(NO)$ (*E* = *N*R, *S*) have also been cited as models for the active sites in nitrogenase enzymes.[649−651] The related cationic complex $[Fe(NO)(\text{“pyS4”})]^+$ (“pyS4” = 2,6-bis(((2-mercaptophenyl)thio)methyl)pyridine(2−)) can be reduced by one electron to form Fe(NO)(“pyS4”), which reacts with CO to form Fe(CO)(“pyS4”).[652]

Derivatives of Fe(NO)(edta) have been utilized as NO scavenging agents,[653−655] and they have been shown to electrocatalytically reduce $[NO_2]^-$ to N_2O, N_2, $[NH_3OH]^+$, and $[NH_4]^+$.[656] Complexes of the form $[(L_4)Fe(NCMe)_2]^{2+}$ (L_4 = macrocyclic 4 N donor ligands) have also been shown to be effective NO scavengers.[657,658]

Magnetic susceptibility and Mössbauer measurements on $[Fe(NO)(salen)]^{2+}$ have detected transitions between the $S = 3/2$ and $S = 1/2$ spin states.[659] In contrast to this behavior, the isoelectronic five-coordinate iron(I) complexes $Fe(NO)(E_2CNR_2)_2$ (E = S, Se) and $[Fe(NO)(S_2CC(CN)_2)_2]^{2-}$ have been found to be pure low-spin species by ESR spectroscopic and magnetic susceptibility methods.[660−668] Kirmse and co-workers have utilized isotopic labeling techniques to prove that trace amounts of $Fe(NO)(S_2CNEt_2)_2$ are responsible for a previously ill-explained triplet at $g = 2.0$ in the ESR spectrum of $Fe(S_2CNEt_2)_3$. The nitrosyl-containing impurity is present as a result of traces of nitrate ions in the $FeCl_3$ starting materials.[664] Only one example of the chemical reactivity of an $Fe(NO)(E_2CNR_2)_2$ system has been reported to date, namely the displacement of a dithiocarbamate ligand by donor molecules (L) to generate the dichloromethane adducts $Fe(NO)(S_2CNR_2)L\cdot nCH_2Cl_2$.[663]

Various $Fe(NO)(L_2)(PPh_3)_2$ and $Fe(NO)(L_2)_2$ complexes (L_2 = cysteine, phenanthroline, dithiolene, bipyridine) have been found to exhibit no antibacterial activity.[669]

Finally, Berke and co-workers have developed two synthetic routes to form iron nitrosyl hydride complexes, namely[670]

$$\begin{array}{l}(OC)_2(Et_3P)_2Fe(H)(OC(O)R) + \text{Diazald} \rightarrow \\ \qquad (OC)_2(Et_3P)_2Fe(NO)(OC(O)R) \\ \qquad \downarrow + LiAlH_4 \\ \qquad (OC)(Et_3P)_2Fe(NO)(H) + (Et_3P)_2Fe(NO)_2\end{array}$$

and

$$\begin{aligned}(OC)_2(R_3P)_2FeCl_2 + {}^tBuLi + [NO][BF_4] \rightarrow \\ (OC)_2(R_3P)_2FeCl(NO) \\ \downarrow + NaBH_4 \\ (OC)(R_3P)_2Fe(NO)(H)\end{aligned}$$

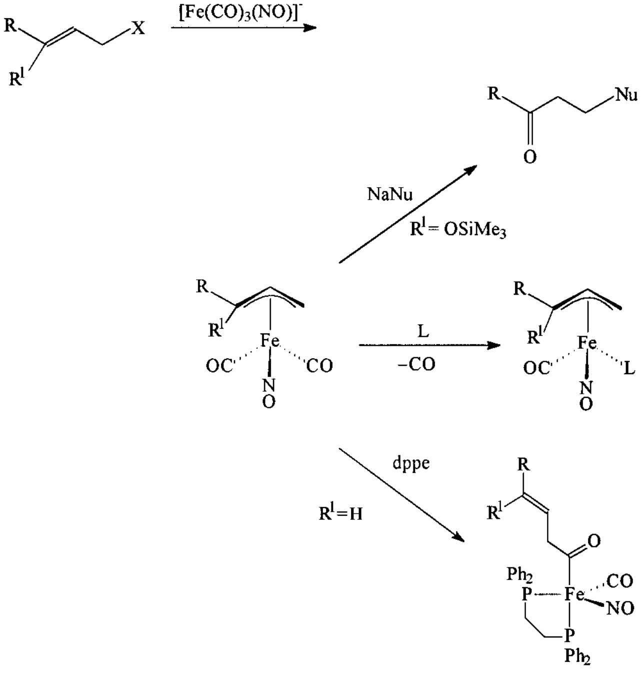
5.1.2. Organometallic Complexes

The tricarbonyl nitrosyl ferrate anion,[671] $[Fe(CO)_3(NO)]^-$, is an efficient carbonylation reagent for the formation of methyl esters and acetamides from alkyl halides.[672,673] The derivative tin complexes $(Cl_{3-n}R_nSn)Fe(CO)_3(NO)$ (R = Me, Ph) have been characterized by IR spectroscopy and crystallographic methods.[674]

Complexes of the form $(\eta^3\text{-allyl})Fe(CO)_2(NO)$ are generated by the reactions of $[Fe(CO)_3(NO)]^-$ with allyl halides[675−677] or allyl transmetalation reagents such as $[(\eta^3\text{-allyl})PdX)]_2$.[678] The η^3-allyl ligands in these nitrosyl complexes react with both carbon- and nitrogen-based electrophiles and nucleophiles and thus serve as synthetically equivalent synthons for carboanions and carbocations.[675,679−684]

As summarized in Scheme 18, $(\eta^3\text{-allyl})Fe(CO)_2(NO)$ undergoes displacement of a carbonyl ligand by phosphines and phosphites (L) to form $(\eta^3\text{-allyl})Fe(CO)(L)(NO)$.[672] In contrast, reaction with bidentate phosphines such as diphenylphosphinoethane (dppe) causes regioselective insertion of a carbonyl ligand into the less-substituted Fe−C σ-bond of the η^1,η^2-allyl resonance form resulting in $(R^1R^2C{=}CR^3C(O))Fe(CO)(dppe)(NO)$.[680,681] Interestingly, the η^3-cyclopropenyl analogues of these systems, $(\eta^3\text{-}C_3Ph_3)Fe(CO)_2(NO)$, react with P^nBu_3 to generate both the carbonyl-substituted complex $(\eta^3\text{-}C_3Ph_3)Fe(CO)(P^nBu_3)(NO)$ and the product of CO insertion $(\eta^3\text{-}C_3Ph_3CO)Fe(CO)(P^nBu_3)(NO)$.[685] The neutral acyl dicarbonyl nitrosyl complexes, $(RC(O))Fe(CO)_2(NO)$, react with allenes to form η^3-allyl complexes which have acyl groups at the central carbon of the allylic ligands.[686]

Scheme 18



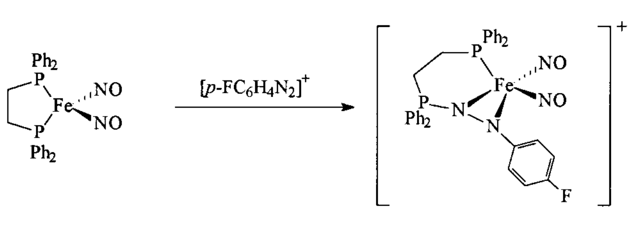
The $[Fe(CO)_3(NO)]^-$ anion also reductively couples α-bromo-*N*-methoxyimines to form diimines via $(\eta^3\text{-1-azaallyl})Fe(CO)_2(NO)$ intermediates.[687] Finally, $[CpFe(P(OMe)_3)(I)(NO)][BF_4]$ has been synthesized by the action of $[NO][BF_4]$ on the neutral carbonyl precursor.[688]

5.1.3. Dinitrosyl Complexes

Iron dinitrosyl complexes have been cited as suitable catalysts for the dimerization of diolefins.[689−692] One of these complexes, the prototypal $Fe(CO)_2(NO)_2$, has been studied by microwave spectroscopy,[693] ionization mass spectrometry,[694] and theoretical methods.[695,696] Novel synthetic methodologies for the production of this toxic liquid via the action of ethylnitrite on $Fe_2(CO)_9$ or silver nitrite on $Fe(CO_4)I_2$ have also been reported.[697] Chemically, $Fe(CO)_2(NO)_2$ is readily oxidized by tetracyanoethylene (TCNE), $[NO]^+$, or electrochemical means to generate mononuclear cations of the form $[Fe(CO)_{2-n}(NO)_2(\text{solvent})_n]^+$. These cationic complexes decompose over the course of a few hours to form trinuclear clusters that are detectable by IR and ESR spectroscopies.[698] Similarly, $Fe(NO)_2(CO)(PR_3)$ complexes undergo rapid oxidation by TCNE to form tetrahedral $Fe(NO)_2(\eta^2\text{-TCNE})(PR_3)$ complexes. These species have been crystallographically characterized, and in solution they exhibit slow rotation of the olefin group at room temperature as detected by NMR spectroscopy.[699,700]

The carbonyl ligands of $Fe(CO)_2(NO)_2$ may be displaced by σ-donor ligands (L) to form $Fe(NO)_2L_2$ complexes.[701−705] This methodology has been utilized for the formation of $Fe(NO)_2(MeIm)_2$ (MeIm = 1-methylimidazole). Monitoring the course of this reaction by ESR spectroscopy reveals the existence of the radical $[Fe(NO)_2(MeIm)_2]^+$, a molecule which exhibits ESR data similar to that displayed by biologically relevant non-heme-iron centers.[706]

The complex $(dppe)Fe(NO)_2$[703] reacts with the diazonium cation $[p\text{-}FC_6H_4N_2]^+$ by undergoing insertion of the terminal nitrogen atom into the Fe−P bond, i.e.[707]



$Fe(NO)_2L_2$ complexes are related to the 17e radical species $Fe(NO)_2LX$ (X = halide) by a redox square in which one-electron oxidation activates the former complexes toward substitution by σ donors and one-electron reduction activates the latter species toward substitution by better π acceptors, i.e.[702]

$$\begin{tikzcd} Fe(NO)_2L_2 \arrow[r, shift left, "-e^-"] & {[Fe(NO)_2L_2]^+} \arrow[l, shift left] \arrow[d, "X^\cdot"] \\ {[Fe(NO)_2LX]^-} \arrow[u, "L"] \arrow[r, shift left] & Fe(NO)_2LX \arrow[l, shift left, "e^-"] \end{tikzcd}$$

These $Fe(NO)_2LX$ species can also be generated by the addition of L to the dinuclear dinitrosyl complexes $[Fe(NO)_2(\mu\text{-}I)]_2$.[708,709] Carrying out these reactions with bidentate phosphines (PP) leads to the formation of $[Fe(NO)_2(\mu\text{-}PP)]_2$.[710] However, if these reactions are performed in the presence of dioxygen, complexes of the form $Fe(O_2NO)_2((O{=}PCH_2)_2)Cl$, in which both nitrosyl and phosphine ligands have been oxidized to nitrates and phosphine oxides, respectively, are obtained.[708,710−713] Similar nitrosyl to nitrate conversions can be effected using bidentate amines such as 2,2′-bipyridine, $Fe(NO_3)_2Cl(bipy)$ being formed in this instance.[714] These and related conversions of bound NO are considered in greater detail in a later section of this review.

The cyclodimerization of 1,3-butadiene has been achieved by using $[Fe(NO)_2Cl]_2$, reduced with zinc, as a catalyst.[715] Addition of bipy to $[Fe(NO)_2Cl]_2$ leads to a disproportionation reaction that forms the paramagnetic complex $[Fe(bipy)_3][Fe(NO)_2Cl_2]_2$.[714,716] These complexes also react with molecular oxygen to convert NO to nitrate.[714] Paramagnetic iron dinitrosyl complexes such as $[Fe(NO)_2I_2]^-$ have been characterized by ESR and IR spectroscopies and X-ray crystallography. On the basis of these studies, the investigators conclude that these species are best described as 17e complexes with a d^9 configuration rather than the d^7 configuration assumed by most previous researchers.[717]

ESR and NMR spectroscopic investigations of iron dinitrosyl complexes containing an amino acid substituent have revealed that the amino acids chelate to the metal center via their amino and carboxylate groups.[718,719]

5.1.4. Clusters

Sulfur-containing nitrosyl complexes are primarily of interest for the numerous roles they play in biological processes.[720] From an inorganic perspective, the archetypal iron sulfur nitrosyl complexes are Roussin's black ($[Fe_4(NO)_7S_3]^-$) and red ($[Fe_2(NO)_4S_2]^{2-}$) salts, so named after their discoverer and colors. The correlation of the counterion size on the solid-state molecular structures and Mössbauer spectra of both varieties of Roussin's salts have been established,[721−723] and the selenium analogue of Roussin's black salt has been structurally characterized.[724] Furthermore, both salts have been investigated for their photolytic,[725−727] electrochemical,[728] and biological[729−732] properties. Solutions of Roussin's red and black salts undergo facile aggregation to form the larger clusters $[Fe_5(NO)_8S_4]^-$ and $[Fe_7(NO)_{10}S_6]^-$, whose structures have been calculated by density functional theory.[733] Roussin's red salt reacts with sources of $[R]^+$ (R = aryl, alkyl, H) to generate the neutral species $[Fe(NO)_2(SR)]_2$. These "Roussin esters" have also been isolated from the reactions of Fe^{II} salts with sulfur-containing amino acids in the presence of $NaNO_2$[734−736] and by other methods.[697] Similar reactions have also generated Roussin's black salt.[732,735] A mononuclear derivative of a Roussin ester, namely $Fe(NO)_2(SC_6H_4\text{-}2\text{-}NH_2)$, has been prepared via the use of a bidentate thiolate ligand.[737] Larger iron sulfur nitrosyl clusters such as $[Fe_6S_6(NO)_6]^{2-}$, which consists of two fused Fe_3S_3 rings[738] and $Cp'_2M_2\{Fe(NO)_2\}S_4$ (Cp′ = Cp, Cp*, C_5Me_4Et; M = Mo, W),[739] have also been crystallographically characterized. Phosphine-containing derivatives of Roussin's black salt have been reported,[740,741] and an S_2O_3-substituted version of Roussin's red salt is also known, i.e., $[Fe_2(NO)_4(S_2O_3)_2]^{2-}$.[742]

The nature of the products resulting from the chemical and electrochemical reduction of $[Fe(NO)_2(SR)]_2$ species has been the subject of some controversy, the products being variously formulated as mono- and dianionic species.[743−746] The tellurium analogues of Roussin esters can be synthesized by the action of $[NO][BF_4]$ on the anion $[Fe(CO)_3(TePh)_3]^-$.[747] Furthermore, reaction of the selenium analogues, $[Fe(NO)_2(SeR)]_2$, with dimeric $[Ni(\mu\text{-}SCH_2CH_2)_2S)]_2$ in the presence of a source of nitrite ions forms the heterobimetallic compound $[(ON)Ni(\mu\text{-}SCH_2CH_2)_2S)Fe(NO)_2]$.[748]

Mild thermolysis of a solution of $[Cp'Fe(\mu\text{-}NO)]_2$ and $Cp'Co(C_2H_4)_2$ ($Cp' = \eta^5\text{-}C_5H_4Me$) leads to the generation of the cluster molecules $Cp'_3Co_2Fe(\mu_3\text{-}NH)(\mu_3\text{-}NO)$, $Cp'_3Co_2Fe(\mu_3\text{-}NH)_2$, and $Cp'_4Co_2Fe_2(\mu_3\text{-}NO)_2$ as the major products. The nitrosyl groups of $Cp'_4Co_2Fe_2(\mu_3\text{-}NO)_2$ bridge the $CoFe_2$ faces of an ideal Co_2Fe_2 tetrahedron.[749] Interestingly, the Cp* analogues of these complexes undergo a different mode of reactivity. Thus, the thermal or photochemical reaction of $[Cp^*Fe(\mu\text{-}NO)]_2$ and $Cp^*Co(C_2H_4)_2$ occurs via the slow transfer of NO from iron to cobalt, giving $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ and $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}NO)$. The related complex $Cp_3^*Co_2Fe(\mu_3\text{-}NH)(\mu_3\text{-}NO)$ was isolated in very low yield as the only iron-containing species. The differences in reactivity between the mono- and pentamethylcyclopentadienyl systems are attributed to steric effects.[750]

