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Recent Organometallic Nitrosyl Chemistry[†]

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Contents

George Richter-Addo (on the left) was born in Glasgow, Scotland, in 1957. He obtained his Honours B.Sc. degree and a Diploma in Education from the University of Cape Coast, Ghana, in 1982. After teaching for a year, he embarked on graduate studies at the University of British Columbia in 1984. He is currently completing his Ph.D. research work, which has been concerned with the determination and synthetic exploitation of the redox properties of a variety of organometallic nitrosyl complexes in nonaqueous media. Peter Legzdins (on the right) was born in Riga, Latvia, on September 24, 1942. His family emigrated to Germany in 1944 and then to Canada in 1949. Dr Legzdins received his Honours B.Sc. from Carleton University (1964) and his Ph.D. from M.I.T. (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, where he is currently Professor of Chemistry. In 1986 Professor Legzdins was awarded a U.B.C. Izaak Walton Killam Memorial Senior Fellowship. His research interests are centered on synthetic, structural, and bonding studies of organometallic compounds that can be utilized as specific reactants or selective catalysts in organic or organometallic syntheses.

I. Introduction

Organometallic nitrosyl complexes are compounds that contain both nitric oxide and organic groups coordinated in some fashion to one or more transition-metal centers. It has been 20 years since these complexes were first the subject of a review.[1] At the time of this first review, the great majority of the organometallic nitrosyls known were simple substitution derivatives of nitrosyl carbonyls such as $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$. Furthermore, the principal emphasis at that time was on the synthesis and characterization of new structural types of these compounds. The intervening years have seen the appearance of an ever increasing amount of information in the chemical literature concerning transition-metal nitrosyl complexes in general,[2] and organometallic nitrosyls in particular. Consequently, a new summary and review of these latter species are both appropriate and somewhat overdue. In this connection it should be noted that the specific topic of organometallic nitrosyl clusters has been addressed in a recent review.[3]

The present article summarizes comprehensively the literature dealing with organometallic nitrosyl compounds (generally excluding clusters) that was published between early 1968 and mid 1987. As outlined in the table of contents, the pertinent information concerning the compounds themselves is first partitioned 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 two general sections that apply, in principle, to all classes of organometallic nitrosyls, namely the characteristic reactivities of bound NO groups and the synthetic ap-

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[†] Unless otherwise stated, the following abbreviations have been used: Cp = η^5-C_5H_5, Cp′ = η^5-$C_5H_4(CH_3)$, Cp* = η^5-$C_5(CH_3)_5$, Ar = aryl, tol = tolyl, py = pyridine, Ph = phenyl, Et = ethyl, Me = methyl, Bu = butyl, and THF = tetrahydrofuran.

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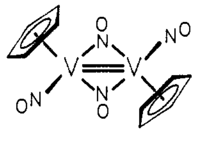
plications of the various types of complexes. The emphasis throughout is on the unique physical and chemical properties imparted to the compounds by the presence of the strongly electron-withdrawing nitrosyl ligands.

II. (Cyclopentadienyl)metal Nitrosyls and Halide Derivatives

A. Vanadium and Titanium

The cyclopentadienyldinitrosylvanadium dimer (1) has been obtained by the treatment of Cp_2V with nitric oxide.[4] The same reaction has also led to the isolation of an insoluble, air-stable brown material of empirical composition $V_3(C_5H_5)_3NO_7$.[5] Reactions of Cp_2V with NOX (X = Cl, Br) produce $Cp_2V(NO)X$ complexes,[4] which are fluxional molecules in which linear and bent VNO groups interconvert.[6] The analogous iodo complexes (X = I, Cp = η^5-C_5H_5;[5] X = I, Cp = η^5-C_5Me_5[7]) are obtainable by the reaction of the vanadocene iodide with nitric oxide. Interestingly, $Cp_2V(NO)I$ decomposes in THF solution to diamagnetic $\{CpVI\}_2\{CpV(NO)\}_2(\mu\text{-}O)_4$, whose X-ray structure has been reported.[5,6]



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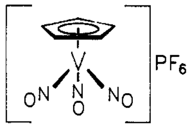

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The cationic complex 2 has been obtained in good yields by the treatment of $CpV(NO)_2(CO)$ with $NOPF_6$.[8] Photolysis of $CpV(NO)_2(CO)$ in methane and argon matrices generates $CpV(NO)(CO)(^*NO)$, where *NO denotes "some type of coordinated nitrosyl, where electron transfer to the nitrosyl ligand has occurred".[9] In a N_2 matrix, however, the primary photoproduct has been identified as $CpV(NO)_2(N_2)$. Displacement of the carbonyl ligand in $CpV(NO)_2(CO)$ by various Lewis bases in solution has been studied by ^{51}V, ^{13}C, and ^1H NMR spectroscopies.[10] The chemical shift $\delta(^{51}V)$ varies over the range of ca. −1300 to −500 ppm, depending on the nature of L (L = P-, S-, N-, and O-donor ligands), and the shielding of the ^{51}V and ^{13}C nuclei decreases as the electronegativity of the ligand atom bound to the metal increases in the order $P < S < N < O$.

Complex 3 has been prepared from $Cp^*_2VBr_2$ and NO.[7] The salt consists of a diamagnetic 18-electron cation and a paramagnetic 16-electron anion whose ESR spectrum is consistent with two unpaired electrons being localized on the vanadium atom.

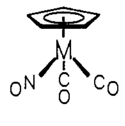
$$[Cp^*_2VBr(NO)]\ [Cp^*VBr_2(NO)]$$

3

A polymeric hyponitrite–titanium compound of composition $[CpTi(NO)]_n$ is formed by treatment of Cp_2Ti with NO.[11]

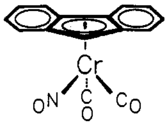
B. Chromium, Molybdenum, and Tungsten

The dicarbonylnitrosyl complexes 4[12] are easily obtainable by a variety of synthetic routes.[13-16] The fluorenyl complex 5[17] results when excess fluorenyllithium is added to $CrCl(CO)_2NO{\cdot}x$THF. Complexes 4 possessing functionalized cyclopentadienyl rings[18] and a polymer (polystyrene)-supported cyclopentadienyl derivative of chromium[19] have been prepared. Furthermore, the preparations and X-ray crystal structures of the pentamethylcyclopentadienyl (Cp*) analogues have also been reported.[20] The ^{95}Mo and ^{14}N NMR spectra of $CpMo(CO)_2(NO)$ and $Cp^*Mo(CO)_2(NO)$ have been recorded and ^{95}Mo–^{14}N spin–spin coupling of ~45 Hz has been observed.[21] However, no coupling between ^{17}O and ^{14}N was detected during this study.



4

(M = Cr, Mo, W)



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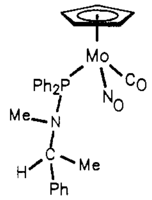
The dicarbonylnitrosyl complexes 4 are prone to lose one or both carbonyl ligands during chemical transformations. Removal of one CO ligand has been achieved photolytically,[9,22,23] and in the presence of phosphine[24,25] to yield CpM(CO)(NO)(L) and $CpM(NO)(L)_2$ compounds (L = phosphine; M = Cr, Mo). One of these, complex 6, has a metal atom that is a stereogenic center.[26] The R_{Mo} and S_{Mo} complexes[27] are separable by preparative liquid chromatography.



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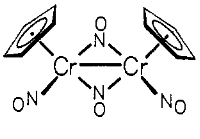
Reactions of 4 with NOCl yield $CpM(NO)_2Cl$ complexes.[12,16,28] These dinitrosyl chloro compounds are also obtainable from the treatment of the corresponding tricarbonyl dimers (M = Mo, W)[29] with NOCl or from exposure of the (cyclopentadienyl)metal dichloride to nitric oxide.[19] Complex 4 (M = Cr) reacts photolytically with NO to afford $[CpCr(NO)_2]_2$ (7) and $CpCr(NO)_2(NO_2)$ (8).[23]



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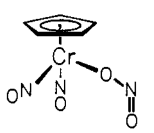
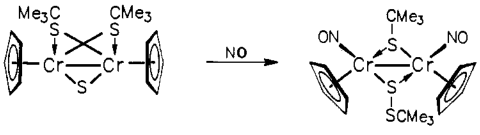


8

The dinitrosyl dimer, 7, is most readily synthesized in high yield by the zinc reduction of $CpCr(NO)_2Cl$.[30] An X-ray crystal structure analysis confirms the dimeric nature of 7 as well as the existence of both terminal and bridging nitrosyl ligands.[31] It can be electrochemically or chemically reduced to the bimetallic radical anion $[7]^{\bullet-}$.[32] The nitrite complex, 8, is also formed when 7 is allowed to react with NO[23] or by treatment of the sulfur-bridged dichromium reagent shown in eq 1 with NO.[33,34] Its crystal structure reveals that the terminal nitrite group is O-bound. The Cp* analogue of 8 has also been reported.[35]