Treatment of iron carbonyls with *N*-nitrosoamines results in homolytic cleavage of the N−N bonds and formation of a number of organoiron products. These products include $Fe(CO)_2(NO)_2$ and $Fe(CO)_4(\mu\text{-}CNR_2)Fe(CO)_2(NO)$.[697] Reactions of $[Fe(NO)(CO)_3]^-$ with $[CpM(CO)_2(CPh)]^+$ (M = Mn, Re) produce the bimetallic bridging-carbene complexes, $CpM(CO)_2(\mu\text{-}CPh)Fe(CO)_2(NO)$. Addition of $Fe_2(CO)_9$ to these bimetallic species generates trinuclear MFe_2 clusters.[751] $[CpFe(CO)(\mu\text{-}CO)]_2$ reacts with NO gas in refluxing xylene to form another trinuclear cluster, namely $(CpFe(\mu\text{-}CO))_3(\mu_3\text{-}NO)$. The ν_{NO} of this cluster species occurs at 1325 cm^{-1} in its Nujol-mull IR spectrum, thereby indicating a highly activated nitrosyl group.[752,753]

Other carbonyl nitrosyl clusters of iron have also been characterized, and these include $Fe_3(CO)_8(NO)_2S$, $Fe_3(CO)_7(NO)_2(S^tBu)$, and $HFe_3(CO)_3(NO)S$. The latter complex readily dissociates a proton in solutions to form the corresponding $[Fe_3(CO)_3(NO)S]^-$ anion.[754] Furthermore, the reaction of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ with $[NO][BF_4]$ provides $[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$. Carbonyl substitution by phosphines and phosphites (L) in these compounds leads to a host of complexes of general formula $[Fe_2(CO)_5(L)(NO)(\mu\text{-}PPh_2)]$ and $[Fe_2(CO)_4(L)_2(NO)(\mu\text{-}PPh_2)]$.[755] It may also be noted that the cluster $Fe_4N(CO)_{11}(NO)$ was briefly reported in 1994.[756]

Rossel and co-workers have described the gold-containing cluster $Fe_6C(AuPPh_3)(CO)_{15}(NO)$ which exhibits a terminal nitrosyl stretch at 1754 cm^{-1} in its IR spectrum (THF). $Fe_4C(AuPPh_3)(CO)_{11}(NO)$ can also be obtained if an excess of $[NO][BF_4]$ is used during the preparation of the former cluster from $[Et_4N][Fe_6C(\mu_3\text{-}AuPPh_3)(CO)_{16}]$[757] The interaction between $CpMn(CO)_2(THF)$ and $Cp_2FeMn(\mu\text{-}NO)_2(NO)$ results in the formation of $Cp_3FeMn_2(\mu\text{-}CO)(\mu\text{-}NO)_2(\mu_3\text{-}NO)$. This complex represents the final link in the series of the isoelectronic clusters $Cp_3Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)$ and $Cp_3Fe_3(\mu\text{-}CO)_3(\mu_3\text{-}NO)$.[758] The related $Cp_3MnFe_2(\mu_2\text{-}CO)_2(\mu_2\text{-}NO)(\mu_3\text{-}NX)$ complexes have been characterized by single-crystal X-ray diffraction, IR, ^1H NMR, laser-desorption, FT mass spectrometric, and electrochemical methods.[759] The trimetallic molybdenum iron cluster $(\eta^5\text{-}C_5H_4Me)Mo(\mu_3\text{-}NH)(\mu_2\text{-}NO)(\mu_2\text{-}CO)Fe_2(CO)_6$ can be synthesized by the reaction of $(\eta^5\text{-}C_5H_4Me)Mo(CO)_3Cl$ with $Na[Fe(CO)_3NO]$, and its solid-state molecular structure has been established by a single-crystal X-ray diffraction analysis.[760]

$[Fe_6N(CO)_{14}(NO)]^{2-}$ has been isolated in 11% yield from the reaction between $[Fe_4N(CO)_{12}]^-$ and $Mo(CO)_3(NCEt)_3$. The source of the NO ligand in the product complex is probably the nitride which is oxidized during the course of the reaction by some as yet unknown agent.[761] Finally, it should be noted that numerous heteropolytungstate molecules containing Fe−NO groups have been reported in recent years.[211,762−764]

5.2. Ruthenium and Osmium Nitrosyls

5.2.1. Coordination Complexes

The ruthenium and osmium analogues of nitroprusside are well-known and exhibit behavior similar to that of their iron congener. For instance, just as for nitroprusside, $[Ru(CN)_5(NO)]^{2-}$ can be excited selectively to form two long-lived, metastable states. The shifts in the nitrosyl-stretching frequencies of these states suggest that the electronic changes are mainly localized at the NO ligands.[765]

$[Ru(CN)_5(NO)]^{2-}$ can be electrochemically reduced to $[Ru(CN)_5(NO)]^{3-}$. In contrast to its iron analogue, the ruthenium complex does not eliminate a cyanide ion. Rather, there is evidence for dimerization of the trianion.[766] The current view is that the unpaired electron density lies mainly on the nitrosyl ligands in these anions, thus formulated as $[M^{II}(CN)_5(NO^\bullet)]^{3-}$ (M = Fe, Ru, Os).[603,767−770] The complex $[trans\text{-}Ru(Cl)(cyclam)(NO)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) forms $[trans\text{-}Ru(Cl)(cyclam)(NO^\bullet)]^+$ when reduced by one electron at low temperature, and the extra electron resides on the NO ligand in the product in a manner similar to that observed for $[Ru(CN)_5(NO)]^{3-}$.[771] Light-induced metastable states have also been studied in octahedral Ru^{II} nitrosyl complexes containing oxalate and ethylenediamine ligands.[772]

$Na_2[Os(CN)_5(NO)]\cdot 2H_2O$ is isostructural with its iron and ruthenium analogues and can be synthesized by photolysis of the hexacyanoosmate(II) anion in the presence of nitrite salts.[773] The $[M(CN)_5(NO)]^{2-}$ (M = Fe, Ru, Os) anions react with hydroxide ions to form equilibria with the *N*-nitrite complexes $[M(CN)_5(NO_2)]^{4-}$.[773−775] An investigation of the reactions of the bimetallic complexes $(H_3N)_5Ru^{II}{-}NC{-}M(CN)_4(NO)$ (M = Ru, Os) and their oxidized forms $[(H_3N)_5Ru^{III}{-}NC{-}M(CN)_4(NO)]^+$ with $[OH]^-$ has revealed that the cationic form contains a significantly more electrophilic nitrosyl ligand.[620]

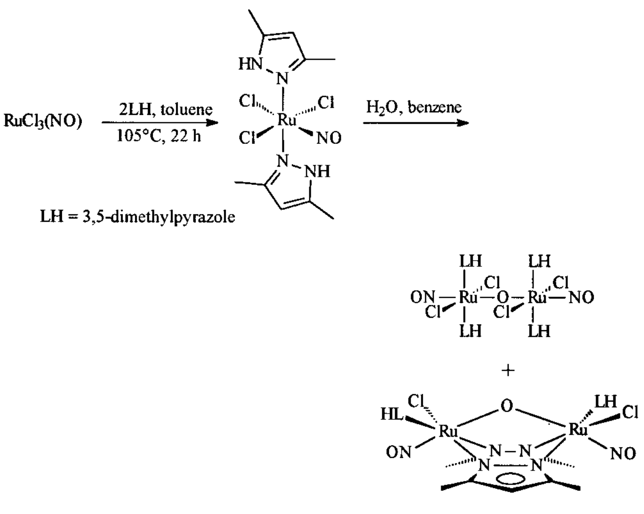
Several structural determinations of the ruthenium- and osmium(II) pentahalo complexes $[M(NO)X_{5-n}Y_n]^{2-}$ (M = Ru, Os; X and Y = halide) have been published in recent years.[776−785] In each of these structures, the most electronegative halogen atom is situated in a position trans to the nitrosyl ligand. The vibrational spectra of these complexes have also been recorded.[776,786−788] The mixed-halide complexes $[M(NO)X_{5-n}Y_n]^{2-}$ are usually formed by the reaction of $[Y]^-$ salts with the $[M(NO)X_5]^{2-}$ precursors. However, treatment of $[Bu_4N]_2[Ru(NO)I_5]$ with $[Bu_4N]Cl$ leads instead to the dimeric, bridging iodo complex $[Bu_4N]_2[\{Ru(NO)(Cl)(I)_2\}_2(\mu\text{-}I_2)]\cdot 2I_2$.[777]

The osmium dianions $[Os(NO)X_5]^{2-}$ are readily oxidized to their monoanionic form, $[Os(NO)X_5]^-$.[780,789] In the case of ruthenium, however, one-electron oxidation in acetonitrile leads to the formation of several products, one of which is $[Ru(NO)Cl_4(NCMe)]^-$ that has been crystallographically characterized.[790] The DMSO derivative of this compound has been synthesized by the reaction of $Ru(NO)Cl_3\cdot nH_2O$ with dimethyl sulfoxide, $Ru(NO)(DMSO)_2Cl_3$ also being generated during this procedure.[791] The Os(DMSO) analogue, namely $[Os(NO)Cl_4(DMSO)]^-$, is formed by the DMSO-for-halide displacement on the $[Os(NO)Cl_5]^{2-}$ precursor.[792,793] Other reported $[M(NO)X_4L]^-$ complexes include $[Ru(NO)(OAc)_3(OC({=}O)\text{-}2\text{-}C_5H_5N)]^-$ [794] and $[Ru(NO)Cl_4(OH_2)]^-$.[795]

The trianionic forms of both the ruthenium and osmium pentahalonitrosyl complexes doped in AgCl powders have been studied by ESR spectroscopy.[796] The $[Ru(NO)Cl_5]^{2-}$ anion liberates NO rapidly under photolysis conditions.[797] The solid-state phase transformations of $[Ph_3PH][Ru(NO)Cl_5]$ have been studied by thermogravimetric analysis and IR spectroscopy, and it has been shown that at 140 °C 2 equiv of HCl are eliminated and $trans\text{-}Ru(NO)(PPh_3)_2Cl_3$ is formed.[798] Theoretical comparisons of the effects of NO vs NS (a stronger π-acid) coordination in these systems have also been published.[782,799]

Numerous octahedral ruthenium- and osmium(II) complexes of compositions $[ML_5(NO)]^{3+}$ and $[ML_4X(NO)]^{2+}$ [monodentate L = pyridine,[800−803] NH_3,[804−815] phosphines,[816−820] arsines,[816] H_2O;[812] bidentate L = bipyridine,[800,821−831] phenanthroline,[829,830,832] (arylazo)pyridine,[833,834] azoamines,[835] oximates,[836−841] diamines,[772,842] diarsines,[829,843] ketoximes;[844] tridentate L = terpyridine,[818,835] 2,6-bis(pyrazol-1-yl)pyridines;[819] tetradentate L = 1,5,9,13-tetraazacyclohexadecane,[845] 1,4,8,11-tetraazacyclotetradecane-5,7-dione;[846] X = halide, OH^-] have been reported. Similar ruthenium(II) complexes containing bidentate monoanionic ligands, e.g. $[Ru(quinolinato)_2(Cl)(NO)]^-$, have also been reported.[832,847−853] The series of related nitrite complexes $[M(NO)(NO_2)_{4-n}X_n]^{2-}$ have been well studied by crystallography,[854,855] ^{99}Ru and ^{15}N NMR

Scheme 19



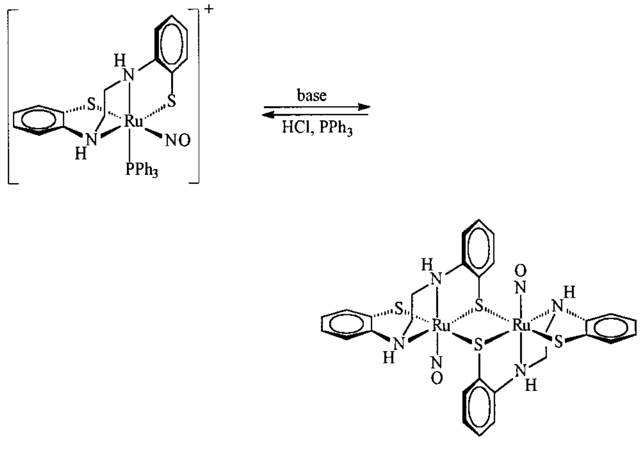
spectroscopy,[856,857] electrochemistry,[858,859] and thermochemistry.[860,861]

One of the most common starting materials in ruthenium(II) nitrosyl chemistry is $Ru(NO)Cl_3 \cdot (OH_2)_x$, which can be readily obtained by passing NO gas through alcoholic solutions of $RuCl_3(OH_2)_x$.[862] This nitrosyl complex holds promise as a carrier of NO in the photodynamic therapy of tumors and in other biological applications.[797,863−866] In general, addition of donor molecules (L) to the hydrous ruthenium nitrosyl trihalide typically affords octahedral $Ru(NO)X_3L_2$ or $[Ru(NO)X_2L_3]^+$ complexes.[867−870] When L is a nitrogen-based ligand such as an amine and X = Cl, the presence of coordinated water leads to further reactivity and diminished yields of $Ru(NO)Cl_3L_2$ complexes. Consequently, Bohle and Sagan have developed a route to anhydrous $Ru(NO)Cl_3$ via the nitrosylation of $Ru(NO)Cl_3 \cdot (OH_2)_x$ in thionyl chloride. This anhydrous trichloro complex reacts with 3,5-dimethylpyrazole (LH) to generate the mononuclear product *trans*-$Ru(NO)(LH)_2Cl_3$ in good yield. As illustrated in Scheme 19, this latter complex rapidly reacts with water to form bimetallic Ru(II) complexes that contain bridging oxo and apical nitrosyl ligands. Furthermore, *trans*-$Ru(NO)(LH)_2Cl_3$ reacts with dibenzyldithiocarbamate to form various isomers having the composition $Ru(NO)(S_2CNBz_2)_2Cl$.[871]

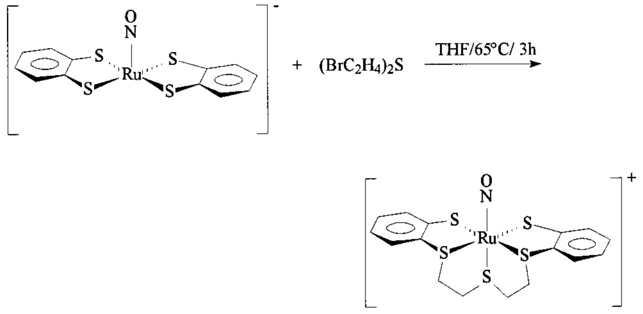
Treatment of $Ru(NO)Cl_3$ with pyrazolylborate anions (Tp′) leads to the formation of $Tp'Ru(NO)Cl_2$ complexes. The ν_{NO} values exhibited by these complexes are at higher energy by ca. 90 cm^{-1} than those displayed by their Cp analogues, thereby indicating a lesser degree of Ru→NO back-bonding in these compounds.[872]

$Ru(NO)X_3L_2$ complexes can also be generated by other synthetic methodologies. For instance, $Ru(CO)_2(bipy)Cl_2$ reacts with nitric acid in HX (X = Cl, F) to form *fac*- and *mer*-$Ru(NO)X_2Cl(bipy)$, the trichloro members of which have been structurally characterized.[873−875] The related $Ru(NO)Cl_3(PPh_3)_2$ reacts with $H_2[S_2N_2H_2]$ [$S_2N_2H_2$ = 1,2-ethanediamine-*N*,*N*′-bis(2-benzenethiolate)] to produce either $[Ru(NO)(PPh_3)(S_2N_2H_2)]Cl$ or the thiolate-bridged bimetallic $[Ru(NO)(S_2N_2H)]_2$ depending on the pH of the reaction mixture. As shown in Scheme 20, $[Ru(NO)(S_2N_2H)]_2$ can be converted to $[Ru(NO)(PPh_3)(S_2N_2H)]^+$ by the addition of PPh_3 under acidic conditions.[876]

Scheme 20



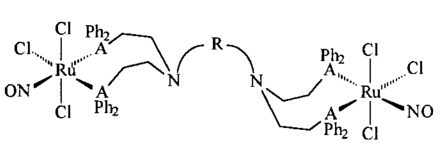
Scheme 21

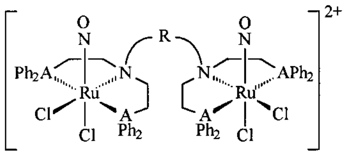


$Ru(NO)Cl_3(PPh_3)_2$ also reacts with 1,2-dithiolatobenzene (S_2^{2-}) to form square pyramidal anionic complexes of the form $[Ru(NO)(S_2)_2]^-$. As illustrated in Scheme 21, further reaction with $(BrC_2H_4)_2S$ leads to template alkylation across a thiolate linkage of each S_2 moiety and the formation of an η^5-dithiolate−trisulfur donor ligand (S_5^{2-}) in the octahedral $[Ru(NO)(S_5)]^+$ complex.[877,878] Related ligand systems have also received some attention.[749,879−881]

The octahedral $Ru(NO)Cl_3(AsPh_3)_2$ has been structurally characterized and shown to exist in the *trans*-arsine configuration in the solid state.[882] This complex and its stibine and phosphine analogues have also been examined by electrospray mass spectrometry[883] and photoelectron spectroscopy.[884] The bidentate diarsine complex *fac*-$Ru(NO)(pdma)Cl_3$ [pdma = 1,2-phenylenebis(dimethylarsine)] reacts with AgX (X = O_2CCF_3, OTf, NO_3) at room temperature to effect halide exchange and form $Ru(NO)(pdma)ClX_2$ in which Cl is situated trans to the NO ligand.[885] In contrast, the use of coordinating solvents such as pyridine or other potential L ligands results in the formation of the cationic species $[Ru(NO)(pdma)ClL_2]^{2+}$.[885]

Nitrosyl complexes containing ligands of general formula $((Ph_2ACH_2CH_2)_2N)_2R$ (A = P, As; R = CH_2CH_2, *m*-xylyl) have been reported. Pictured as follows, these complexes are of two types, either $[Ru(NO)Cl_3(\mu\text{-}L)]_2$ in which each metal center is coordinated by two phosphine or arsine arms of the ligand or $[\{Ru(NO)Cl_2(\mu\text{-}L)\}_2]^{2+}$ in which the bridging ligand also coordinates to the metal center via its amine functionality:[886]





The dimeric complex $\{Ru(acac)_2\}_2(\mu\text{-}NO)_2$ can be electrochemically oxidized in acetonitrile to obtain 2 equiv of *cis*-$[Ru(NO)(NCMe)(acac)_2]^+$.[887] The acetylacetonate complexes $[M(NO)Cl_{5-2n}(acac)_n]^m$ [M = Ru, Os; $n = 0$ ($m = 2$), $n = 1$ ($m = 1$), $n = 2$ ($m = 0$)] have also been electrochemically characterized.[888]

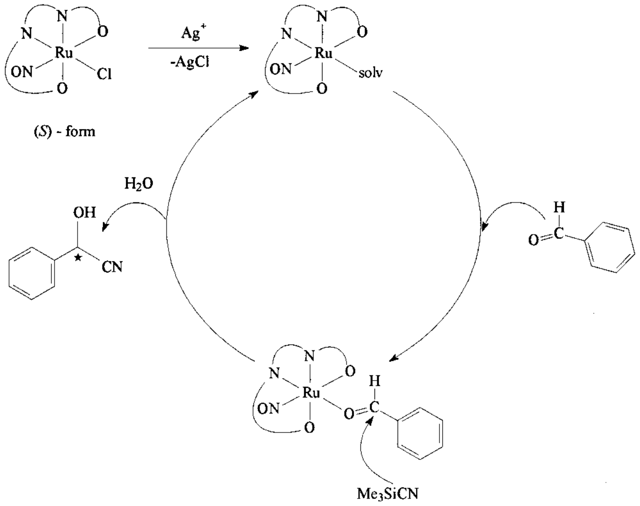
Ru(NO)(salen)Cl is an effective catalyst for Diels–Alder reactions, even in water.[889] Furthermore, upon photoactivation, a chiral variant of this complex[890] exhibits catalytic activity toward asymmetric epoxidation,[891] cyclopropanation,[892] and hetero Diels–Alder reactions.[893,894]

The Ru–Ru multiply bonded species $Ru_2(Fap)_4(NO)Cl$ [Fap = 2-(2-fluoroanalino)pyridinate] has been synthesized and structurally characterized. The Ru–N–O angle was found to be 155.8(6)°.[895]

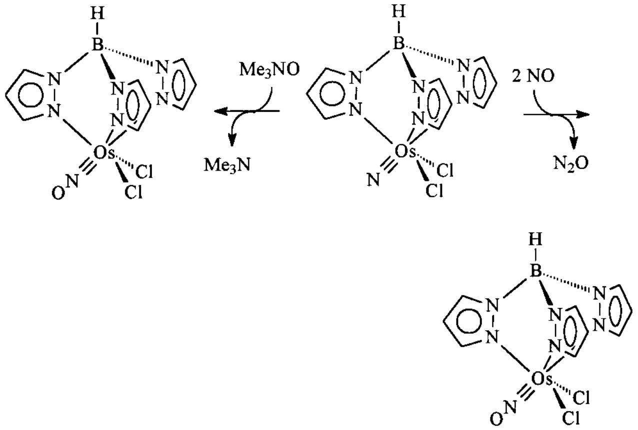
Reaction of $Ru(NO)Cl_3(PPh_3)_2$ with binaphthyl Schiff base salts ($[SB]^{2-}$) generates complexes of the form Ru(NO)(SB)Cl. Several of these have been structurally characterized and found to exist as the cis-isomers with the NO ligands trans to oxygen atoms. As depicted in Scheme 22, these complexes are effective catalysts for the asymmetric trimethylsilylcyanation of aldehydes.[896]

Reactions of $Ru(NO)X_3{\cdot}xOH_2$ (X = Cl, Br) with diethylenetriamine (dien) yield either $[Ru(NO)(dien)Cl_2]^+$ or $[Ru(NO)(dienH)Br_3]^+$ cations.[869] In other work, RuL_2X_4 complexes such as those containing tridentate (LX_2) pyridinedicarboxamide ligands have been treated with nitrite ions in methanol to form $Ru(NO)(LX_2)(PPh_3)(NO_2)$.[897]

Scheme 22



Scheme 23



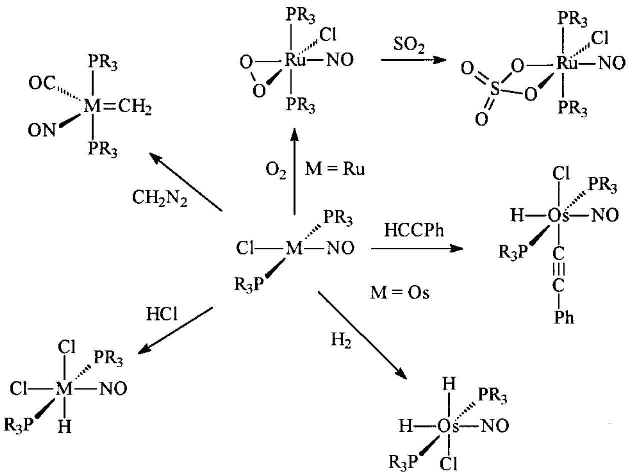
Coordinated NH_3 groups have been electrochemically oxidized to nitrosyls on a number of different ruthenium and osmium centers. Thus, the six-electron oxidation of coordinated ammonia in $[Os^{II}(terpy)(bipy)(NH_3)]^{2+}$ results in the formation of a nitrosyl ligand in the product $[Os^{II}(terpy)(bipy)(NO)]^{3+}$. Cyclic voltammetry measurements on this system suggest that an Os(IV) complex, namely $[Os^{IV}(terpy)(bipy)(NH_2)]^{3+}$, is an intermediate that is subsequently hydrated to form a hydroxylamine ($-NH_2OH$) complex. Further oxidation of this hydroxylamine complex leads to the final nitrosyl product.[898] Similarly, $Os(terpy)Cl_2(NH_3)$ undergoes a sequence of two reversible one-electron oxidations followed by a proton-coupled two-electron oxidation to form an Os(IV) nitrido complex.[899] This nitrido complex is then oxidized to the nitrosyl by reaction with trimethylamine *N*-oxide in acetonitrile.[900] The ruthenium ammine complex $[Ru(bipy)_2(NH_3)_2]^{2+}$ can be converted to $[Ru(bipy)_2(NH_3)(NO)]^{3+}$ either via electrochemical oxidation[901] or by oxidation with aqueous Cl_2 and HOCl.[827]

As illustrated in Scheme 23, oxygen-atom transfer to a terminal osmium nitride is also known for $TpOs(N)Cl_2$. In this instance reaction of the nitride with Me_3NO generates the nitrosyl $TpOs(NO)Cl_2$.[902] If S_8 or Se metal is used in place of Me_3NO, the corresponding chalcogenonitrosyls are generated. The same osmium nitride complex has also been shown to exhibit remarkable reactivity toward NO(g). When $TpOs(N)Cl_2$ is reacted with 2 equiv of NO, nitrogen-atom abstaction occurs to form N_2O and $\{TpOsCl_2\}$, which is trapped by the second 1 equiv of NO to form the known $TpOs(NO)Cl_2$.[903]

Relatively few $Os(NO)X_3L_2$ complexes have been reported in the past decade. Unlike its ruthenium congener, $Os(NO)Br_3(Et_2S)_2$ has not been isolated from the reaction of $[OsBr_6]^{2-}$ with NO gas and Et_2S. Instead, the oxidation product $Os(NO)Br_3(Et_2S)(\eta^1\text{-}Et_2SO)$ (ν_{SO} = 940 cm^{-1}) is obtained in small amounts.[904] Nitrosylation of $[OsCl_6]^{2-}$ in 2-methoxyethanol followed by addition of PEt_2Ph affords $Os(NO)Cl_2(PEt_2Ph)_2(OCH_2CH_2OMe)$.[904]

$Ru(NO)Cl_3(PPh_3)_2$ may be reduced by Zn/Cu to generate the extremely reactive square-planar Ru^0 complex $Ru(NO)Cl(PPh_3)_2$. This species subsequently undergoes phosphine exchange with added PR_3 to

Scheme 24



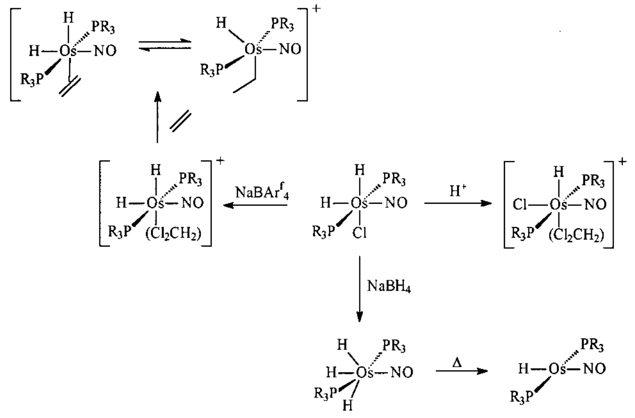
form $Ru(NO)Cl(PR_3)_2$.[905] These $Ru(NO)Cl(PR_3)_2$ compounds react with π-acidic molecules (Y) to form the 18e adducts $Ru(NO)(Y)Cl(PR_3)_2$ (Y = TCNE, CO, CH_2, η^2-O_2). When Y = O_2, the complexes are highly oxidizing and react with SO_2 to form $Ru(NO)(\eta^2\text{-}SO_4)Cl(PR_3)_2$. The $Ru(NO)Cl(PR_3)_2$ complexes also undergo oxidative addition with HCl to form the Ru(II) hydrides $Ru(NO)Cl_2(H)(PR_3)_2$.[906]

An osmium analogue of this system, namely $Os(NO)Cl(P^iPr_3)_2$, is formed by ligand displacement from either the 18e precursor $Os(NO)Cl(PPh_3)_3$ or the peroxocarbonylosmium(II) derivative $Os(NO)Cl(PPh_3)_2$(*C*(O)O*O*). As illustrated in Scheme 24, there are some striking differences in the reactivity displayed by the second- and third-row species. For instance, in contrast to its ruthenium counterpart, the square planar osmium complex reacts readily with H_2 to form the octahedral dihydride species,[907–909] and it undergoes other oxidative addition reactions more readily.[910]

$Os(NO)(H)_2Cl(P^iPr_3)_2$ reacts with $[H]^+$ at a hydride ligand to eliminate H_2 and form the $[Os(NO)(H)Cl(P^iPr_3)_2]^+$ cation. The dihydrido analogue of this cation, $[Os(NO)(H)_2(P^iPr_3)_2]^+$, is obtainable via halide abstraction from the neutral chloro precursor. Both of these hydrido cations are very electrophilic and reversibly coordinate CH_2Cl_2 in solution. The dihydride complex reversibly binds H_2 and forms the $[Os(NO)(H)_2(H_2)(P^iPr_3)_2]^+$ cation, which exhibits a large barrier to hydride exchange.[911] Furthermore, as shown in Scheme 25, the dihydrido cation coordinates ethylene to form an η^2-ethylene dihydrido complex which exists in equilibrium with its ethyl monohydrido tautomer.[912]

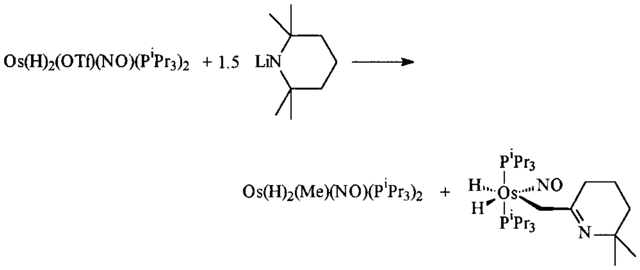
Sodium borohydride reacts with $Os(NO)(H)_2Cl(P^iPr_3)_2$ to form the trihydride complex $Os(NO)(H)_3(P^iPr_3)_2$. The ruthenium analogue of this species is produced quantitatively by the reaction of excess H_2 with $Ru(NO)Me(P^iPr_3)_2$. NMR and IR spectroscopies characterize the molecular geometries of these trihydrides as being pseudooctahedral with significantly compressed H−M−H angles. Theoretical calculations rationalize these geometries as being due to increased H→M σ-donation and the presence of the strongly π-accepting NO ligand. The hydride ligands in these complexes undergo site exchange via a dihydrogen intermediate.[913]

Scheme 25



As depicted in Scheme 25, thermal elimination of H_2 from $Os(NO)(PPh_3)_2H_3$ affords square-planar $Os(NO)(PPh_3)_2H$. Oxidative addition of the Sn−H bond of $(p\text{-tolyl})_3SnH$ to this Os(0) complex or its chloro analogue generates the Os(II) stannyl complexes $Os(NO)(Sn(p\text{-tolyl})_3)(PPh_3)_3HX$ (X = H, Cl). The high trans influence of the hydride ligands in these complexes confers lability to one of the phosphine ligands, thereby enabling its ready substitution by CO or dithiocarbamates.[914]