The dinitrosyl cations, $[CpM(NO)_2]^+$ (M = Cr, Mo, W) (9), are preparable by halide abstraction from the



+ 8 (1)

corresponding neutral chloride complexes,[36,37] oxidative cleavage of the dinitrosyl dimer, 7,[32] or protonation of the alkyl complexes $\mathrm{CpCr(NO)_2R}$.[38] These 16-electron, cationic Lewis acids readily form adducts with Lewis bases such as acetonitrile[32,38] or phosphine (M = Cr).[39] The $[\mathrm{CpCr(NO)_2L}]^+$ (L = phosphine) species also result from addition of L to the bis(fluorosulfonyl)amido complex, $\mathrm{CpCr(NO)_2N(SO_2F)_2}$.[39] A series of $[\mathrm{CpM(NO)_2L}]^+$ cations are readily preparable by NO^+ attack on the neutral CpM(NO)(CO)L complexes (M = Mo, W; L = CO, phosphine)[40] (M = Cr, Mo, W; L = CNR).[41,42]

Not surprisingly, treatment of the $[\mathrm{CpM(NO)_2L}]^+$ cations with halide anions yields the neutral $\mathrm{CpM(NO)_2X}$ complexes.[40] However, treatment with alkoxide (for M = W) and other reducing agents produces the 19-electron $\mathrm{CpW(NO)_2L}$ (L = phosphine) neutral complexes.[43] The solid-state molecular structure of the complex when L = $\mathrm{P(OPh)_3}$ shows the N–W–N angle (102.7°) to be substantially larger than for the 18-electron $\mathrm{CpW(NO)_2Cl}$ (92.0°). A concomitant increase of 0.05 Å in the N–O bond lengths in the 19-electron complex is also consistent with the added electron being delocalized over the $\mathrm{W(NO)_2}$ fragment.

An X-ray PES study[44] of the $\mathrm{CpM(NO)_2Cl}$ (M = Cr, Mo, W) complexes reveals that in going from Cr to W, M→NO back-bonding increases as electron density is withdrawn from the Cl atoms. As for complexes 4, electron density is transferred equally to both the N and O atoms when M = Cr, but more to the oxygen atom when M = Mo or W. This phenomenon may well account for the ready loss of oxygen from these nitrosyl ligands (vide infra).

Iodine reacts with CpCr(CO)(NO)L (L = CO, $\mathrm{PPh_3}$; Cp = Cp or Cp*) to give $[\mathrm{CpCr(NO)I}]_2$ and $\mathrm{CpCr(NO)_2I}$.[45] The paramagnetic mononitrosyl dimer is cleaved by phosphines to afford the 17-electron CpCr(NO)(L)I compounds (L = $\mathrm{PPh_3}$, $\mathrm{P(OPh)_3}$, $\mathrm{P(OEt)_3}$). Reactions of CpCr(CO)(NO)L with $\mathrm{Cl_2}$ and $\mathrm{Br_2}$, on the other hand, only generate the dinitrosyl chloride and bromide complexes, respectively.[45] In contrast, when M = Mo or W, the mononitrosyl dihalo complexes 9 (M = Mo)[13] and 10 (M = W)[46] are obtained by treatment of 4 (M = Mo, W) with halogens (eq 2).

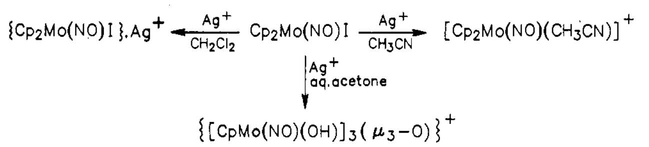
$$\mathrm{CpM(CO)_2NO} \xrightarrow{X_2} [\mathrm{CpM(NO)X_2}]_2 \qquad (2)$$

9 M=Mo; X=Cl, Br, I
10 M=W; X=I

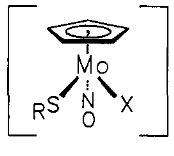
Complexes 9 and 10 are usually formulated as halide-bridged dimers in the solid state, and they are cleaved readily by a variety of Lewis bases in solutions to form the corresponding $\mathrm{CpM(NO)X_2L}$ adducts[47–49] (L = phosphines, arsines, isocyanides, or halides). When M = Mo, further reaction with L generates $[\mathrm{CpMo(NO)XL_2}]^+\mathrm{X}^-$ salts.[47] Displacement of Cp from $[\mathrm{CpMo(NO)I_2}]_2$ by CNR (R = alkyl)[50] and trimethylphosphine[51] has also been observed.

Replacement of halide in complexes 9 and 10 by Cp^- is quite facile.[46,52] Similar replacements by dithioacid ligands produce the mono- and disubstituted derivatives CpM(NO)I(S–S) and $\mathrm{CpM(NO)(S\text{–}S)_2}$ (M = Mo, W).[53] Analogous hydroxide-[54] and alkoxide-substituted[55] derivatives are also known, and interactions of 9 with hydrazines form adducts and/or hydrazido complexes.[54,56]

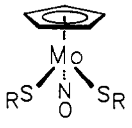
SCHEME I



Reactions of 9 (X = I) with 1 or 2 equiv of NaSR (R = alkyl, aryl) produce 11 and 12, respectively.[49] Complex 11 is also obtainable by treatment of $\mathrm{(C_5H_5)_2Mo(NO)I}$ with RSH.[57] Reduction of 11 (X = Br, I) by zinc generates bimetallic $[\mathrm{CpMo(NO)(SR)}]_2$.[57] This dimeric complex can exist in either a *cis*- or *trans*-nitrosyl form, depending on the nature of R[58] as determined by single-crystal X-ray crystallographic analysis. Heating 12 also generates $[\mathrm{CpMo(NO)(SR)}]_2$.[49]



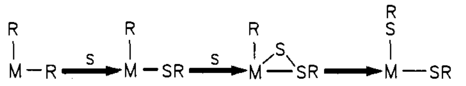
11



12

(R = alkyl, aryl)

The formally 16-electron complex 12 (R = Ph) has been crystallographically determined to be monomeric,[59] and its thermal stability has been attributed to the existence of S→Mo pπ–dπ bonding interactions on the basis of Fenske–Hall MO calculations. This bonding interaction raises the LUMO energy and renders it less susceptible to nucleophilic attack. The related dithiolate complex, $\mathrm{CpW(NO)(SCH_2SiMe_3)_2}$,[60] has been obtained by the sequential insertion of sulfur into the metal–carbon bonds of the unusual 16-electron complex $\mathrm{CpW(NO)(CH_2SiMe_3)_2}$[61] (eq 3).

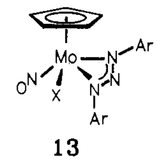


(3)

$[\mathrm{M} = (\eta^5\text{-}\mathrm{C_5H_5})\mathrm{W(NO)};\ \mathrm{R} = \mathrm{CH_2SiMe_3}]$

Reduction of 9 and 10 (X = I) in the presence of Lewis bases (L) produces the $\mathrm{CpM(NO)L_2}$ (M = Mo, W) complexes,[62] which are formally 18-electron compounds. The chromium congener is obtainable by employing $[\mathrm{CpCr(NO)I}]_2$ analogously.

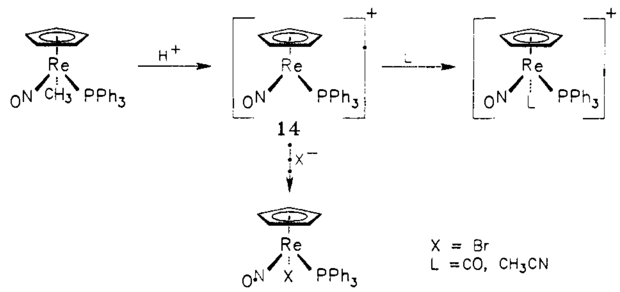
Stoichiometric amounts of silver(I) triazenides react with 9 to give complexes 13, which are stereochemically rigid on the NMR time scale. It has been proposed that the electron-withdrawing nitrosyl ligand in 13 inhibits its fluxionality.[63] Fluxional processes have, however, been observed for $\mathrm{(C_5H_5)_3Mo(NO)}$ by NMR spectros-



13

copy. At room temperature, all three cyclopentadienyl rings are equivalent, but at lower temperatures (0 to −50 °C), one adopts an η^1 configuration, the other two being η^4, a deduction confirmed by solid-state crystallographic analysis.[64] Other complexes that have η^5-Cp and η^1-Cp rings include $Cp_2Mo(NO)(S_2CNR_2)$ (R = Me or *n*-Bu)[65] and $Cp_2Cr(NO)_2$.[23] In the case of $Cp_2Mo(NO)I$, static structures such as $(\eta^5\text{-}Cp)(\eta^3\text{-}Cp)Mo(NO)I$, $(\eta^4\text{-}Cp)_2Mo(NO)I$, and $(\eta^5\text{-}Cp)(\eta^1\text{-}Cp)Mo(NO)I$ are possible. Interestingly, halide abstraction from this complex by Ag(I) salts gives a variety of products depending on the solvent used in the reaction (Scheme I).[66]