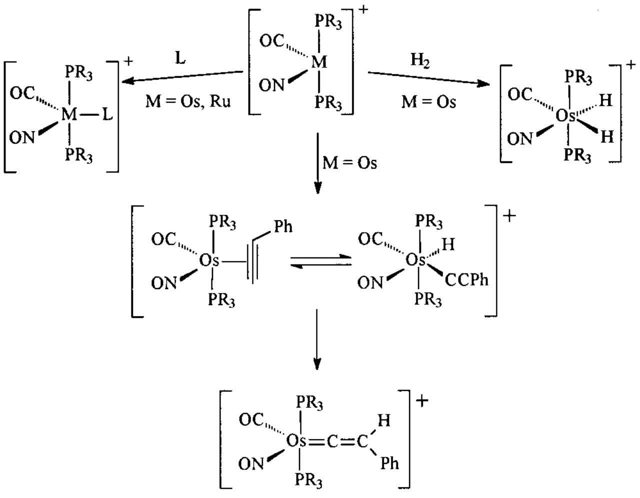
$Os(H)_2(OTf)(NO)(P^iPr_3)_2$ reacts with lithium 2,2,6,6-tetramethylpiperidide to give $Os(H)_2(Me)(NO)(P^iPr_3)_2$ and $Os(H)_2(C_8H_{14}N)(NO)(P^iPr_3)_2$ via an interesting C−C bond cleavage reaction, i.e.[915]



The complexes $Os(NO)Cl(PPh_3)_2(OSA)$ (A = O, CH_2, S, NR; R = *p*-tolyl, *o*-tolyl, SO_2-*p*-tolyl) have been reported, and $Os(NO)Cl(PPh_3)_2(\eta^2\text{-}OSNC_6H_4Me\text{-}4)$ has been crystallographically characterized. The iminooxosulfurane ligand is coordinated to the metal center in a psuedoolefinic fashion.[916,917]

$Ru(NO)Cl(PPh_3)_2$ reacts with diazomethane in Et_2O to afford the methylene complex $Ru(NO)Cl(=CH_2)(PPh_3)_2$. This complex reacts with electrophiles in a manner that is dominated by the nucleophilic character of the methylene carbon. Thus, reactions of this complex with various molecules lead to addition of polar bonds across the metal−methylene linkage and formation of the octahedral complexes $Ru(NO)Cl(Y)(CH_2X)(PPh_3)_2$ (XY = HCl, ClHgCl, OSO). The ruthenium methylene complex reacts with olefins and acetylenes to produce $Ru(NO)Cl(CH_2PPh_3)(PPh_3)(R_xCCR_x)$ [R = Ph (x = 1); R = F (x = 2)] via the migration of PPh_3 to the methylene carbon and the coordination of the unsaturated reagent.[918] This reactivity contrasts with that of the osmium analogues which fail to form tractable products when treated with olefins.

Scheme 26

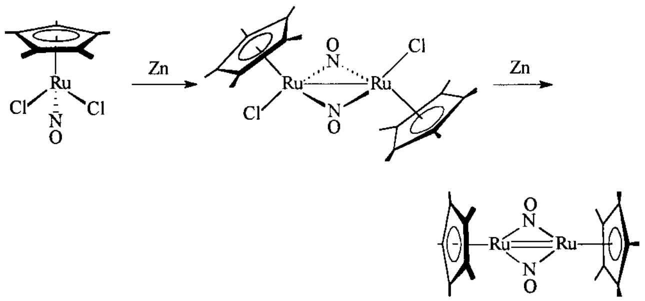


Ru(NO)Cl(PPh$_3$)$_2$ reacts with thiirane *S*-oxide (C$_2$H$_4$SO) to give Ru(NO)Cl(SO)(PPh$_3$)$_2$, which contains a linear nitrosyl ligand and a bent Ru−S−O linkage. This complex can be oxidized with *m*-chloroperbenzoic acid to form Ru(NO)Cl(η^2-SO$_2$)(PPh$_3$)$_2$, Ru(NO)Cl(SO$_4$)(PPh$_3$)$_2$, and a small amount of Ru(NO)Cl(η^2-O$_2$)(PPh$_3$)$_2$.[919] This latter complex can also evidently be obtained by the reaction of Ru(NO)Cl(SO$_4$)(OH$_2$)$_2$ with triphenylphosphine.[830]

The square-pyramidal complexes M(NO)Cl(CO)(PR$_3$)$_2$ (M = Ru, Os) are preparable by the reaction of M(H)Cl(CO)(PR$_3$)$_2$ with Diazald in refluxing ethanol. Subsequent treatment of these complexes with 1,1-dithiolates results in nitrosyl ligand substitution and the formation of RuCl(η^2-dithiolate)(CO)(PR$_3$)$_2$.[920] Alternatively, chloride abstraction by [Na]$^+$ or [Ag]$^+$ salts of weakly coordinating anions generates the four-coordinate cationic species [M(NO)(CO)(PR$_3$)$_2$]$^+$ which exist in a sawhorse molecular geometry and, unlike the precursor chlorides, contain a linear NO ligand. The lability of the chloro ligand during this transformation is enhanced by the alteration of the bonding mode of the NO ligand, i.e., from bent to linear. The formal oxidation state of the metal center changes from +2 to 0 upon nitrosyl-straightening, and so this is an example of an *intramolecular* redox process. The cationic complexes readily form adducts with H$_2$O, MeCN, CO, [F]$^-$, and [H]$^-$ in both the ruthenium and osmium systems. However, as illustrated in Scheme 26, reactivity differences do exist between the second- and third-row congeners. The osmium complex is more electron-rich, more Brønsted basic, and more readily oxidized than its ruthenium analogue. Consequently, [Os(NO)(CO)(PR$_3$)$_2$]$^+$ readily undergoes oxidative addition with H$_2$ to form [Os(H)$_2$(NO)(CO)(PR$_3$)$_2$]$^+$. Furthermore, reaction of the osmium complex with acetylenes (H−C≡C−R, R = H, Ph) forms [Os(NO)(CO)(η^2-HCCR)(PR$_3$)$_2$]$^+$ which in the case of R = Ph establishes an equilibrium with the hydrido alkynyl isomer. Over time this equilibrium mixture slowly converts to the vinylidene form. None of this reactivity occurs for the ruthenium analogues.[910,921−924]

It may also be noted that *fac*-RuH(NO)(P$_3$) (P$_3$ = tridentate phosphine donor) complexes are active hydrogenation catalysts for aldehydes and ketones.[925−928]

Scheme 27



Treatment of [Ru(Hedta)Cl]$^-$·2H$_2$O with hydroxamic acids in aqueous solution results in the formation of brown [Ru(NO)(edta)Cl]$^{2-}$. This complex was synthesized as part of a study designed to test the ability of hydroxamic acid to act as a nitric oxide donor.[929] The analogous Ru(III) complex, Ru(NO)(edta), is a highly effective catalyst for the transfer of oxygen atoms from O$_2$ to unsaturated hydrocarbons, e.g. during the transformation of 1-hexene to 2-hexanone.[930,931]

Finally, Shepherd and co-workers have studied the series of complexes [Ru(hedta)(*NO*)]$^{n-}$ [hedta = *N*-(hydroxyethyl)ethylenediaminetriacetate; *NO* = NO$^+$ (n = 0), NO (n = 1), or NO$^-$ (n = 2)]. This study provided the first comparison of the entire set of NO$^{+/\bullet/-}$ as ligands on the same metal center in a constant ligand environment.[932]

5.2.2. Organometallic Complexes

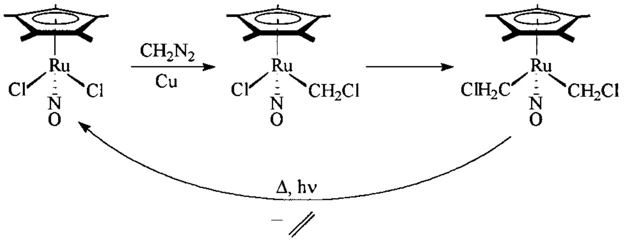
The dicationic Ru(II) complexes [Cp′Ru(NO)L$_2$]$^{2+}$ (Cp′ = Cp or Cp*; L = Lewis base) have been synthesized by a number of routes. One such route involves treatment of neutral Cp′RuL$_2$X or monocationic [Cp′RuL$_3$]$^+$ and [Cp′RuL$_2$]$^+$ complexes with nitrosonium salts.[933−939] Another popular method of synthesis is the reduction of the nitrite ligands in Cp′Ru(NO$_2$)L$_2$ complexes with protic sources.[934,940] Furthermore, the triflate ligands of Cp*Ru(NO)(OTf)$_2$ can be displaced by bidentate L$_2$ ligands to generate [Cp*Ru(NO)L$_2$]$^{2+}$.[941] The phenazine derivative [Cp*Ru(NO)(dppz)]$^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) is particularly interesting since it intercalates DNA with a binding constant of $>10^6$ M^{-1}.[941]

The neutral dichloro complex CpRu(NO)Cl$_2$ can be made by the reaction of Ru(NO)Cl$_3$ with CpH.[942] As depicted in Scheme 27, this complex and its Cp* congener may be reduced with Zn dust to form the bridging nitrosyl complexes [Cp′Ru(μ-NO)]$_2$.[942,943] In the case of the Cp* system, the intermediate [Cp*Ru(μ-NO)Cl]$_2$ has been isolated and crystallographically characterized.[943]

Reaction of [Ru(RH)Cl$_2$]$_2$ (RH = η^4-cyclooctadiene, η^6-cycloheptatriene, η^6-benzene) with NOCl reportedly affords the corresponding cationic nitrosyls [(RH)Ru(NO)Cl$_2$]$^+$. The thionitrosyl analogues can be synthesized by a similar methodology utilizing (NSCl)$_3$.[942]

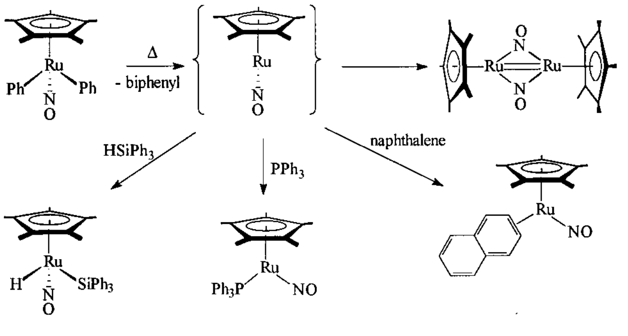
Chloride substitution by H$_2$O occurs when Cp′Ru(NO)Cl$_2$ complexes are dissolved in water, resulting in an equilibrium mixture of $[Cp'Ru(NO)Cl_2]_{aq}$ plus the $[Cp'Ru(NO)Cl(OH_2)]^+$ and $[\{Cp'Ru(NO)(\mu\text{-}OH)\}_2]^{2+}$ cations. H/D exchange in the Cp* methyl groups occurs when $Cp^*Ru(NO)Cl_2$ is dissolved in D_2O. It is proposed that this exchange occurs via a ring slippage of the Cp* ring to a η^4-fulvene coordination mode, a process that is facilitated by the π-donor ability of the OH^- and H_2O ligands.[944] Similar OTf ligand displacement by water occurs with the $Cp'Ru(NO)(OTf)_2$ complexes.[944]

Reaction of $Cp^*Ru(NO)Cl_2$ with ethereal diazomethane over a copper catalyst leads to the stepwise insertion of methylene units into the Ru–Cl bonds (vide infra). Photolysis or thermolysis of the resulting $Cp^*Ru(NO)(CH_2Cl)_2$ complex leads to the elimination of ethylene via an intramolecular coupling of CH_2 groups with concomitant formation of the dichloro-starting material.[945]

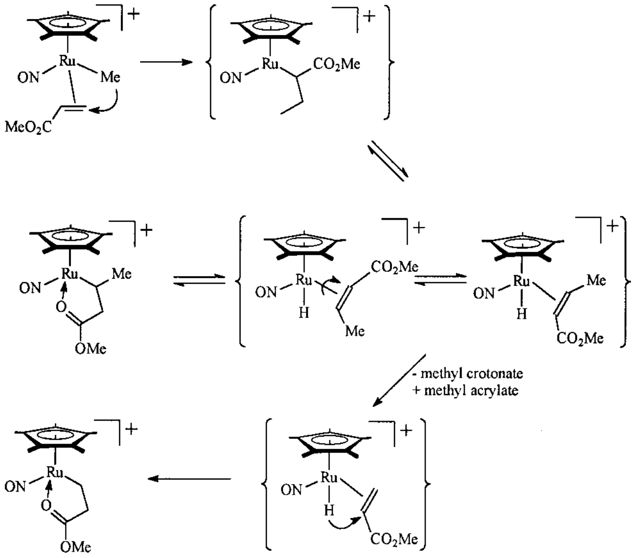


The thermally induced reductive elimination of biphenyl from the coordination sphere of $Cp^*Ru(NO)Ph_2$ results in the generation of the 16e transient species Cp*Ru(NO) which subsequently dimerizes to $[Cp^*Ru(\mu\text{-}NO)]_2$ (Scheme 28). Bergman and coworkers have detected the intermediate $Cp^*Ru(NO)(\eta^2\text{-}C_6H_6)$ complex by careful monitoring of the reaction in aromatic solvents by ^1H NMR spectroscopy. Addition of naphthalene to solutions of the intermediate complex results in displacement of benzene and formation of $Cp^*Ru(NO)(\eta^2$-naphthalene), the solid-state molecular structure of which has been determined. This complex can be independently synthesized by the reaction of Cp*Ru(NO)Me(OTf) with $LiHBEt_3$ in benzene, followed by the addition of naphthalene.[946] The bound arenes reversibly dissociate from the coordination sphere of the metal, thereby generating Cp*Ru(NO), which can be trapped with phosphines and oxidatively adds the silicon–hydrogen bond of Ph_3SiH or a carbon–hydrogen bond of CH_2Cl_2.[943,946] Reaction of $Cp^*Ru(NO)(\eta^2$-arene) complexes with dialkyl disulfides leads to the formation of the dithiolato complexes $Cp^*Ru(NO)(SR)_2$.[946]

Scheme 28



Scheme 29

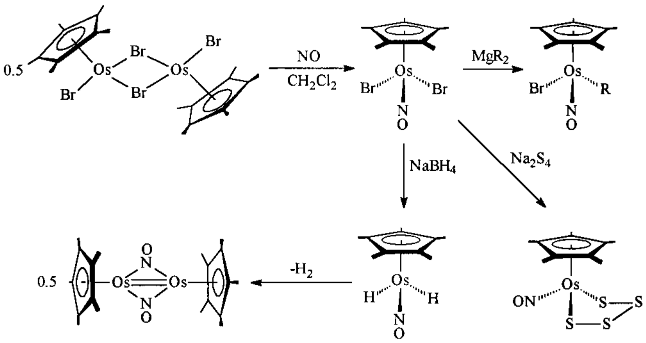


The hydrocarbyl ligands of $Cp'Ru(NO)R_2$ (R = Me, Ph, p-tolyl) complexes readily undergo protonolysis upon addition of suitable acids.[944,947,948] For example, treatment of $Cp^*Ru(NO)R_2$ with 1 equiv of triflic acid generates Cp*Ru(NO)R(OTf). Significant amounts of $Cp^*Ru(NO)(OTf)_2$ are produced when R = aryl, thereby indicating that the monoaryl complex is more susceptible to protonolysis than is the diaryl precursor. Cp*Ru(NO)R(OTf) dissociates its triflato ligand in solution and forms the reactive electrophilic fragment $[Cp^*Ru(NO)R]^+$.[947] Attempts to trap this fragment when R = Me with methyl acrylate lead to three ruthenium species that are detectable by NMR spectroscopy, namely the olefin complex $[Cp^*Ru(NO)Me(\eta^2\text{-}CH_2CH(CO_2Me))]^+$ and the metallacycles $[Cp^*Ru(NO)(\mathit{C}H(CH_3)CH_2C(\mathit{O})OCH_3)]^+$ and $[Cp^*Ru(NO)(\mathit{C}H_2CH_2C(\mathit{O})OCH_3)]^+$. The olefin complex converts to the α-Me metallacycle via migratory insertion of the olefin into the Ru–Me bond over 0.5 h. The α-Me metallacycle in turn converts to the α-H metallacycle over 15 h at room temperature. As illustrated in Scheme 29, the latter process occurs via deinsertion of the α-Me metallacycle to form the olefin hydrido cation $[Cp^*Ru(NO)(H)(\eta^2\text{-}CH_3CH{=}CHCO_2Me)]^+$. Elimination of the coordinated methyl crotonate from the cation followed by coordination of another 1 equiv of methyl acrylate and subsequent migratory insertion then forms the thermodynamic product.[948]