SCHEME II



C. Manganese and Rhenium

The tricarbonyl complexes $CpM(CO)_3$ are the logical precursors to $[CpM(CO)_2(NO)]^+$ derivatives for rhenium[67] and manganese[29,68,69] by nitrosonium substitution of carbonyl. The thiocarbonyl complex $[CpMn(CO)(CS)(NO)]^+$ (Cp = Cp or Cp′) is similarly obtained by treatment of $CpMn(CO)_2(CS)$ with nitronium or nitrosonium salts.[70] All these organometallic nitrosyl cations undergo facile carbonyl substitution reactions with various nitrogen- and phosphorus-donor ligands.[70,74] An exception is the reaction of $[CpMn(CO)_2(NO)]^+$ with triethylamine, which only affords the dimer $[CpMn(CO)(NO)]_2$.[71]

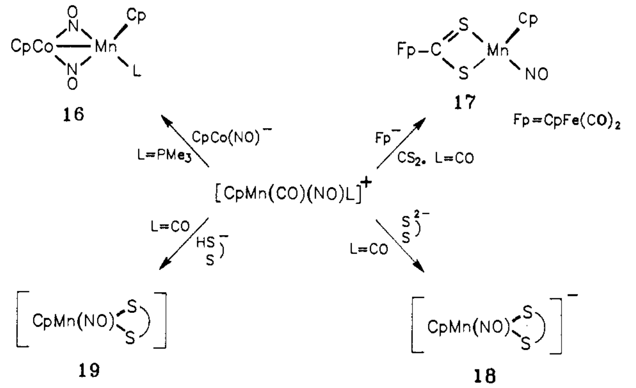
The 16-electron, coordinatively unsaturated, pyramidal cation $[CpRe(NO)(PPh_3)]^+$ (**14**) is formed upon electrophilic cleavage by H^+ of a Re–C bond as shown in Scheme II.[75] As expected, the cation **14** readily forms adducts with Lewis bases and reacts with halides to generate the neutral $CpRe(NO)(PPh_3)X$ complexes. These product complexes are generated in enantiomerically pure form and have metal-centered chirality (Scheme II). The manganese-containing analogues of **14** are also well-known, and these also retain their configuration on adduct formation with donor ligands.[76]

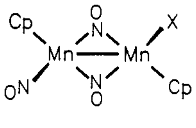
In passing, it may be noted that the "gauche effect" has been used to explain the conformation of the phosphide ligand in $CpRe(NO)(PPh_3)(PPh_2)$. Extended-Hückel MO calculations on $CpRe(NO)(PH_3)(PH_2)$ showed it to possess a significant and nondegenerate 2-fold $Re\text{–}PH_2$ rotational barrier.[77]

Iodide reacts with $[CpMn(CO)_2(NO)]^+$ to give $CpMn(CO)(NO)I$, and this subsequently reacts with triphenylphosphine to generate $CpMn(PPh_3)(NO)I$.[78] The thiocarbonyl analogue, $CpMn(CS)(NO)I$, has been synthesized similarly.[73] Surprisingly, the carbonyl ligand in the analogous rhenium complex, $CpRe(CO)(NO)I$, is inert to substitution by Lewis bases.[79]

The bimetallic complexes **15** are also obtainable by X^- attack on $[CpMn(CO)_2(NO)]^+$ under appropriate conditions, and they exist as a mixture of cis and trans isomers.[79] Replacement of X^- in **15** by cyclopentadienyl anion can be effected, the $\eta^1\text{-}C_5H_5^-$ being subsequently replaceable by Ph^-.[80]

SCHEME III





15

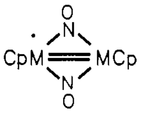
(X = Cl, Br, I, NO_2)

In aqueous solution, however, $[CpMn(CO)_2(NO)]^+$ reacts with NO_2^- to give a material formulated as polymeric $[CpMn(NO)_2]_n$ ($n > 1$).[81] A monomeric analogue of this polymer, namely $LMn(NO)_2$ (L = an asymmetric tridentate ligand),[82] has been prepared.

Finally, reactions of $[CpMn(CO)(NO)L]^+$ with transition-metal anions of cobalt and iron produce heterobimetallic complexes **16**[83] and **17**,[84] respectively (Scheme III). Similar reactions with dithiolate and dithiocarbamate reagents produce the neutral paramagnetic species **19**. Monoanionic diamagnetic complexes **18** can be obtained by employing suitable dianionic reagents,[85] a particular example being shown schematically in Scheme III.

D. Iron and Ruthenium

The mononitrosyl dimers **20**[86] and **21**[87] result from treatment of their dicarbonyl dimer precursors with NO at elevated temperatures. The X-ray molecular structure of **20a** establishes that the entire $Fe(\mu\text{-}NO)_2Fe$ group is virtually coplanar and perpendicular to the Cp ligands.[88a] The MO description of the bonding in **20a** suggests that the metal–bridge bond consists "almost exclusively of metal orbitals interacting with bridge 2π orbitals".[88b] Indeed, the current view of the bonding in complexes containing $M(\mu\text{-}NO)_2M$ bridges is that such π interactions involving the bridging nitrosyls are



20 a: M=Fe
b: M=Fe; Cp=Cp*

21 a: M=Ru
b: M=Ru; Cp=Cp*

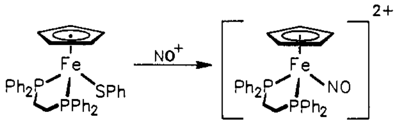
dominant, direct M–M σ interactions being minimal.[89] Complex **20a** undergoes a 1-electron reduction process to give $[CpFe(NO)]_2^{\bullet-}$.[90]

Nitrosylation at room temperature of $[CpFe(CO)_2]_2$ in benzene solution yields a greenish-brown solid formulated as $[CpFe(NO)(CO)]_2$.[91] However, nitrosylation of $[CpFe(CO)_2(EPh_3)]^+$ (E = P, As, Sb) reportedly produces the dinitrosyl cation $[CpFe(NO)_2(EPh_3)]^+$, whose IR nitrosyl stretching frequencies (1724, 1638 cm^{-1}) are indicative of terminal nitrosyl ligands.[91] The mode of attachment of the cyclopentadienyl ring to the Fe center is not clear, but if it remains η^5-bonded, then the dinitrosyl cation must be considered to be a formal 20-electron complex.

The neutral 19-electron $CpFe(NO)_2$ has not yet been reported, but its pyrazolylgallate analogue $LFe(NO)_2$ (L = a uninegative, 6-electron, tridentate pyrazolylgallate ligand) has been synthesized and its crystal structure determined.[82]

Returning to complexes **20** and **21b**, it may be noted that they are also produced upon reductive elimination of R–R from $CpM(NO)R_2$ derivatives.[86,92] The corresponding dihalides, $CpM(NO)X_2$, are obtained (for M = Fe, X = I) upon oxidative cleavage of the dimers **20** with iodine,[86,93] by nitrosylation (for M = Ru) of $CpRu(CO)_2X$ (Cp = Cp or Cp*) under UV irradiation,[94] or by NOCl reaction with $Cp^*Ru(CO)_2Cl$ to give $Cp^*Ru(NO)Cl_2$.[95]

Monocarbonyl substitution of $CpFe(CO)_2I$ by treatment with NO to give CpFe(CO)(NO)I has also been reported.[91] On the other hand, attempted nitrosylation of the phosphine-substituted cations $[CpRu(PPh_3)L]^+$ (L = PPh_3, 2,2′-bipyridine) only results in the removal of the Cp ligand.[96,97] However, incorporation of the nitrosonium cation does occur in the rather unusual reactions outlined in eq 4 and 5. The unusual feature is that *reactions 4*[98] *and 5*[99] *involve formal SPh^- and Cl^- anion replacement by the NO^+ cation.* The neutral Cp*Ru(dmpe)NO (dmpe = 1,2-bis(dimethylphosphino)ethane) has been prepared by a different route and contains a bent NO ligand [ν_{NO} 1386 cm^{-1}].[92]



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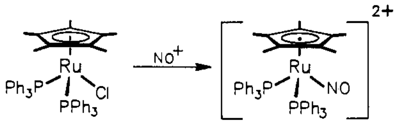
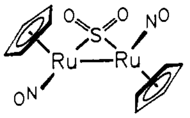


(5)

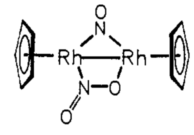
Diazomethane reacts with **20a** to give the methylene-bridged bimetallic complex in which the nitrosyl ligands are terminal.[100] Further studies with a variety of substituted diazoalkanes, $N_2{=}CR_2$, show that the initially bridging nitrosyls in **20a** either may remain so (R = bulky groups) or may become terminal (R = a sterically less demanding group).[101,102] These CR_2-bridged nitrosyl complexes of ruthenium are also formed by using the respective hydrazone reagents in the presence of MnO_2.[103] Likewise, in place of the diazoalkanes, sulfur dioxide reacts with **21a** to give **22**. However, diazomethane reacts with monomeric $CpRu(NO)X_2$ (Cp = Cp or Cp*; X = Cl, Br or I) to give mono- and diinserted halomethyl products in high yields.[104]



22

E. Cobalt and Rhodium

The bimetallic $[CpM(NO)]_2$ complexes are obtained by nitric oxide treatment of their carbonyl precursors for both cobalt[105] and rhodium.[106] In the case of rhodium, the reaction is catalyzed by air, and a second complex, **23**, which contains both bridging nitrosyl and nitrite groups, is also isolable. A discussion of the electronic structure of $[CpCo(NO)]_2$ has been made in relation to its solid-state molecular structure. The $Co(\mu\text{-}NO)_2Co$ core, which is planar in the solid phase (with no formal Co–Co bond),[108] is proposed to be bent in the vapor phase (with a Co–Co bond).[107,109] Its electrochemical reduction proceeds in a single two-electron, irreversible step, generating monomeric $[CpCo(NO)]^-$ in accord with the valence bond view, which predicts homolytic cleavage of the dimer upon reduction.[89] This reduction has been accomplished on a preparative scale with sodium amalgam,[110] and the crystal structure of the related $Na^+[Cp'Co(NO)]^-$ salt synthesized in this way has been reported.[83] In contrast, the rhodium dimer, $[CpRh(NO)]_2$, undergoes a reversible one-electron reduction in THF to give the corresponding bimetallic monoanion.[111]



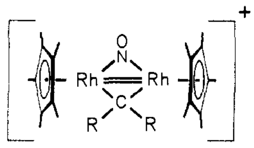
23

A wide variety of cationic mono- and bimetallic nitrosyl complexes have been obtained by NO^+ treatment of CpM(CO)L (L = CO, phosphine) complexes,[111-116] among which are the $[CpM(NO)]_2^{2+}$ dications and the $[CpM(NO)]_2^+$ monocations.[111,113,117,118] The molecular structure of $[CpCo(NO)]_2^+$ has been determined[119] in the solid state, and the $Co(\mu\text{-}NO)_2Co$ core is found to be planar with only a very slight shortening of the Co–Co distance as compared to its neutral form (vide supra).[107] The neutral $[CpCo(NO)]_2$ dimer reacts with halogens to produce CpCo(NO)X derivatives (X = I,[93] Br[119]), and the iodide complex inserts $M'I_2$ (M′ = Ge, Sn) into its Co–I bond to generate $CpCo(NO)M'I_3$ type compounds.[120]

Finally, in closing this section, we note that the unsaturated alkylidene complex **24** is obtained by diazoalkane attack on $[(Cp^*Rh)_2(\mu\text{-}NO)(\mu\text{-}CO)]^+$ and subsequent decarbonylation of the intermediate so formed.[116] Also, $CpCo(CO)_2$ abstracts NO from $[CpFe(NO)]_2$ to produce the unique tricobalt nitrosyl cluster, $[CpCo]_3(\mu_3\text{-}NO)_2$.[121]

III. Nitrosyl Hydrides

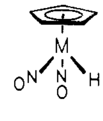
Some 15 years ago, the only organometallic nitrosyl hydride known was CpRe(NO)(CO)H.[122] (Its PPh_3



24

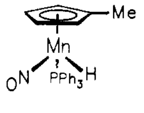
(R=H, Me, Ph)

analogue is now also known.[123]) The preparation of both monomeric and bimetallic nitrosyl hydrides has since received considerable attention. For instance, the gentle reducing agent sodium dihydridobis(2-methoxyethoxy)aluminate (also known as Red-Al or Vitride) has been found to be a suitable source of H^- for the syntheses of the monomeric hydrides **25**[124] and **26**[125] from their chloride and iodide precursors, respectively.



25

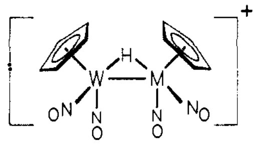
(M=Mo, W)



26

However, $CpCr(NO)_2Cl$ and $CpMn(CO)(NO)I$ react with Red-Al to give the known $[CpCr(NO)_2]_2$ and $[CpMn(CO)(NO)]_2$ dimers, respectively, presumably via initial formation of the thermally unstable $CpCr(NO)_2H$ and $CpMn(CO)(NO)H$ species.

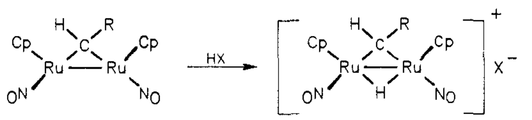
The bimetallic nitrosyl cations **27** are obtained by reactions of **25** with 0.5 equiv of Ph_3C^+, or adduct formation with the 16-electron $[CpM(NO)_2]^+$ cations.[126] The hydride ligands in the cations **27** undergo rapid exchange between the two metal sites, the minimum lifetime for each isomer having a terminal H ligand having been estimated to be ~1.2 ms.[127] Nevertheless, Lewis bases (L) cleave these bimetallic cations to the $CpM(NO)_2H$ and $[CpM(NO)_2L]^+$ monomers.



27

(M=Mo, W)

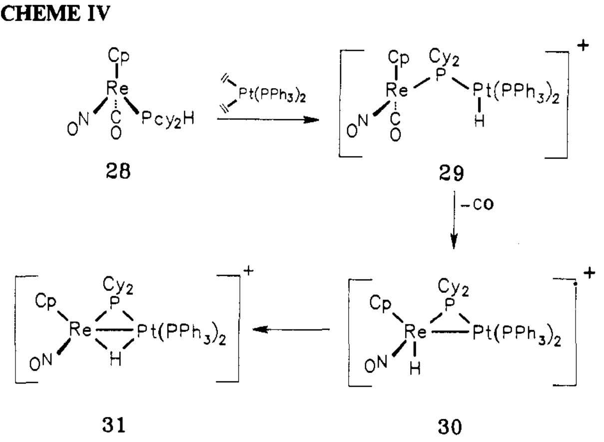
A diruthenium cationic complex containing a bridging H ligand has been generated by HX (X = BF_4, CF_3SO_3) addition to a bridging alkylidene complex (eq 6). When R = H and X = Br in eq 6, the bridging methylidene-hydride complex rearranges to the neutral bromo(methyl) product.[103] An unusual hydrogen atom transfer reaction has been found to occur in a rhenium–platinum heterobimetallic complex (Scheme IV).[128] Treatment of the secondary phosphine rhenium complex **28** with $(C_2H_4)_2Pt(PPh_3)_2$ gives **29**, in which the "$Pt(PPh_3)_2$" entity has formally inserted into the phosphorus–hydrogen bond. Hydrogen atom transfer from platinum to rhenium then occurs with the concomitant loss of CO to generate **30**. This transfer *does not* occur under rigorous exclusion of moisture and air and is catalyzed by base. The final rearrangement of **30** → **31** is promoted by the addition of halide ions, and the relative rate of the process is in the order $Cl^- > Br^- > I^- \gg F^-$, fluoride having no effect.



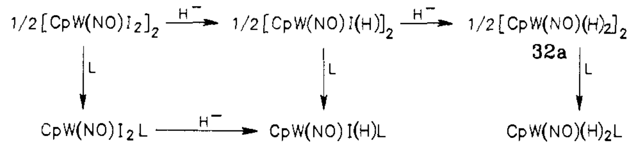
(6)

(R=H, Me)

SCHEME IV

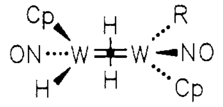


SCHEME V



(L = phosphine)

Neutral bimetallic hydrides of tungsten are obtainable by Red-Al treatment of $[CpW(NO)I_2]_2$ in the sequence outlined in Scheme V (L = phosphines, or phosphites).[129] A new bonding formulation has been proposed for the bimetallic hydrides **32** consistent with the $W(\mu\text{-}H)_2W$ core being considered as *a single four-center bonding unit*.[127,130] Finally, thermally stable alkyl hydrides of compositions CpW(NO)(H)(R)L (R = CH_2SiMe_3; L = phosphine) have been synthesized by hydrogenation of the 16-electron $CpW(NO)(CH_2SiMe_3)_2$ complex in the presence of L. These complexes have been used to effect intra- and intermolecular C–H bond activation.[130]



32 a: Cp=Cp, Cp*; R=H
b: Cp=Cp*; R=CH_2SiMe_3

IV. Complexes Containing Only σ-Alkyls and σ-Aryls

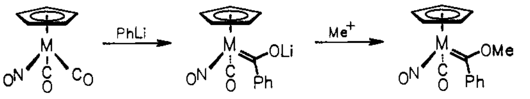
Notable isolable members of this class of compounds include $RFe(CO)_3(NO)$[131] (R = alkyl) and the benzylnitrosylmanganese complex having the composition $PhCH_2Mn(NO)$.[132] The manganese complex is prepared from dibenzylmanganese (as the dioxane solvate) and nitric oxide, and contains manganese in the formal zero oxidation state. The arylnickel compound **33**[133] is made by reacting PhLi with the appropriate bromide precursor (eq 7).