The $[Cp^*Ru(NO)R]^+$ cations also react with alkynes. For instance, reaction with PhC≡CPh generates the ruthenacyclopentadiene complexes $Cp^*Ru(NO)(\mathit{C}(Ph){=}C(R)\mathit{C}_6H_3X)$ (X = H, Me). These conversions occur via migratory insertion of the alkyne into the Ru–R bond followed by deprotonation at the ortho position on a phenyl ring.[947]

Treatment of $Cp^*Ru(NO)Cl_2$ with disodium dithiolates leads to chloride metathesis and the isolation of ruthenium dithiolate complexes.[949–952] Similar methods have been employed for the preparations of

Scheme 30



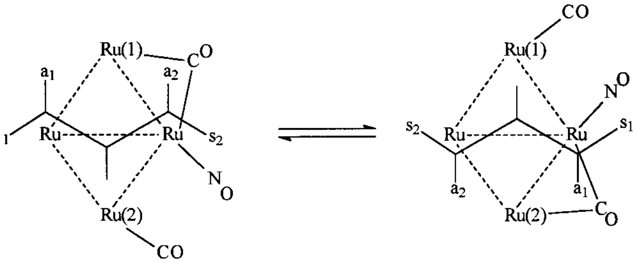
related oxygen-donor diolate complexes.[953] Cyclic voltammetry indicates that all these complexes display reversible one-electron oxidation and reduction couples.

As shown in Scheme 30, reaction of the bimetallic complex $[Cp^*OsBr(\mu\text{-}Br)]_2$ with nitric oxide in CH_2Cl_2 affords the dibromonitrosyl compound $Cp^*Os(NO)Br_2$.[954] Treatment of this complex with $NaBH_4$ yields $Cp^*Os(NO)H_2$. This dihydrido complex undergoes H_2 elimination over a few days in solution, ultimately producing $[Cp^*Os(\mu\text{-}NO)]_2$. The Os=Os bond length in this latter complex is 2.359(1) Å.[955] Attempted metathesis of the halide ligands of $Cp^*Os(NO)Br_2$ with R_2Mg reagents leads only to the formation of the monoalkylated products, $Cp^*Os(NO)(R)Br$, even when large excesses of alkylating reagent and extended reaction times are employed. The dimethyl complex, $Cp^*Os(NO)Me_2$, is accessible by the treatment of $Cp^*Os(NO)MeBr$ with AgOTf followed by metathesis of the triflato ligand with Me_2Mg.[955] $Cp^*Os(NO)Br_2$ reacts with Na_2S_4 or $[Et_4N]_2Se_6$ to generate the metallacyclic tetrachalcogenido complexes $Cp^*Os(NO)(E_4)$ (E_4 = *S*−S−S−*S* or *Se*−Se−Se−*Se*) (vide supra). Dechalcogenation of these compounds with $^nBu_3P$ leads to the formation of $[Cp^*Os(NO)(\mu\text{-}E)]_2$, the tellurium analogue of which can also be formed by the reaction of the dibromo complex with Li_2Te.[956]

Hydrometalation of $RuH(NO)(PPh_3)_3$ with 1,3-butadienes and allenes proceeds regio- and stereoselectively to produce the corresponding η^3-allyl complexes in good yields.[957]

5.2.3. Clusters and Dinitrosyls

The dianionic carbide carbonyl cluster $[Ru_6C(CO)_{16}]^{2-}$ reacts with 1 equiv of NO gas to form $[Ru_6C(CO)_{15}(NO)]^-$. Further reaction with gaseous NO results in the production of a neutral pentanuclear cluster having NO and NO_2 ligands, i.e., $Ru_5C(CO)_{14}(NO)(NO_2)$. Similar chemistry occurs upon nitrosylation of the hexanuclear allyl complex $[Ru_6C(CO)_{15}(C_3H_5)]^-$.[958,959] The resulting $[Ru_6C(CO)_{14}(C_3H_5)(NO)]^{2-}$ anionic cluster is stereochemically nonrigid, and its fluxionality is believed to involve the rapid migration of a CO and an NO ligand around the cluster framework as well as rotation of the allylic fragment, i.e.[960,961]

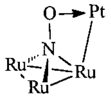


Nitrosyl-containing clusters are often synthesized by the reaction of nitrosonium salts with neutral or anionic precursor clusters. For instance, $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]^+$ is formed by the reaction of $Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)$ with nitrosonium tetrafluoroborate, and it has been structurally characterized.[962]

$[Ru_3(\mu\text{-}NO)(CO)_{10}]^-$ reacts with 1 or 2 equiv of tertiary silanes and stannanes to afford trinuclear $[Ru_3(\mu\text{-}NO)(\mu\text{-}H)(ER_3)(CO)_9]^-$ or $[Ru_3(\mu\text{-}NO)(\mu\text{-}H)_2(ER_3)_2(CO)_8]^-$ (ER_3 = $SiEt_3$, $SiPh_3$, $SnBu_3$, $SnPh_3$), respectively. Spectroscopic data indicate that the monohydrido complexes are isostructural and that the structures of the disilyl dihydrido derivatives (C_s) differ from those of the distannyl dihydrido derivatives (C_1).[963]

While $Ru(NO)_2(PPh_3)_2$ has been known for over 30 years, new methodologies for its synthesis have been developed in the past decade. These methodologies involve the action of HNO_3 or $AgNO_3$ on $RuCl_3$ or $RuH(SO_4)_2(OH_2)_6$ followed by treatment with triphenylphosphine.[964] This dinitrosyl complex reacts with excess HgX_2 by substitution of one nitrosyl and one phosphine ligand and oxidation to the formal Ru(II) complex $RuX_2(HgX)(NO)(PPh_3)$. An exception to this generalization is the reaction with $Hg(SCN)_2$, which forms $Ru(SCN)(HgSCN)_2(NO)(PPh_3)$.[965]

Last, the tetrametallic nitrosyl cluster $Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}NO)(CO)_{10}(P^iPr_3)$ has recently been formed in 12% yield by the reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}NO)(CO)_{10}$ with $Pt(nb)_2(P^iPr_3)$ (nb = bicyclo[2.2.1]hept-2-ene).[966] This complex exhibits the interesting NO-binding mode shown as follows:



6. Group 9 Nitrosyls

6.1. Cobalt Nitrosyls

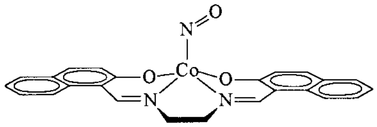
Numerous investigations involving the archetypal cobalt nitrosyl complex, the d^{10} $Co(CO)_3(NO)$, have been reported in recent years. These include chemical vapor deposition studies,[967] photochemical studies,[968−970] thermal decomposition studies,[971−973] theoretical studies,[695] microwave spectroscopic studies,[974] its deposition onto Mo/Al_2O_3 surfaces,[975] its use as a precursor to Fe_xCo_y particles,[976] and its photodissociation.[977]

The substitution of the carbonyl ligands in $Co(CO)_3(NO)$ by chiral phosphines and isocyanides has been effected.[978−980] The Co−CO and Co−NO bond lengths and L−Co−C(CO) and L−Co−N(NO) bond angles of several such substituted complexes have been established, and distinct differences exist between the parameters involving the CO and NO ligands, thereby affording a method of differentiating the two ligands.[981] The carbonyl ligands of $Co(CO)_3(NO)$ can also be displaced by $PHPh_2$. The disubstituted species, $Co(CO)(NO)(PHPh_2)_2$, can be isolated in 44% yield, and it has been structurally characterized. Deprotonation of this species with 2 equiv of ^{n}BuLi, followed by the addition of 2 equiv of MeI, cleanly generates $Co(CO)(NO)(PMePh_2)_2$.[395]

The η^2-hydroxylamine complex $[(MeC(CH_2PPh_2)_3)Co(\eta^2\text{-}NH_2O)]^+$ reacts with O_2 to produce $(MeC(CH_2PPh_2)_3)Co(NO)$, a phosphine-substituted variant of $Co(CO)_3(NO)$, which exhibits a ν_{NO} (Nujol mull) of 1630 cm^{-1}.[982] In a related transformation, the six-electron oxidation of $[Os(terpy)(bipy)(NH_3)]^{2+}$ produces $[Os(terpy)(bipy)(NO)]^{3+}$, presumably through a similar η^2-hydroxylamine intermediate.[898]

The substitution of water in the d^8 aquo complex $[Co(NO)(CN)_4(H_2O)]^{2-}$ can be effected by a variety of donor ligands,[983–985] and the thermolysis of the parent complex $[Co(CN)_5(NO)]^{3-}$ in the solid-state results in dissociation of NO.[986]

The prototypal Schiff base nitrosyl complex Co(salen)(NO) dissociates NO when photolyzed in toluene.[987] The complexes $Co(o\text{-}OC_6H_4CH{=}NR)_2(NO)$ (R = Me, Et, ^{n}Bu, Ph, CH_2Ph) have also been prepared by adding NO to the cobalt Schiff-base precursor. They have been shown to contain a bent Co−N−O linkage by X-ray crystallographic analyses, and they have also been thoroughly characterized by ^{59}Co solution and ^{15}N solid-state NMR spectroscopies.[988] Co(naphth-en)(NO) [naphth-en = $(o\text{-}OC_{10}H_6CH{=}NCH_2)_2$] (vide infra) can be synthesized in the same manner as Co(salen)(NO). Just as in the salen case, it also contains a bent nitrosyl ligand as confirmed by ^{15}N NMR spectroscopy.[659]

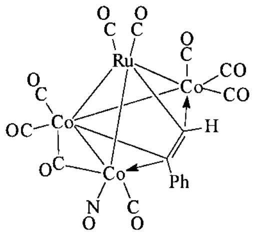


The d^8 complexes $[Co(NO)(L{-}L)_2]^{2+}$ (L−L = numerous diphosphine ligands) disproportionate in the presence of nucleophiles, $[X]^-$, to give the dinitrosyl cations $[Co(NO)_2(L{-}L)_2]^+$ and the cobalt(III) species *trans*-$[CoX_2(L{-}L)_2]^+$.[989] The disproportionation reaction probably proceeds via a bent-nitrosyl intermediate, $[Co(X)(NO)(L{-}L)]^+$.

$$\begin{aligned} &2[Co(NO)(L{-}L)_2]^{2+} + 2[X]^- \rightarrow [Co(NO)(L{-}L)]^+ + \\ &\quad L = \text{phosphine} \\ &\quad [X]^- = \text{halide} \\ &\qquad\qquad\qquad\qquad \textit{trans}\text{-}[CoX_2(L\text{-}L)]^+ + L{-}L \end{aligned}$$

The related Co(NO)(6,13-di(ethoxycarbonyl)-7,12-dimethyldibenzo[b.i.]-1,4,8,11-tetraaza[14] annulene) complex is also known, and it has been structurally characterized.[990] Furthermore, $Co(NO)(NO_2)_2(PR_3)_2$ (R = Me, Et) reacts with O_2 to generate $Co(NO_3)_2(PR_3)_2$, a transformation which may involve the conversion of the nitrosyl to a nitrate.[991] Also, IR spectroscopic and mass spectral evidence suggests that the reaction of $[Co(CN)_5]^{3-}$ with NO(g) may well proceed through a dimeric cobalt complex containing bridging nitrosyls.[992]

The mixed-metal cluster $[RuCo_3(CO)_{12}]^+$ reacts with $[NO][BF_4]$ to produce $RuCo_3(CO)_{11}(NO)$, which contains a linear terminal nitrosyl (ν_{NO} = 1820 cm^{-1}, hexanes solution).[993,994] Both the ^{59}Co and ^{99}Ru NMR spectra of the neutral cluster have been recorded.[993] This cluster reacts with phenylacetylene to form $RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CH)$ whose molecular structure is as follows:[995]

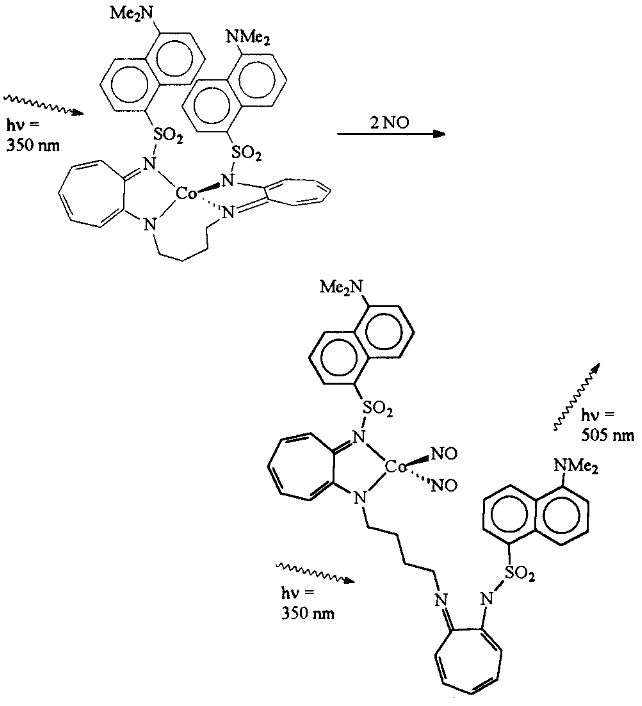


IR spectroscopic studies suggest that the cobalt ions in the zeolites Co−APO-18 and Co−APO-5 form dinitrosyl species when exposed to NO gas.[996]

The structurally characterized $[Co(NO)_2(py)_2]^+$ cation can be prepared from $[Co(NO)_2I]_2$, [Na][BPh$_4$], and pyridine,[997] but it slowly decomposes in CH_2Cl_2 in the absence of excess pyridine. The related $[(dppf)Co(NO)_2]^+$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] has been prepared in a similar manner, and it has been characterized by Mössbauer spectroscopy and X-ray crystallography.[704,705]

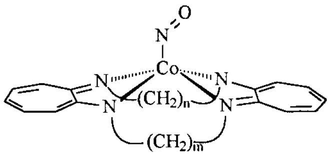
The complex $Co(DATI\text{-}4)_2$ [DATI-4 = 1,4-bis(*N*-dansyl-*N*-amino-*N*′-troponimino)butane] reacts with NO to generate $Co(NO)_2(DATI\text{-}4)$ (Scheme 31).[998] The net result of this transformation is that half of the ligand, specifically the part that contains the fluorophore, is pushed away from the quenching

Scheme 31



metal center. Consequently, the fluorophore can then be observed by fluorescence emission spectroscopy. This strategy may well serve as the basis for a useful method of detecting NO in situ in real time.