$$(PPh_3)_2Ni(NO)Br + PhLi \longrightarrow (PPh_3)_2Ni(NO)Ph + LiBr \quad (7)$$

33

V. Carbene Complexes

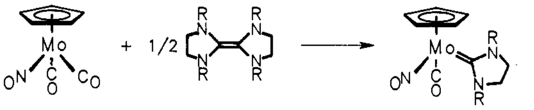
Group 6 carbene complexes **35** can be made the usual nucleophilic addition of a carbanion to the carbonyl precursor **4** and subsequent methylation of the resulting acylcarbonyl metalate **34** (eq 8).[134] Only one carbonyl ligand in **4** reacts with PhLi to form the methoxyphenyl carbene complex, and this is believed to be a manifestation of the greater positive charge on the C(carbonyl) atom relative to the N(nitrosyl) atom.[134] The molybdenum carbene complexes **36** have been obtained by the thermal interaction of the dicarbonyl nitrosyl with electron-rich olefins (eq 9).[135] The second carbonyl in **36** cannot be substituted to obtain a bis(carbene) complex, however. The stable chromium complex **37** has been synthesized from CpCr(CO)(NO)(THF) and diphenyldiazomethane.[22] Its solid-state molecular structure shows the carbene ligand plane to be almost coplanar with the N–Cr=C plane and nearly perpendicular to the C(carbonyl)–Cr=C plane. NMR studies of this complex have shown the Cr=C conformation to be locked in this form (i.e., there is no rotation of the carbene ligand). This behavior contrasts with that exhibited by the isoelectronic analogue CpMn(CO)$_2$CPh$_2$, in which fast rotation of the CPh$_2$ group about the Mn=C bond occurs.[22] Again, the nitrosyl-containing compound is the more stereochemically rigid of the two.



(8)

4 34 35

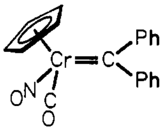
(M = Cr, Mo, W)



(9)

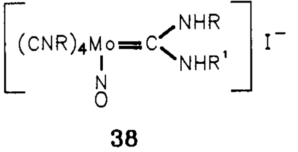
(R = p-tol, Me)

36



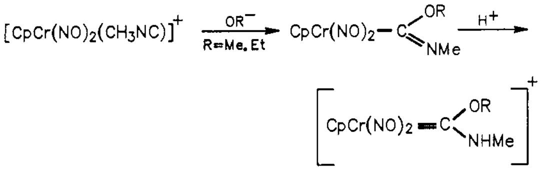
37

Other molybdenum mononitrosyl carbene complexes **38**[50] have resulted from primary amine (NH$_2$R′) addition to bound isocyanide ligands in the [Mo(CNR)$_5$(NO)]I complexes. Curiously, only one example of a group 6 metal dinitrosyl complex possessing carbene-type ligands has been described in the literature to date.[136] This complex results from the sequential reaction of the isocyanide ligand in [CpCr(NO)$_2$(CH$_3$NC)]$^+$ with alkoxide and then acid (eq 10).[38]



38

(R, R′ = alkyl, aryl)



(10)

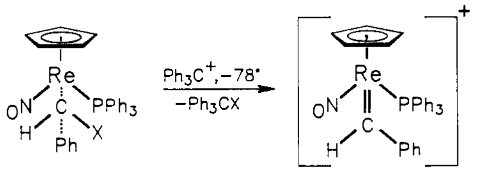
The trityl cation, Ph$_3$C$^+$, has been employed to abstract hydride from a number of rhenium alkyl complexes of the type CpRe(NO)(PPh$_3$)CH$_2$R (R = alkyl, aryl). Both η^1-alkylidene and η^2-alkene complexes may be formed, depending on the nature of R.[137] With the aim of gaining mechanistic insight into the nature of the hydride abstraction, a detailed study of the electrochemistry of the rhenium alkyl complexes was carried out. The relatively easy, and somewhat reversible, oxidations observed in these systems provide evidence for the occurrence of an initial electron transfer from the rhenium alkyl complex to the trityl cation (eq 11).[138]

$$RCH_2\text{–[Re]} + Ph_3C^+ \rightleftharpoons RCH_2\text{–[Re]}^{\cdot+} + Ph_3C\cdot \quad (11)$$

$$\text{[Re]} = CpRe(NO)PPh_3$$

However, no correlation exists between the potentials at which these rhenium alkyls oxidize and the selectivity that they exhibit for the formation of alkylidene or alkene complexes.[137] Chemical isolation of the radical cation depicted in eq 11 has not yet been successful, but electrochemical and mechanistic studies support its formulation.[138]

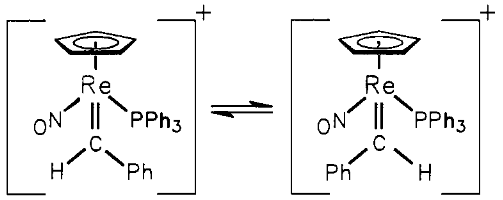
Of great interest, however, are the stereospecific interconversions that these alkyl or carbene complexes undergo. For example, hydride abstraction from the benzyl complexes occurs with complete stereochemical control (eq 12). The kinetic product is the benzylidene cation, which is initially stereospecifically generated. It is converted thermally to the thermodynamic isomer **40** and back to the kinetic form by UV irradiation.[139]



(12)

(X=H, D)

39

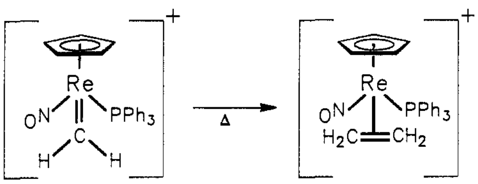


39 40

Furthermore, these benzylidene cations stereospecifically add nucleophiles such as methoxide and hydride anions to the alkylidene carbon atom.[140]

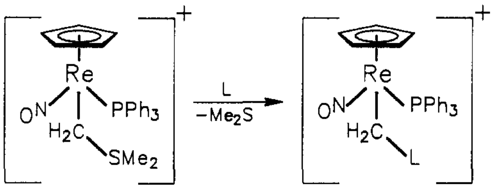
Stable methylene complexes of the type [Cp*Re(NO)(L)(=CH$_2$)]$^+$ have been obtained similarly, and their crystal structures have been determined (L =

PPh_3, $P(OPh)_3$).[141] The $=CH_2$ plane in the triphenyl phosphite derivative is essentially parallel to the Re–NO bond (compare with complex **37**; vide supra) and the bands due to CH_2 antisymmetric stretches observable in the compound's IR spectrum provided the "first definitive determination of the stretching ν_{C-H} for a methylidene complex".[141] The methylidene ligand in the cyclopentadienyl triphenylphosphine complex, however, couples to generate an ethylene complex (eq 13).[142] The ethylene complex is formed in about 50% yield with retention of configuration at rhenium. The rate of coupling is second order in the methylidene complex, and crossover experiments disfavor phosphine dissociation or methylidene scrambling prior to coupling. Consequently, the formation of a dimeric form of the $[Re{=}CH_2]^+$ complex is proposed to be the rate-determining step in this coupling reaction.[142]



+ 14 (13)

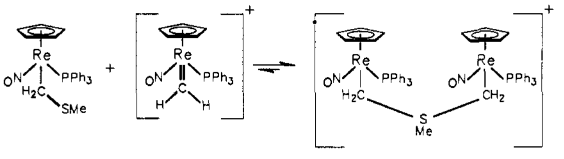
Dimethyl sulfide (Me_2S) forms a 1:1 adduct with the methylidene complex, generating the sulfonium salt **41**.



41

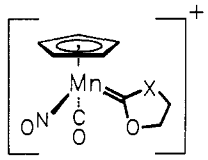
(L = PPh3, py, SR⁻)

Displacement of coordinated Me_2S from **41** occurs readily upon treatment with triphenylphosphine, pyridine, or even SR^- (R = Me, Ph, CH_2Ph). For L = SMe^-, the resulting complex **42** then becomes formally R′SMe (R′ = $CpRe(NO)(PPh_3)CH_2$), and this compound reacts in a similar fashion with another molecule of the starting methylidene complex to produce the bimetallic sulfonium salt **43** (eq 14). A single-crystal, X-ray crystallographic analysis of **43** confirms the atom connectivity shown.[143] Warming of this bimetallic complex results in hydride transer to form $CpRe(NO)(PPh_3)CH_3$ and $[CpRe(NO)(PPh_3)({=}C(H)SMe)]^+$.

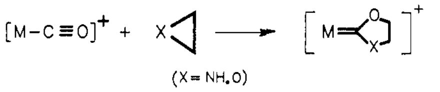


42 43 (14)

The manganese carbene complexes **44** have been obtained by aziridine or oxirane addition to one of the carbonyl groups in $[CpMn(CO)_2(NO)]^+$, as exemplified by the overall reaction depicted schematically in eq 15.[144] The reaction proceeds in the presence of a halide salt. The cyclic aminooxycarbene (**44a**) and the dioxycarbene (**44b**) complexes are isolable as thermally stable, crystalline compounds. In the case of **44b**, the unchanged carbonyl ligand can be further converted to the analogous bis(carbene) complex, which can also be isolated in a crystalline state.

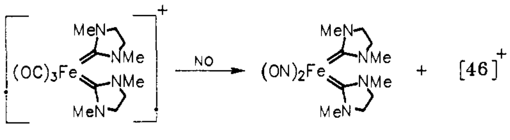


44 a: X = NH
b: X = O

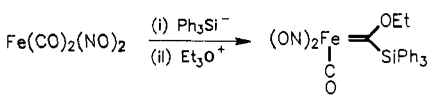


(15)

Electron-rich olefins can be used to displace triphenylphosphine (in a manner identical with that shown in eq 9) to form various mono- and oligocarbene complexes of ruthenium, osmium, and nickel[145] that contain one or two nitrosyl ligands. A logical extension of this chemistry involves nitrosylation of the bis(carbene) complex of iron **45** to give both the cationic and neutral dinitrosyl bis(carbene) complexes **46** (eq 16).[146] Complex $[\mathbf{46}]^+$ is also obtainable by the Ag^+ oxidation of **46**. Surprisingly, replacement of one of the carbene ligands in **45** with PPh_3 results in only one of the carbonyl ligands being expelled in the above reaction to yield a mononitrosyl monocarbene complex. Finally, the carbonyldinitrosyliron carbene complex **47** has been made in the conventional manner by initial nucleophilic addition of a silyl group onto the coordinated carbonyl of $Fe(CO)_2(NO)_2$ (eq 17).[147]



45 46 (16)



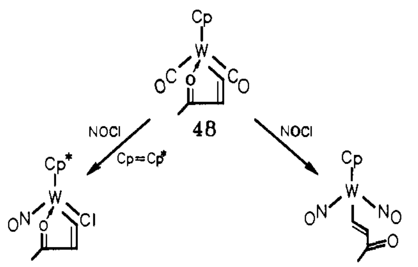
47 (17)

It is worth noting that the chemistry of organometallic nitrosyl carbene complexes remains largely unexplored. The presence of the nitrosyl ligand (and its pronounced electron-withdrawing effect) in these complexes may well be responsible for the hindered rotation about the metal–carbene bond. The exploitation of this phenomenon for specific organic applications such as olefin metathesis and cyclopropanation may lead to transformations that are not feasible with the more fluxional carbonyl carbene analogues.

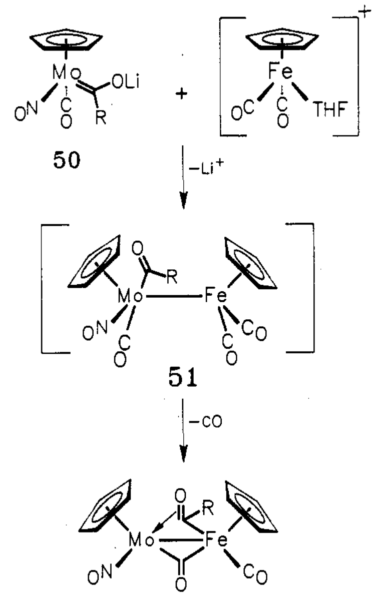
VI. Complexes with Acyl, Acetate, and Related Heteroatomic Ligands

Acetate complexes of molybdenum of the type $CpMo(NO)(\eta^2\text{-}O_2CR)X$ (X = Br or I) have been obtained either by removal of a η^1-cyclopentadienyl ligand from $(C_5H_5)_2Mo(NO)I$ by carboxylic acids RCO_2H (R = alkyl or aryl) or by metathesis of halide in complex **9** (X = I).[55] The acetate ligands are formulated as being η^2-bound on the basis of their IR spectra. Similar reaction of $Cp_2Mo(NO)(\eta^2\text{-}S_2CNMe_2)$ with trifluoroacetic

SCHEME VI



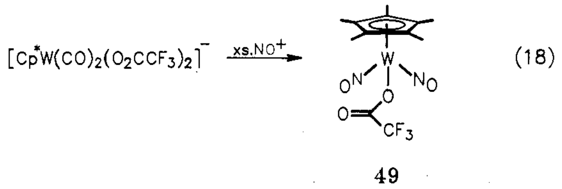
SCHEME VII



52

acid affords the mixed $CpMo(NO)(O_2CCF_3)(\eta^2\text{-}S_2CNMe_2)$ species, which contains a monodentate trifluoroacetate group.[55]

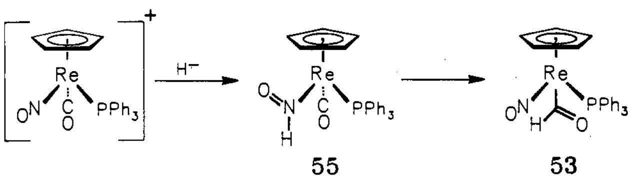
Reactions of nitrosyl chloride with the carbonyl complexes **48** generate mono- or dinitrosyl complexes of tungsten containing a bidentate or monodentate alkenyl ketone ligand, respectively, depending upon the cyclopentadienyl ligand employed (Scheme VI).[148] The related complex **49** has been obtained from a diacetate carbonyl anion (as its trimethylphosphonium salt) by treatment with excess $NOBF_4$ (eq 18).[149] A heterobimetallic compound containing a rare π-bound acyl group has been isolated and fully characterized by spectroscopic and X-ray data.[150] This compound (Scheme VII) results from the reaction of the molybdenum carbene complex **50** with the Lewis acid $[CpFe(CO)_2(THF)]^+$, which generates the bimetallic intermediate **51**. This in turn rearranges with carbonyl loss from molybdenum to give the isolable complex **52**. A rare feature of this reaction is the acyl group migration from molybdenum to iron (Scheme VII). The carbamoyl complex $CpCr(NO)_2[C(O)NHMe]$ has been generated by hydroxide ion attack on a coordinated isocyanide ligand.[38]



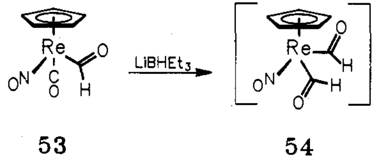
(18)

49

SCHEME VIII

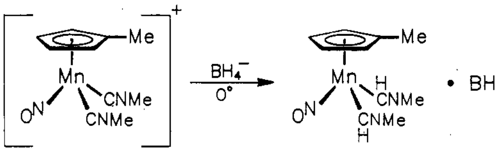


Nucleophilic attack of hydride on the cationic complex $[CpRe(NO)(CO)_2]^+$ produces the neutral formyl complex $CpRe(NO)(CO)(CHO)$ (**53**). Its subsequent reduction and decomposition reactions[123] have been extensively studied and are the principal subject of an enlightening review article.[151] Hydride reduction of the second carbonyl group in **53** has been achieved to produce a diformyl complex **54** (eq 19). This diacyl complex cannot be isolated, but it has been fully characterized by IR and ^1H NMR spectroscopies. A manganese analogue of the diformyl complex **54**, i.e. **54b**, has been prepared as an air-stable, crystalline solid by an entirely different route (eq 19b).[153]



(19)

53 54

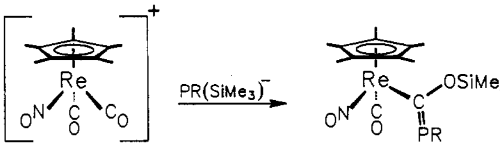


(19b)

54b

The mechanism of hydride attack on the triphenylphosphine complex cation $[CpRe(NO)(CO)(PPh_3)]^+$ has been the subject of Fenske–Hall MO calculations.[154] The results of these calculations indicate that the coordinated nitrosyl ligand in the cationic complex is the preferred site of H^- attack, leading to the generation of an HNO ligand in complex **55** (Scheme VIII). This kinetic product then rearranges to the final isolable formyl complex **53**.