The tropocoronand complexes Co(NO)(TC-n,m) (n, m = 3, 3; 4, 4) can be obtained by reacting the parent complexes, Co(TC-n,m) with NO, and both complexes have been structurally characterized. When $n = m = 3$, a paramagnetic square pyamidal complex is generated, but when $n = m = 4$, a diamagnetic trigonal bipyamidal complex is formed. In both cases the nitrosyl ligand is bent, i.e.[999]



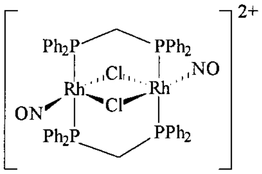
$Cp^*_3Co_3(\mu\text{-}H)_4$ reacts with gaseous NO to afford $Cp^*_3Co_3(\mu_3\text{-}NO)_2$, which has been structurally characterized.[1000] This same cluster can also be made by the reaction of $[Cp^*Fe(\mu\text{-}NO)]_2$ with $Cp^*Co(C_2H_4)_2$. Also formed in this latter reaction is $Cp^*_3Co_3(\mu_3\text{-}NO)(\mu_3\text{-}CCH_3)$, which has also been structurally characterized.[750,1001] In the same vein, the thermolysis of a mixture of $[(\eta^5\text{-}C_5H_4Me)Fe(\mu\text{-}NO)]_2$ and $(\eta^5\text{-}C_5H_4Me)Co(C_2H_4)_2$ generates $(\eta^5\text{-}C_5H_4Me)_4Co_2Fe_2(\mu_3\text{-}NO)_2$ as one of the products. The solid-state molecular structure of this tetrametallic species has also been established.[749] The reaction of $CoCl_2$, $[Na][C_5H(^iPr)_4]$ or $[Na][C_5H_2(^tBu)_3]$, and NO(g) produces a number of nitrosyl-containing products. Among these are $[Cp'Co]_2(\mu\text{-}NO)_2$ and $[Cp'Co]_2(\mu\text{-}NO)(\mu\text{-}Cl)$, which have been structurally characterized for $Cp' = C_5H_2(^tBu)_3$.[1002,1003]

6.2. Rhodium and Iridium Nitrosyls

The most common coordination compounds for rhodium and iridium nitrosyls are those having the general formula $M(NO)(X)_2(L)_2$ (X = halide or pseudohalide; L = Lewis base). Thus, both square-pyramidal $Rh(NO)(NO_2)_2(PPh_3)_2$ and $Rh(NO)(OAc)(Cl)(PPh_3)_2$ are known, and both possess bent apical nitrosyl ligands.[1004,1005] Photolysis of the complexes $M(NO)(X_2)(Ph_3E)_2$ (M = Rh, Ir; E = P, As; X = Cl, Br, I) results in the loss of NO from the metal, but no tractable products have been isolated from these reactions.[884] Furthermore, $Rh(NO)Cl_2(PPh_3)_2$ reacts with $[Rh(CO)_2Cl]_2$ to produce the bimetallic $Rh(CO)(PPh_3)(\mu\text{-}Cl)_2Rh(NO)(Cl)(PPh_3)$.[1006] Treatment of $Ir(NO)Cl_2(PPh_3)_2$ with [Na][SMes] (Mes = mesityl) results in the production of the d^8 nitrosyl complex $Ir(NO)(SMes)_2(PPh_3)$, which is square planar probably because of the steric bulk of the mesityl substituents.[1007] Unlike the starting material, this complex also contains a linear nitrosyl ligand. Other complexes in this class are $Ir(NO)(SH)_2(PPh_3)_2$, which is formed by the reaction of NaSH with $Ir(NO)Cl_2(PPh_3)_2$, and $[Ir(NO)(\mu\text{-}S^tBu)(PPh_3)]_2$, which is a metal–metal-bonded dimer with linear nitrosyl ligands.[1008]

The reaction of $Rh_2(OAc)_4(H_2O)_2$ with KNO_2 and HNO_3 gives $Rh_2(OAc)_4(NO)(NO_2)$,[1009] and $Rh(H)(P^iPr_3)_3$ reacts with Diazald to form $Rh(NO)(P^iPr_3)_3$, which is unstable and reacts with one molecule of $Rh(H)(P^iPr_3)_3$ to produce the dimer $Rh_2(\mu\text{-}NO)(\mu\text{-}H)(P^iPr_3)_4$.[1010]

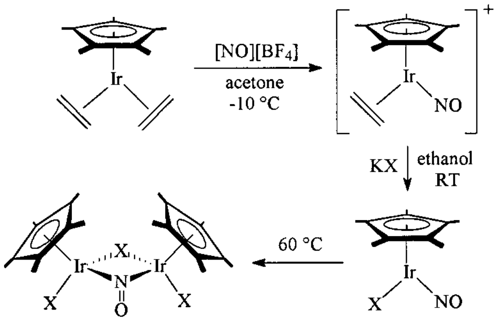
Two SO_2 molecules in $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-}dppm)_2$ are displaced by 2 equiv of $[NO]^+$ to give $[Rh_2(NO)_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2]^{2+}$ (vide infra), which contains linear nitrosyl ligands.[1011]



The cluster anion $[Ir_6(CO)_{11}(\mu\text{-}CO)_3(NO)]^-$ has been prepared by the one-electron oxidation of $[Ir_6(CO)_{15}]^{2-}$, followed by addition of NO(g). It has been structurally characterized and shown to contain a linear nitrosyl ligand.[1012]

As summarized in Scheme 32, $Cp^*Ir(\eta^2\text{-}C_2H_4)_2$ reacts with 1 equiv of $[NO][BF_4]$ to afford $[Cp^*Ir(NO)(\eta^2\text{-}C_2H_4)]^+$ in high yield [ν_{NO} = 1822 cm^{-1} (acetone)]. This cationic molecule reacts with KX (X = Cl, Br, I) to give the neutral Cp*Ir(NO)X species [ν_{NO} = 1751 cm^{-1} (EtOH) for X = I], which slowly convert to $[Cp^*Ir(X)]_2(\mu\text{-}NO)(\mu\text{-}X)$ upon warming. Furthermore, $[Cp^*Ir(NO)(\eta^2\text{-}C_2H_4)]^+$ reacts with NaOEt to give $Cp^*Ir(NO)(CH_2CH_2OEt)$.[1013,1014]

Scheme 32



In a similar manner, $Cp^*IrMe_2(PPh_3)$ reacts with $[NO]^+$ to produce $[Cp^*IrMe_2(NO)]^+$. Curiously, this reaction appears to be reversible since $[Cp^*IrMe_2(NO)]^+$ reverts to the starting material in the presence of 1 equiv of PPh_3.[1015,1016] The related dication $[Cp^*IrMe(PR_3)(NO)]^{2+}$ is also known, and it can be reduced with Cp_2Co to obtain a 19e monocationic complex that is detectable by ESR spectroscopy.

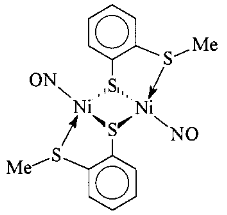
7. Group 10 Nitrosyls

7.1. Nickel Nitrosyls

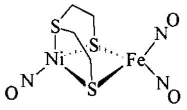
Cp′Ni(NO) is undoubtedly the best studied class of group 10 nitrosyl complexes, and they have been the subject of many investigations, including those involving photoelectron spectroscopy,[1017−1019] EXAFS,[1020] and mass spectrometry.[1021] Their formation at a nickel electrode under an NO atmosphere has also been documented.[1022] The metastable isomer Cp*Ni(η^2-NO) has recently been characterized by X-ray crystallography.[1023]

$Ni(NO)_{1-3}$ species have been detected by guided ion beam mass spectrometry.[1024] Most nickel nitrosyls, however, are of the form $[Ni(NO)L_3]^+$, are tetrahedral, and contain a linear nitrosyl ligand. For instance, $[NiL_3(NO)]^+$ (L = PH_2Mes) has been synthesized by reacting NiL_4 with $[NO]^+$.[1025] The related complex with L = 1,3,5-triaza-7-phosphaadamantane can be prepared in a similar manner.[1026] Also known are complexes of the type $[Ni(NO)(L)(L-L)]^+$ (L = a phosphine)[1027] and NiX(NO)(L−L) [X = Cl, Br, I, CN; L−L = 1,2-$C_6H_4(PMePh)_2$].[1028] The related Ni(NO)-(PPh_3)(L) (L = 3,6-di-*tert*-butyl-*o*-benzosemiquinone) has been synthesized by reaction of TlL with Ni(NO)-$Br(PPh_3)_2$ and has been characterized by ESR spectroscopy.[1029] However, the identity of the products formed during the reaction between $Ni(NO)Cl(PPh_3)_2$ and $Hg(CN)_2$ has yet to be established conclusively.[1030]

Ni(*o*-(MeS)$C_6H_4S)_2$ reacts with $[NO]^+$ or NO to generate the dimer [Ni(*o*-(MeS)C_6H_4S)(NO)$]_2$ shown as follows:[1031]



Also known is the heterometallic complex Ni(NO)-(μ-$S(CH_2)_2S(CH_2)_2S$)$Fe(NO)_2$ in which the geometry around the d^{10} Ni center is tetrahedral, i.e.[748]

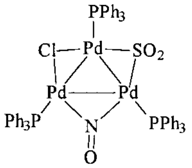


7.2. Palladium and Platinum Nitrosyls

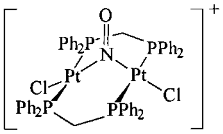
The adsorption of NO on Pd-exchanged H−ZSM-5 generates NO-containing species with ν_{NO} values at 2126 and 1881 cm^{-1}.[1032,1033] $M(NO)_{1,2}$ (M = Pd, Pt) species have been detected in an argon matrix.[1034]

The square pyramidal $Pt(C_6Cl_5)_2Cl_2(NO)$ has been synthesized and structurally characterized. It contains an apical bent NO ligand that displays a stretching frequency of 1776 cm^{-1} (Nujol mull).[1035] Indirect kinetic evidence for the existence of [Pd-$(NO)Cl_3]^{2-}$ has also been collected.[1036,1037]

The palladium cluster *triangulo*-Pd_3(μ-NO)(μ-SO_2)-(μ-Cl)$(PPh_3)_3$ is formed by the reaction between $[NO]^+$ and $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$.[1038]



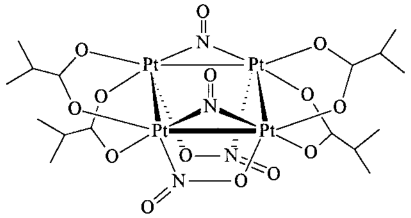
The first A-frame nitrosyl complexes, $[M_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]^+$ (M = Pd, Pt),[1039,1040] have also been made by reacting $[NO][BF_4]$ with $Pt_2(\mu\text{-}dppm)_2Cl_2$, contrary to unfavorable theoretical predictions.[1041] Both of the d^8 metal centers in this compound are square planar, i.e.



The double-A-frame complexes $[Pt_3(\mu\text{-}NO)_2(RNC)_2(\mu\text{-}dpmp)_2]^{4+}$ (dpmp = bis(diphenylphosphino)phenylphosphine; R = xylyl, mesityl) are also known.[1042]

The large cluster anion $[Pt_{19}(CO)_{21}(NO)]^{3-}$ is made by substitution of a CO by $[NO]^+$ in $[Pt_{19}(CO)_{22}]^{4-}$. Surprisingly, it contains a bent nitrosyl ligand which results from an intramolecular redox reaction, whereby two electrons that were delocalized over the metal cluster are transferred to the nitrosyl group.[1043]

Several oligomeric platinum species containing μ-NO and μ-NO_2 groups are known,[1044−1048] and of these $Pt_4(\mu\text{-}NO)_2(\mu\text{:}\eta^2\text{-}N,O\text{-}NO_2)_2(\mu\text{-}{}^iPrCO_2)_4$ has been structurally characterized, i.e.

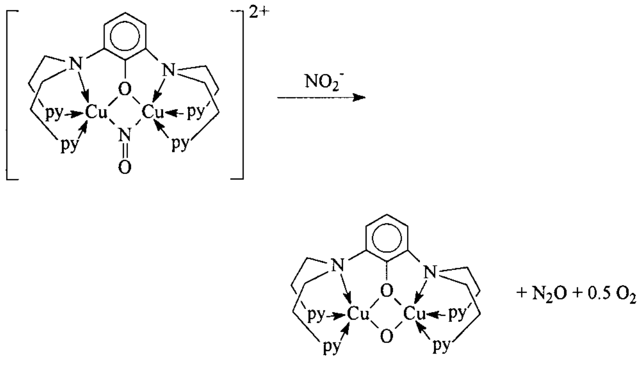


8. Group 11 Nitrosyls

8.1. Copper Nitrosyls

Several theoretical and matrix-isolation studies on copper nitrosyls have been reported.[1049−1052] These investigations have found that N-bound nitrosyls are more stable than O-bound nitrosyls and that the ground-state geometry for Cu−NO is bent while that for $[Cu-NO]^+$ is linear. Also, copper-containing zeolites have been found to form mono- and dinitrosyl species when exposed to NO.[1053−1056]

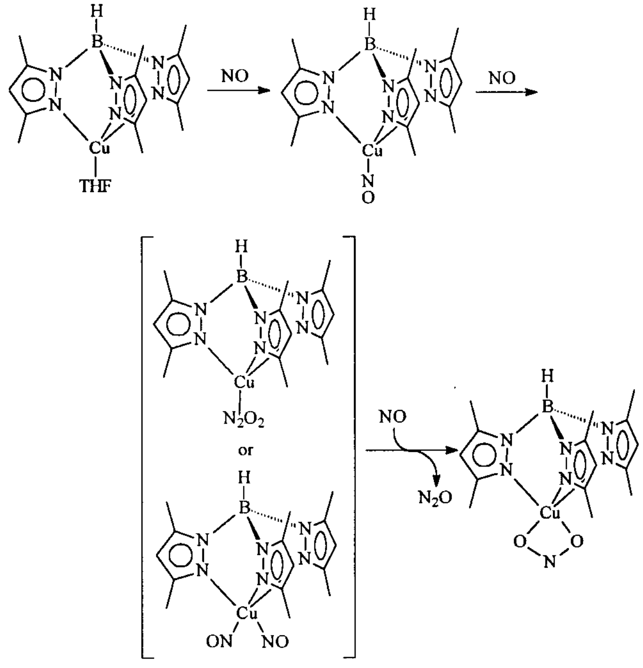
The first copper nitrosyl, synthesized in 1983, was a heterobimetallic copper−iridium bridging nitrosyl complex.[1057] The first homometallic copper nitrosyl to be structurally characterized was $[Cu_2(XYL\text{-}O)(\mu\text{-}NO)]^{2+}$ [XYL-O = 2,6-bis(bis(2-pyridylethyl)aminomethyl)phenolate)] (vide infra), formally a d^9 complex.[1058] This complex reacts with $[NO_2]^-$ to form the bridging oxo species $[Cu_2(XYL\text{-}O)(\mu\text{-}O)]^+$, N_2O, and 0.5 O_2.[1059] This conversion is important since it is thought to mimic the mode of action of nitrite reductase, a metalloenzyme containing two copper centers. Indeed, one of the intermediates in the nitrite reductase mechanism is believed to be a copper nitrosyl.[1060]



Further progress in copper–nitrosyl chemistry occurred when the first terminal nitrosyl complex, Cu(HB(^{t}Bu-pz)$_3$)(NO), was fully characterized.[1060–1063] This compound exhibits a ν_{NO} at 1720 cm^{-1} (KBr) and contains a linear nitrosyl ligand. On the basis of electronic spectra, ESR studies, and theoretical calculations, the favored view of the bonding extant in this molecule is Cu(I)–NO•, as opposed to Cu(II)–NO$^-$ or Cu(0)–NO$^+$. The NO ligand can be easily displaced by MeCN or CO, and it can also be removed by simply placing the complex under a gentle vacuum. In the presence of excess NO, the related molecule Cu(HB(Me$_2$-pz)$_3$)(NO) undergoes NO disproportionation, yielding N$_2$O and Cu(HB(Me$_2$-pz)$_3$)(η^2-O,O-NO$_2$) (Scheme 33).[1064,1065] This conversion is thought to proceed via a *cis*-dinitrosyl/hyponitrite intermediate (vide infra). Examples of this disproportionation reaction are known for triazacyclononane derivatives as well,[1066] but the nitrosyl intermediates have not been detected spectroscopically for these transformations.