The differing configurations of the metalloester complexes $CpM(NO)(PPh_3)(COOR)$ of rhenium[155] and manganese[156,157] (obtained from OR^- attack on coordinated carbonyl ligands) have been established, and comparisons with isostructural chiral organometallic compounds have been made.[155] Following the patterns outlined above, the phosphorus-containing nucleophiles $PR(SiMe_3)^-$ (R = $SiMe_3$, *t*-Bu, Ph) add to $[Cp^*Re(NO)(CO)_2]^+$ to produce the phosphaalkenyl complexes **56** (eq 20).[158]

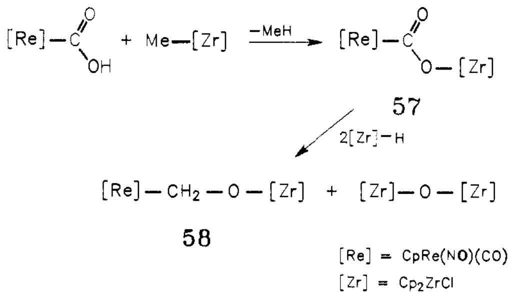


(20)

56

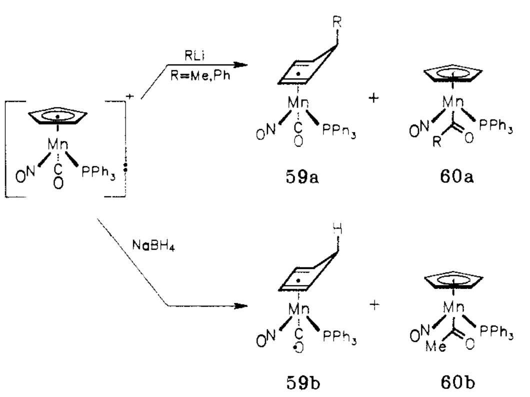
The reactions of other organorhenium nitrosyls have been used to model the binding of CO_2 between two metal centers. For instance, bimetallic μ-carboxylate,

SCHEME IX



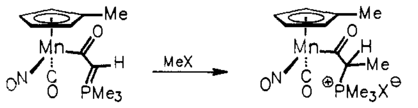
57, and μ-formaldehyde, 58, complexes have been made as shown in Scheme IX.[159]

Complexes of manganese belonging in this section are preparable in a variety of ways. Thioacyl complexes have been proposed[73] as products of insertion of bound CS into the manganese–alkyl bond of $Cp'Mn(NO)(CS)(C(CF_3){=}C(F)CF_3)$. Ring addition products **59** and acyl products **60** result from carbanion addition to $[CpMn(NO)(PPh_3)(CO)]^+$ (eq 21). In complexes **59a** the carbanion adds exo to the ring, but the origin of the acetyl group in **60b** is not clear.[160] The Wittig reagent $Me_3P{=}CH_2$ reacts with $[Cp'Mn(NO)(CO)_2]^+$ to yield **61**, which further reacts with MeX (X = I, SO_3F) to yield exclusively **62** (eq 22).[161] The related complex **63**, which contains an arylglyoxyl ligand, results from nitrite addition to the carbyne complex $Cp'Mn(CO)_2({\equiv}CR)$ [R = Ph, tol].[162] The formation of the arylglyoxyl ligand from the oxidized carbyne coupling with CO is unprecedented. In the case of rhenium, only the acyl complex is produced in this reaction.



59a 60a (21)

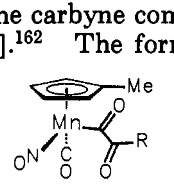
59b 60b



(22)

61 62

(X=I, SO3F)

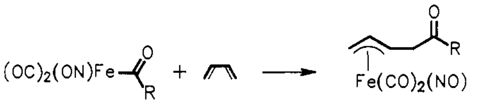


(R=Ph, tol)

63

Liquid ammonia reacts as a nucleophile toward $[CpMn(CO)_2(NO)]^+$ to give the carbamoyl complex $CpMn(CO)(NO)[C(O)NH_2]$[163] whose solid-state structure reveals dimerization via hydrogen bonding involving the carbamoyl ligands of two molecules. The carbamoyl ligand formation (from amines) is reversible if the manganese cation bears a phosphine ligand,[164] and a similar reaction has been used to synthesize a carbamoyl nitrosyl complex of osmium.[165]

Acyl nitrosyl complexes of cobalt[166] and iron[167] have been obtained by carbanion and carbocation attack on their carbonyl nitrosyl precursors, respectively. Furthermore, the iron complex **64** reacts with dienes *without substitution of CO* to give the allyl complexes **65** (eq 23) (R = Me, $PhCH_2$).



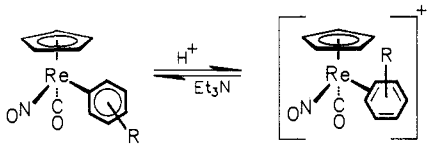
(23)

64 (R=Me, PhCH2) 65

A series of ruthenium acyl and acyl acetate complexes has been made by the oxidative addition of acyl chlorides and activated carboxylic acid anhydrides to $RuCl(NO)(PPh_3)_2$ under mild conditions.[168,169]

VII. Olefin and Alkyne Complexes

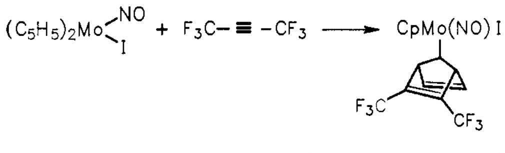
A fair number of organometallic nitrosyl olefin complexes results from simple 1:1 adduct formation between the olefin and the metal–nitrosyl complex. Specific examples include activated-olefin addition to $RuCl(NO)L_2$ (L = phosphine),[169,170] ethylene addition to $[Os(CO)(NO)L_2]^+$ (L = PPh_3),[171] cyclooctene addition to $[CpW(NO)_2]^+$,[37] and ethylene addition to $[CpRe(NO)(PPh_3)]^+$.[75] These ruthenium and osmium[172] precursor complexes also form 1:1 adducts with a number of alkynes without ligand displacement. In contrast, the η^2-arene complex of rhenium **66** is generated in the metal's coordination sphere by protonation of a σ-aryl complex (eq 24) (R = H, Me, CF_3).[173] Deprotonation studies provide evidence that the η^2-arene complex **66** is in equilibrium with small amounts of an η^1-arenium species.



(24)

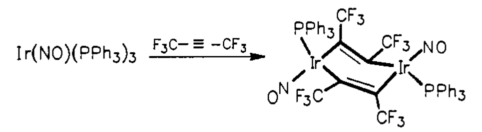
(R=H, Me, CF3) 66

The activated alkyne $CF_3C{\equiv}CCF_3$ forms a 1:1 adduct with $(C_5H_5)_2Mo(NO)I$ by addition across one of the cyclopentadienyl rings (eq 25),[174] and similar reactivity of the organometallic nitrosyl reactant is observed with tetracyanoethylene (TCNE).



(25)

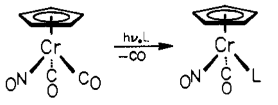
Complex formation with concomitant ligand displacement is more common, however. The iridium complex $Ir(NO)(PPh_3)_3$ (like its cobalt and rhodium analogues) loses phosphine during adduct formation with $CF_2{=}CF_2$.[175] Its reaction with hexafluorobut-2-yne is more complex; the product contains two ethylene bridges and each Ir environment is essentially square-planar (eq 26) as determined by a single-crystal X-ray crystallographic analysis.[170] Dimerization of the acetylene occurs, possibly via an initial η^2-acetylene com-



(26)

plex, when diphenylacetylene is reacted with HRu(NO)$(PPh_3)_3$.[176]

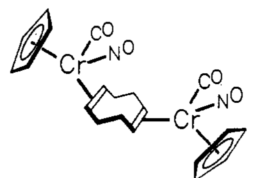
Cyclooctene replaces carbonyl in $[Re(CO)_2(NO)Cl_2]_2$ in the presence of L (L = P-, N-, and As-donor ligands) to give monomeric, olefin-substituted complexes LRe(CO)(NO)Cl_2(cyclooctene), which readily lose the cyclooctene in the presence of excess L.[177] Carbonyl replacement by TCNE occurs in $(RNC)_2Co(CO)(NO)$ (R = aryl) to give a complex in which the magnetic equivalence of the isocyanide ligands has been attributed to the free rotation of the TCNE ligand in solution rather than to the dissociative exchange of ligands.[178] Numerous olefins and acetylenes coordinate to the chromium center in the reaction summarized by eq 27 (L = olefin, acetylene).[179] If L = cyclooctene, then the



(27)

(L = olefin, acetylene)

bound olefin is readily displaceable by other nitrogen-donor ligands.[180] A related tungsten acetylene complex has been obtained by an entirely different route.[148] The complex containing 1,5-cyclooctadiene, i.e. CpCr(CO)(NO)(η^2-C_8H_{12}), can be thermally converted to the bimetallic product **67** containing a bridging diolefin ligand.[179] Similar transformations occur with the η^5-fluorenyl complex, (η^5-$C_{13}H_9$)Cr$(CO)_2$(NO) (**5**), to eventually produce an analogue of **67**.[17]

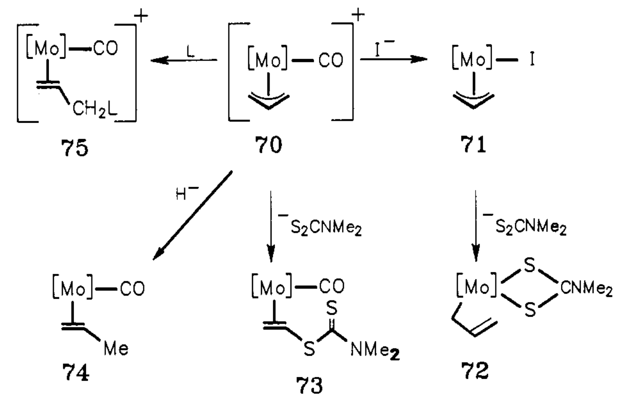


67

Photolytic displacement of carbonyl by olefins in $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$ in liquid xenon solution has resulted in the generation of the monosubstituted η^2-olefin species (olefin = 1-butene).[181] In the case of iron, displacement of two CO ligands is observed to produce a compound identified spectroscopically as $Fe(NO)_2(\eta^2\text{-1-butene})_2$. This compound is thermally unstable at −55 °C, however, losing olefin and reacquiring the carbonyl ligands. When 1,3-butadiene is employed, both η^2- and η^4-diene complexes result.[182] The resulting iron complex $Fe(NO)_2(\eta^4\text{-diene})$ is also thermally unstable, decomposing in solution at temperatures above −50 °C. The related η^2-diene complex Cp*Ru(NO)(η^2-diene) is formed by the reaction of Cp*Ru(NO)Cl_2 with 2 equiv of CH_2=CHMgBr,[92] putatively via an unstable divinyl complex.