The remarkable feature about Cu(HB(^{t}Bu-pz)$_3$)(NO) is that it is a {Cu–NO}^{11}, 19e species. This feature is in striking contrast to the niobium and tantalum nitrosyls, the other periphery of known nitrosyl complexes, since they rigorously obey the 18e rule.

Scheme 33



Treatment of the complex (^{i}Pr$_3$-tacn)Cu(N-NO$_2$) (^{i}Pr$_3$-tacn = 1,4,7-triisopropyl-1,4,7-tiazacyclononane) with 2 equiv of acid (HX) results in the production of 1 equiv of NO(g) and the concomitant formation of (^{i}Pr$_3$-tacn)Cu(X)$_2$ and H$_2$O. Presumably, this reaction proceeds via a nitrosyl intermediate.[1067,1068] A related nitrosyl intermediate has also been proposed for the disproportionation of NO by alcoholic solutions of [(^{i}Pr$_3$-tacn)Cu(MeCN)]$^+$. This reaction is catalytic and affords N$_2$O, aldehyde, and H$_2$O as products.[1069]

The synthesis of Cu(AsPh$_3$)$_2$(NO)Cl has been claimed, but given its incomplete characterization and putative air stability, its existence remains to be proven.[1070]

8.2. Silver and Gold Nitrosyls

No well-defined silver or gold nitrosyl complexes are known to exist. There are, however, reports concerning the formation of silver and gold nitrosyls in zeolites. Thus, Ag(I)–ZSM-5 forms Ag(NO) upon exposure to NO (ν_{NO} = 1882 cm^{-1}) at 100 K. The interaction is deemed to be weak and electrostatic in nature.[1071] Similarly, AuCl-impregnated NaY zeolite exhibits a strong IR absorption at 1820 cm^{-1} when exposed to NO. However, this absorption band disappears upon exposure of the system to vacuum.[1072,1073]

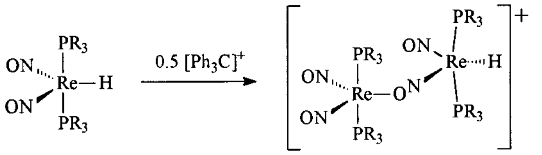
9. Nitrosyl Ligand Reactivity

9.1. Interaction with Lewis Acids

The ability of nitrosyl ligands to form adducts with hard Lewis acids was first documented by Legzdins and co-workers over 30 years ago.[1074,1075] Since then the ability of a nitrosyl oxygen atom to function as a Lewis base has been well established.[1] In all cases the coordination of the Lewis acid to the nitrosyl ligand results in a drain of σ electron density from the N–O linkage and a concomitant increase in M→NO back-bonding into the π^* orbitals of the NO ligand. The resultant lowering of the N–O bond order is readily observed spectroscopically by the decrease in the value of ν_{NO} which can range from 50 to several hundred wavenumbers.

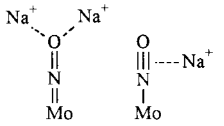
Several examples of nitrosyl–borane adducts have been reported in recent years, namely CpRe(SiMe$_2$Cl)(PR$_3$)(NOBCl$_3$),[547,1076] Re(H)(P^{i}Pr$_3$)(NO)(NOBF$_3$),[457] and Cp*WR$_2$(NOBF$_3$) (R = CH$_2$SiMe$_3$, CH$_2$Ph).[1077] Complexation of a borane to the nitrosyl oxygen leads to a lowering of the ν_{NO} by 159 to 264 cm^{-1}. The decrease in the N–O bond order is also evident in the solid-state molecular structures of these adducts. Typically, the N–O bond is increased in length (ca 0.07 Å), and there is a less pronounced decrease in the metal–N distance. The solid-state molecular structure of CpRe(SiMe$_2$Cl)(PPh$_3$)(NOBCl$_3$) displays more drastic distortions of the metrical parameters relating to the M–N and N–O distances than do the other examples,[547,1076] though Berke and co-workers have suggested that this discrepancy may be due more to the relatively low quality of the crystallographic data set obtained for the rhenium complex rather than any chemically meaningful change in bonding parameters.[457]

Nitrosyl ligands can also bridge metal centers via isonitrosyl interactions. For instance, hydride abstraction from $Re(NO)_2(P^iPr_3)_2H$ with 0.5 equiv of trityl cation generates the bimetallic cation $[Re(NO)_2(P^iPr_3)_2\{ONRe(NO)(P^iPr_3)_2H\}]^+$ in which the unreacted starting material acts as a ligand to a cationic rhenium center via an isonitrosyl interaction, i.e.[463,1078]



Alkali and alkaline-earth metals often complex the nitrosyl ligands of formally anionic complexes. Reaction of $Cp^*M(NO)(CH_2SiMe_3)_2$ (M = Mo, W) with lithium bases generates a variety of nitrosyl "ate" species. These complexes fall into two main categories, namely monomeric species containing a M−NO−Li(THF)$_3$ linkage and dimeric species in which two nitrosyl ligands are bridged by two solvated Li cations in a O−Li−O−Li− square. Inspection of the IR data for these complexes as KBr pellets reveals consistently lower NO-stretching frequencies for those complexes containing bridging $[\mu_2\text{-Li(THF)}_x]_2$ moieties (1350−1399 cm^{-1}) as compared to those containing terminal Li(THF)$_3$ groups (1463−1481 cm^{-1}). Examples of each of these interactions have been structurally characterized, and in accord with the proposed accommodation of charge in the π^* MO's of the nitrosyl fragment, they exhibit shorter M−N bond lengths and longer N−O bond lengths than do their parent nitrosyl complexes.[345,368,369,1079]

Wieghardt and co-workers have reported an interesting variation on the bonding of alkali-metal cations to nitrosyl ligands. The tetrameric cluster $[\{MoL(NO)(O)(OH)\}_4Na_2(H_2O)_2]^{2+}$ [L = tris(*N*-isopropyl)triazacyclononane] consists of two sets of crystallographically independent molybdenum complexes. While the nitrosyl ligand of one of these complexes coordinates the sodium cation in an orthodox end-on manner [ν_{NO} = 1476 cm^{-1} (KBr)], the other exhibits a novel side-on bond [ν_{NO} = 1529 cm^{-1} (KBr)], i.e.[1080]



Treatment of the lithium isonitrosyl complex $[Cp^*MoMe_3(NO\text{-}\mu\text{-}Li)]_2$ with a trimethyloxonium salt results in the formation of a methoxylimido ligand in the complex $Cp^*MoMe_3(NOMe)$. This complex exhibits an intense IR absorption at 1260 cm^{-1}, which is attributed to the nitrosyl-derived ligand on the basis of labeling studies.[1079] Only one other class of complex containing a terminal alkoxylimido ligand has been reported, namely $Cp'NbX_2(NO^tBu)$ (Cp′ = Cp, CpMe; X = Cl, CH_2SiMe_3), although these complexes were not derived from a nitrosyl-containing precursor.[1081]

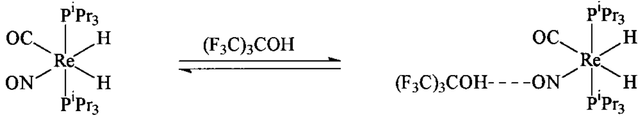
Gladfelter and co-workers reported an example of the bridging methoxylimido complex $[Ru_3(CO)_{10}(\mu_3\text{-}NOMe)]$ in 1990. This complex is preparable by the reaction of $[Ru_3(CO)_{10}(\mu_2\text{-}NO)]^-$ with 1 equiv of MeOTf.[1082,1083] The nitrosyl-cleaved product $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)(\mu_4\text{-}NH)\{\mu_3\text{-}\eta^2\text{-}CO_2Me\}]$ can be isolated in low yield if 1.5 equiv of MeOTf is employed to effect the methylation.[1084] Furthermore, thermolysis and pyrolysis of $Ru_3(CO)_{10}(\mu_3\text{-}NOMe)$ generates a variety of nitrosyl-cleaved cluster molecules.[1084−1086]

The reaction of $CpMnFe_2Cp'_2(\mu_2\text{-}CO)_2(\mu_2\text{-}NO)(\mu_3\text{-}NO)$ with MeOTf produces $[CpMnFe_2Cp'_2(\mu_2\text{-}CO)_2(\mu_2\text{-}NO)(\mu_3\text{-}NOMe)]^+$. The μ_3-NOH analogue of this cation is also formed during this reaction, reportedly as a result of insufficiently dry solvents.[759]

9.2. Interaction with Protons

In 1990 Gladfelter and co-workers reported that the reaction of the anionic cluster $[Ru_3(CO)_{10}(\mu\text{-}NO)]^-$ with HOTf generates the O-protonated nitrosyl complex $Ru_3(CO)_{10}(\mu\text{-}NOH)$. In contrast, reaction with the weaker acid CF_3CO_2H affords the hydride complex $Ru_3(CO)_{10}(\mu\text{-}NO)(H)$.[1082,1083] Subsequent reinvestigation of this system by Hash and Rosenberg has shown that the kinetic site of protonation in both cases is the nitrosyl oxygen atom.[1087]

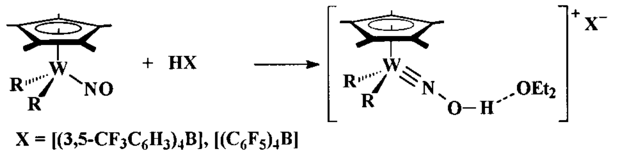
IR spectroscopy indicates that the hydroxyl proton of $(CF_3)_3COH$ hydrogen bonds to a terminal nitrosyl ligand of $Re(NO)(CO)(PR_3)(H)_2$ complexes (vide infra). The nature of the phosphine ligands has a surprising effect on this interaction. When R = Me, hydrogen bonding to a hydride ligand is favored over hydrogen bonding to the nitrosyl, but when R = ^{i}Pr, the NO···HOC(CF$_3$)$_3$ complex is exclusively formed.



When $Re(PPh_3)_2(CO)_2(NO)$ is reacted with HCl, the N-protonated nitrosyl complex, $Re(PPh_3)_2(CO)_2(Cl)(NH{=}O)$, can be obtained in 79% yield. Use of HOTf in place of HCl results instead in the isolation of $[Re(PPh_3)_2(CO)_2(NO)H]^+$, which has been structurally characterized.[1088] The HNO ligand is also formed when $[Ru(NO)(\text{"pybuS4"})]^+$ ["pybuS4" = 2,6-bis((2-mercapto-3,5-di-*tert*-butylphenyl)thio)dimethylpyridine(2−)] is reacted with $[Na][BH_4]$ in MeOH. The structurally characterized product, Ru(HNO)("pybuS4"), can be reconverted to the starting material by reaction with Brønsted acids.[1089]

The first fully characterized examples of O-protonated terminal nitrosyl complexes have recently been described. As illustrated in Scheme 34, treatment of $Cp^*WR_2(NO)$ (R = CH_2SiMe_3, CH_2Ph) with the oxonium acids of weakly coordinating counterions forms the hydroxylimido complex $[Cp^*WR_2(NOH\cdots OEt_2)]^+$, thereby showing that the nitrosyl ligand is a stronger base than diethyl ether. These

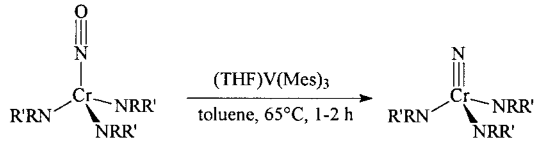
Scheme 34



X = [(3,5-CF$_3$C$_6$H$_3$)$_4$B], [(C$_6$F$_5$)$_4$B] complexes are unstable with respect to protonolysis of an alkyl ligand. The ^1H NMR signal of the hydroxylimido protons is exhibited between 12.5 and 14.5 ppm depending on solvent and counterion, and the ν_{NO} of the dibenzyl cation is centered at 1302 cm^{-1}.[1077]

9.3. Activation and Cleavage

The activation and cleavage of nitrosyl ligands is of fundamental importance in inorganic chemistry and of relevance to biological and environmental chemistry. Recently, the nitrosyl ligand of $[Cp_2Fe_2(NO)]^+$ was observed to undergo N−O bond cleavage by tandem mass spectrometry. The products thus generated are $[CpFe_2O]^+$ and pyridine, the latter presumably being formed by insertion of nitrogen into the Cp ring.[1090] Furthermore, the nitrosyl ligands of cluster molecules are known to undergo nitrosyl-ligand cleavage to form nitrido species.[1091] However, there are remarkably few examples of monomeric or dimeric nitrosyl complexes undergoing similar N−O bond dissociation processes. Cummins and co-workers have deoxygenated the nitrosyl ligands of $Cr(N^iPr_2)_3(NO)$ and $Cr(NRAr)_3(NO)$ [R = $C(CD_3)_2Me$; Ar = 2,5-C_6H_3FMe, 3,5-$C_6H_3Me_2$] with the highly oxophilic reagent $(THF)V(Mes)_3$ to generate nitrido complexes, i.e.[1092]

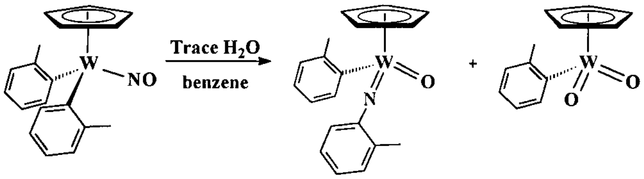


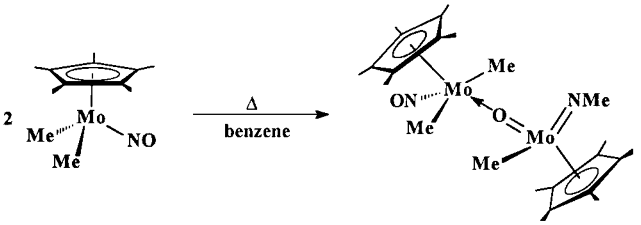
A similar transformation occurs when $W(NO)(silox)_3$ (silox = $^tBu_3SiO$) is reacted with $V(silox)_3$ to obtain $W(N)(silox)_3$ and $V(O)(silox)_3$.[1093]

A review of NO cleavage in $Cp'M(NO)R_2$ (M = Mo, W) complexes has been published,[357] and the highlights of this account are presented below. There are only two examples of reactions in which well-defined (R−)[M](−NO) complexes convert into their thermodynamically more stable (RN=)[M](=O) isomers. As shown in Scheme 35, $CpW(NO)(o\text{-tolyl})_2$ reacts with trace deaerated water to generate both the expected $CpW(O)_2(o\text{-tolyl})$ complex and the nitrosyl-cleaved product CpW(O)(N-*o*-tolyl)(*o*-tolyl). Labeling studies have shown that two distinct reaction pathways form these two species. Remarkably, despite extensive investigations, no other bis(hydrocarbyl) complexes have been discovered to undergo a similar transformation upon treatment with H_2O.[1094,1095]

Very recently, $Cp^*M(NO)Me_2$ (M = Mo, W) complexes have been found to be thermally unstable with respect to their $Cp^*M(O)(NMe)Me$ isomers. Thus, solutions of $Cp^*Mo(NO)Me_2$ afford the bimetallic species $Cp^*Mo(NO)Me_2(\mu\text{-}O)MoCp^*Me(O)(NMe)$, which can be isolated as a solid in high yield (vide infra). The isomerization process is inhibited by the presence of Lewis bases in solution. Consequently, formation of the oxo imido product with its Lewis basic oxo ligand dramatically slows the transformation. The currently available evidence points to a bimetallic mechanism being operative, possibly one involving Mo−NO−Mo interactions. The tungsten congener isomerizes far faster than does the Mo complex, and so $Cp^*W(NO)Me_2$ is not isolable free of a supporting donor interaction.[1079]

Scheme 35

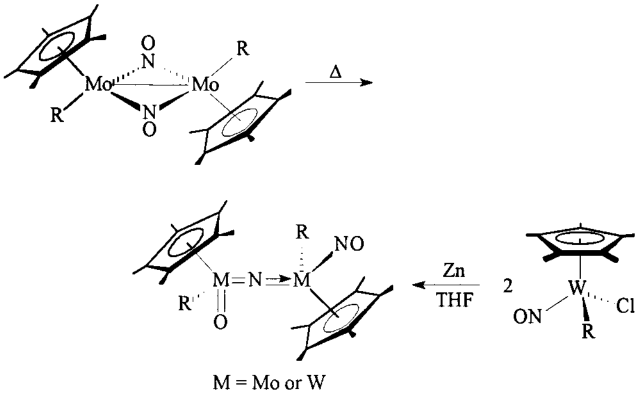




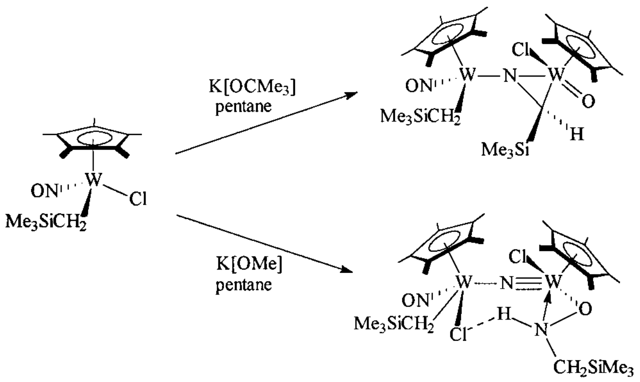
The diphenyl complex $Cp^*W(NO)Ph_2$ undergoes thermal conversion to a number of nitrosyl-cleaved products including $[Cp^*W(NO)Ph](\mu\text{-}N)[Cp^*W(O)Ph]$.[1096] This complex and the analogous alkyl species can also be generated by the reduction of $Cp^*W(NO)(R)Cl$ (R = Ph, CH_2SiMe_3, CH_2CMe_3) with Zn powder (Scheme 36).[1097] Furthermore, the bridging nitrosyl complexes $[Cp^*MoR(\mu\text{-}NO)]_2$ (R = CH_2CMe_3, CH_2CMe_2Ph) are thermally unstable with respect to the formation of the analogous molybdenum compounds, $[Cp^*MoR(NO)](\eta\text{-}N)[MoCp^*(O)R]$.[367,1097] These transformations may well occur via an intermediate containing a $Mo(\mu\text{-}NO)(\mu\text{-}\eta^1{:}\eta^2\text{-}NO)Mo$ bridge. One example of a complex containing such an activated NO ligand has been reported, namely $[Cp^*Mo(NO)](\mu\text{-}\eta^1{:}\eta^2\text{-}NO)(\mu\text{-}CHCMe_3)[MoCp^*(=CHCMe_3)]$, and it results from the spontaneous thermal decomposition of $Cp^*Mo(NO)(CH_2CMe_3)_2$.[371,372]

The products of the treatment of $Cp^*W(NO)(CH_2SiMe_3)Cl$ with metal alkoxide salts are highly dependent on the nature of both the alkoxide reagent and the solvent used for the reaction. Reaction in an ethereal solvent generates the chloride metathesis products $Cp^*W(NO)(CH_2SiMe_3)(OR)$. However, if the reaction with either $KOCMe_3$ or KOMe is attempted in pentane, the bimetallic NO-cleaved species $[Cp^*W(NO)(CH_2SiMe_3)](\mu^2\text{-}\eta^1{:}\eta^2\text{-}NC\{H\}SiMe_3)[Cp^*W(Cl)$-

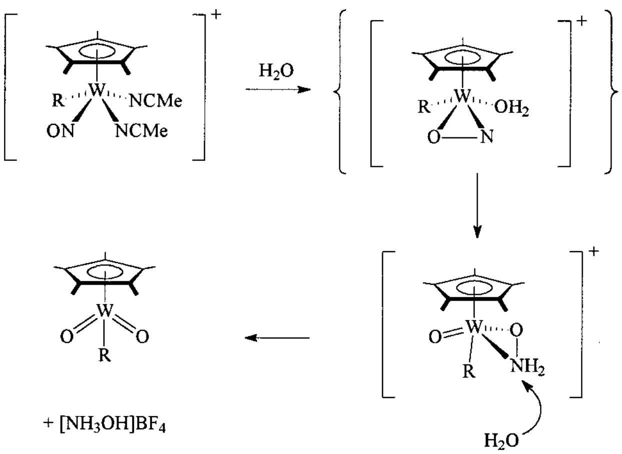
Scheme 36



Scheme 37



Scheme 38

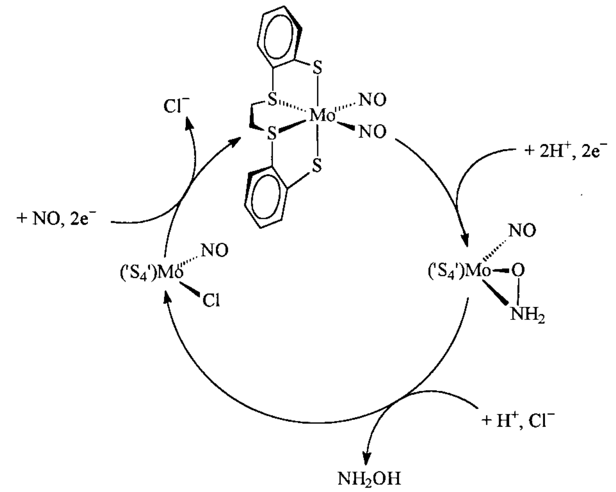


(O)] and [Cp*W(NO)(CH$_2$SiMe$_3$)Cl](μ-N)[Cp*W(Cl)-(η^2-N{O}{H}CH$_2$SiMe$_3$)] are formed instead (Scheme 37). The mechanisms of these reactions are unclear, but it has been suggested that coordination of [K]$^+$ is important since the expected metathesis products are obtained when lithium or sodium alkoxide salts are used.[1098]

Legzdins and co-workers have reported the stepwise hydrolysis of a terminal nitrosyl ligand. Careful reaction of the cationic nitrosyl complex [Cp*W(NO)-(CH$_2$SiMe$_3$)(NCMe)$_2$][BF$_4$] with 1 equiv of water produces the hydroxylamido compound [Cp*W(O)(η^2-NH$_2$O)(CH$_2$SiMe$_3$)][BF$_4$]. As depicted in Scheme 38, it is believed that this reaction occurs via the displacement of acetonitrile from the metal's coordination sphere by H$_2$O, followed by hydrogen-atom transfer from the coordinated water to the nitrosyl nitrogen atom and bending of the nitrosyl to an η^2-coordination mode. The hydroxylamido species reacts further with water to ultimately form the dioxo complex, Cp*W(O)$_2$(CH$_2$SiMe$_3$).[1099]

Mo(NO)$_2$('S$_4$') ['S$_4$' = 2,2′-(ethylenedithio)dibenzenethiolate] can be converted to Mo(η^2-NH$_2$O)(NO)-('S$_4$') in a 2-electron-2 H$^+$ process in which the NO ligand is hydrogenated to an η^2-hydroxylamido ligand (Scheme 39).[1100] Treatment of this latter complex with HCl results in the expulsion of the hydroxylamido group from the metal's coordination sphere and the formation of Mo(NO)(Cl)('S$_4$'). The byproducts of this reaction, [N$_2$H$_5$]Cl and [NH$_4$]Cl, are formed by hydrolysis and acidolysis of the liberated hydroxylamine.[1101] Electrochemical studies on

Scheme 39



related molybdenum thiolate complexes have demonstrated the reduction of NO ligands to form free NH$_3$.[150]

The reaction of [{(ON)$_2$Fe(μ-SR)}$_2$]$^{2-}$ with an excess of alkyl iodide (R′I) leads to the formation of [(ON)$_2$Fe]-(μ-SR)(μ-NHR′), allegedly via the reduction of coordinated NO.[743,745,746] Furthermore, several examples of the reduction of the bridging nitrosyl ligands of clusters and bimetallic species to μ-amido and μ-imido ligands have also been reported.[749,759,1102]

9.4. Insertion of Bound NO

Hall and co-workers have used theoretical methods to investigate the migratory insertion of NO into the cobalt–carbon bond in the model complex CpCo(NO)-Me, both with and without the assistance of an incoming ligand (PH$_3$).[1103,1104] In agreement with the experimental results of Bergman and co-workers,[1105,1106] insertion is found to occur without prior phosphine association.[1103]

Upon treatment with [NO][BF$_4$], the complexes [CpMo(CO)(NO)(η^3-allyl)]$^+$ undergo oxidative decomplexation of the π-allyl ligand to form organic isooxazole compounds. It has been claimed that insertion of the coordinated nitrosyl fragment into the allyl ligand is a key mechanistic step during this transformation.[1107,1108]

9.5. Metal-Catalyzed NO Disproportionation

The disproportionation of nitric oxide into N$_2$O and NO$_2$ is thermodynamically downhill. However, NO gas is kinetically inert, and a metal catalyst is generally required to effect this transformation.

Tolman and co-workers have investigated the reactions of Tp^{X}Cu(L) [Tp^X = substituted tris(pyrazolyl)-borate; L = MeCN, THF] complexes with nitric oxide. When the Tp ligand is sterically demanding, the nitrosyl complexes Tp^{X}Cu(NO) are reversibly formed. Complexes containing less bulky Tp ligands also form mononuclear nitrosyl species initially, but upon reaction with excess NO these cleanly convert to Cu^{II}-(NO$_2$) species with the evolution of N$_2$O. Mechanistic studies on this system have ruled out a mechanism involving rate-limiting dimerization of the copper species and instead support a process in which a further 1 equiv of NO gas reacts with the initially formed mononitrosyl species. The dinitrosyl or hyponitrite (N_2O_2) complex thus formed quickly reacts with further NO to generate the observed products.[1060,1062,1064,1065]

Manganese and iron tropocoronand complexes also catalyze the disproportionation of NO to N_2O and NO_2. The metal nitrosyl−nitrito species *cis*-M(NO)(NO_2)(tropocoronand) (M = Mn, Fe) is formed in each case. The NO ligand of the manganese product is labile, and so the nitrito complex M(NO_2)(tropocoronand) is the ultimate product. In contrast, the iron complex loses NO_2 from its coordination sphere, and this further reacts to nitrate the tropocoronand ligand. The mechanism postulated for the overall NO disproportionation reaction is similar to that proposed in the Tp^{X}Cu(NO) system shown in Scheme 33. However, an NO-exchange step was detected in the manganese and iron systems, and this supports the existence of a dinitrosyl intermediate along the reaction pathway.[1109,1110] During these studies it was also discovered that the $\{MnNO\}^6$ tropocoronand complex transfers its nitrosyl ligand to Fe(tropocoronand). A kinetic analysis of the transfer indicates that it occurs via a dissociative mechanism.[1111]

Reaction of $Co(qn)_2{\cdot}2H_2O$ or $Co(NO)(qn)_2$ (qn = 8-quinolinolate) with nitric oxide in pyridine generates the nitrate complex $Co(NO_3)(qn)_2(py)$ with liberation of N_2O. The same products are formed upon the reaction of $Co(NO)(qn)_2(py)$ with NO gas.[1112]

9.6. NO Reduction

A number of homogeneous systems catalyze the reduction of NO by CO to produce N_2O and CO_2. The aqueous $PdCl_2$–$CuCl_x$-HCl ($x = 1, 2$) systems are among the simplest and most effective of these catalysts.[1113,1114] Trogler and co-workers have investigated the nature of the active intermediate in these catalytic systems. Work in nonaqueous solvents has identified $[Pd_2Cl_4(NO)_2]^{2-}$ as a key intermediate. However, this dimeric species exists primarily as the mononuclear complex $[PdCl_3(NO)]^{2-}$ in aqueous conditions.[1036] A detailed kinetic study of the overall reaction has revealed that NO reduction by Cu^{I} is the rate-limiting step.[1037]

The reduction of coordinated NO by sulfite and bisulfite ions has been studied for ferrous chelate nitrosyl complexes. The products of this reaction are Fe^{III}, N_2O, N_2, sulfate, and $S_2O_6^{2-}$.[1115] Electrochemical reduction of *cis*-$[Os(tpy)(Cl)_2(NO)]^+$ results in the formation of the ammine complex *cis*-$[Os(tpy)(Cl)_2(NH_3)]^+$.[900]

$[Re(NO)_2(dppe)_2][BF_4]$, a 20-valence-electron compound containing the unusual *trans*-di(linear)nitrosyl fragment, reacts with protic sources to effect reduction of the NO ligand to nitrous oxide.[431]

Nitroprusside reacts with hydrazine in water to form $[Fe(CN)_5(OH_2)]^{3-}$, NH_3, and N_2O. A kinetic study of this system found the reaction to be first-order both in nitroprusside and N_2H_4. The reaction evidently occurs via nucleophilic attack of hydrazine at the nitrosyl nitrogen. The $\{Fe{-}N(O)NH_2NH_2\}$ intermediate thus formed rapidly deprotonates at the bound nitrogen of hydrazine. After tautomerization and elimination of ammonia, $[Fe(CN)_5(N_2O)]^{3-}$ results, but it is unstable with respect to loss of nitrous oxide.[775] Other researchers have also reported the reduction of the NO ligand of nitroprusside by hydroxylamine.[1116]

9.7. Conversion of NO to NO_2 and NO_3

Reaction of a pyridine solution of bis[(phthalocyaninato)iridium], $(Ir(pc))_2$, with NO gas generates nitrosyl-containing species that are immediately oxidized by air to Ir(py)(NO$_2$)(pc).[1117] Other examples of M−NO to M−NO_2[823,827,835,897,901,1118−1122] or M−NO_3[991] conversions are known.

Reaction of *trans*-$[ReCl(N_2)(dppe)_2]$ with NO gas in THF yields the nitrosyl product *trans*-$[ReCl(NO)(dppe)_2][NO_3]_2$. Thus, in addition to substitution of coordinated dinitrogen for nitrosyl, NO gas has been oxidized to nitrate ions.[430]

Examples of intramolecular oxygen exchange between nitrosyl and nitrite ligands are well-known.[1123] For instance, the labeled complex $CpCr(NO)_2(^{15}NO_2)$ converts into $CpCr(NO)(^{15}NO)(NO_2)$ both in the solid state and in solutions.[1124,1125]

9.8. Release of NO

Since the discovery that nitric oxide is a physiologically important molecule, there has been great interest in the use of metallonitrosyl complexes as pharmaceuticals.[1126] Particularly interesting are those complexes which can deliver NO to biological targets on demand.[1127,1128] The nitrosyl ligand of Ru(salen)Cl(NO) dissociates upon photolysis,[1129] as do the NO ligands in nitroprusside and Roussin's red and black salts.[726] Furthermore, reduction of $[RuCl(NO)(cyclam)]^{2+}$ results in the rapid loss of Cl^- ($k = 1.5\ s^{-1}$) followed by the slower loss of NO ($k = 6.1 \times 10^{-4}\ s^{-1}$).[1130]

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