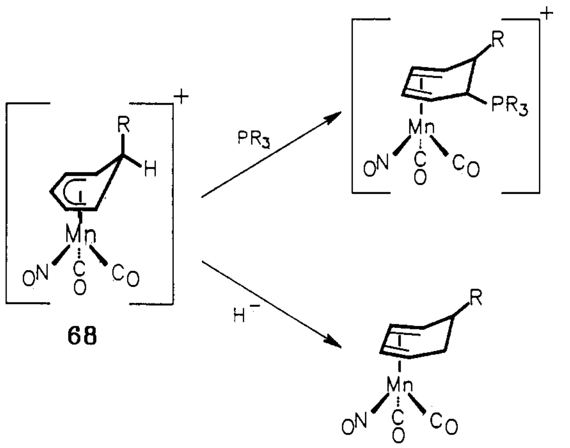
cis- and *trans*-diene complexes of molybdenum of the type CpMo(NO)(η^4-diene) result from the Na/Hg reduction of the diiodides **9** (X = I) in the presence of the appropriate diene.[183,184] MO calculations on the model CpMo(NO)(η^4-butadiene) complex show the *trans*-diene isomer to be more thermodynamically stable than the corresponding cis form. This result is in accord with the experimental observation that the isolable *cis*-diene isomers are indeed the kinetic products and isomerize irreversibly to the favored trans isomers upon standing in solution under ambient conditions.

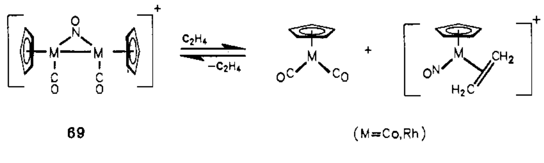
SCHEME X



[Mo] = CpMo(NO)

Diene complexes of manganese can be generated by nucleophilic exo attack of the η^5-bonded ring in complexes **68** by nucleophiles such as phosphines and hydride. Triphenyl phosphite, on the other hand, substitutes a carbonyl ligand instead of adding onto the organic ring.[185] Finally, reversible ethylene addition resulting in the fragmentation of a binuclear complex has been observed for **69** (M = Co, Rh) and their Cp* analogues (eq 28).[113]

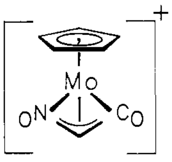




(28)

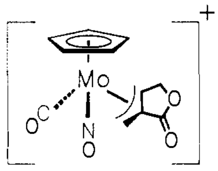
VIII. Allyl Complexes

The allyl ligand can adopt either static η^1 (σ-bound) or η^3 ($\sigma + \pi$ or π only) type linkages to metal centers, or it may rapidly interconvert between the two, thereby exhibiting fluxionality. One of the most studied nitrosyl allyl complexes known is the cationic molybdenum allyl **70** (and its substituted analogues), which is preparable by the reaction of allyl bromide and $AgPF_6$ with CpMo$(CO)_2$(NO) (**8**).[186,187] Its characteristic reactions with representative anionic and neutral nucleophiles are summarized in Scheme X. Attack of halides (for example, iodide) on **70** displaces the carbonyl ligand to

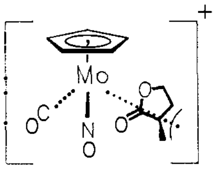


70

give the neutral allyl iodo complex **71**.[186a] A detailed study of this reaction using the neomenthylcyclopentadienyl analogue revealed that carbonyl displacement occurs with *retention of configuration* at the metal center.[188,189] An analysis of the conformational isomers of the type **70** and **71** has been performed by using ^{95}Mo NMR spectroscopy.[190] These complexes exhibit ^{95}Mo NMR resonances in the ranges −1326 to −1576 ppm and −790 to −1100 ppm, respectively. Hence, the molybdenum center becomes more deshielded upon iodide replacement of the carbonyl. Furthermore, this study also established that for a given allyl ligand in complexes of the type **70** and **71**, the exo isomers exhibit ^{95}Mo NMR signals upfield of those displayed by their corresponding endo isomers.[190] The tungsten congener of **71** can be synthesized from tetraallyltin and the diiodide dimer **10** and is found to contain a very asymmetric allyl ligand.[191] Iodide can be removed from **71** by Ag^+ in the presence of nitriles to generate analogues of **70**. More interesting is the iodide replacement in **71** by dithiocarbamate ligands to give **72** in which the allylic group is η^1-bound and the dithiocarbamate is bidentate. This latter complex is stereochemically rigid over the temperature range −60 to +110 °C.[187] A similar reaction of a dithiocarbamate ligand with the cation **70** gives the product complex **73**. The formation of this product is most consistent with the occurrence of nucleophilic attack at the coordinated allyl group.[186] Such attacks, demonstrated during the reactions of **70** with $[M(CO)_5]^-$ (M = Mn, Re) nucleophiles,[186b] also probably occur during the formation of **74** and **75**. Very high regioselectivity has been observed when the allyl is cyclooctenyl, the formation of the nucleophile–carbon bond occurring cis to NO in both the exo and endo isomers.[192,193] On the other hand, only the endo conformer **76b** (formed as the kinetic product from nitrosonium for carbonyl replacement in its precursor) reacts with nucleophiles via attack at the methylene carbon to form an η^2-lactone complex analogous to **75**. The isolation of only one diastereoisomeric product also confirmed the stereospecificity of the reaction.[194] The thermodynamically more stable **76a** exo conformer does not react similarly. Electrophiles have been found to insert into the Mo–allyl σ-bond in **72** (electrophile = SO_2, $CF_3C{\equiv}CCF_3$) or to form *addition products at the allyl ligand* resulting in cyclization (electrophile = TCNE, $(CF_3)_2C{=}O$).[195]

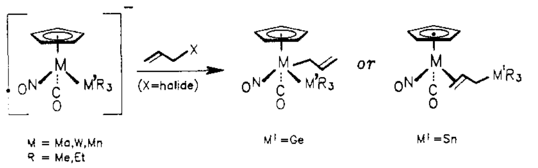


76a exo



76b endo

Other allyl complexes of Mo, W, and Mn are obtainable by the reaction of allyl halides with nitrosyl anion precursors (eq 29) (R = Me, Et; X = halide).[86]



(29)

Reactions of the allyl complexes $(\eta^3\text{-allyl})Fe(L)(CO)(NO)$ (L = CO or phosphine) with phosphines, PR_3, may result in either (i) substitution of a carbonyl ligand or (ii) attack on the coordinated allyl to form a zwitterionic olefin complex of the type $Fe^-(CH_2{=}CHCH_2{}^+PR_3)$.[197] If CO substitution occurs, the five-coordinate addition complex formed by phosphine attack at Fe has been detected as an intermediate in some cases.[198,199] Alternatively, when a chelating phosphine is used, insertion of CO into the Fe–allyl bond is known to occur on occasion.[198] Hydride attack on $(\eta^3\text{-allyl})Fe(L)(CO)(NO)$ results in displacement of the coordinated allyl group.[200] Nitrosonium ion substitution for carbonyl in a series of such Fe–allyl complexes results in the generation of the fluxional $[(\eta^3\text{-allyl})Fe(L)(NO)_2]^+$ cations, which undergo facile allyl displacement upon treatment with nucleophiles.[201] The fluxionality of these cations involves slow allyl group rotation, as established by spin saturation transfer ^{1}H NMR spectroscopy.[202] Replacement of allyl for nitrosyl (both formally three-electron donors) in a related diallyl iron complex has also been achieved.[203]

The complexes **77a** and **77b** are obtained by the reaction of tetrallyltin with $[Fe(NO)_2Cl]_2$ and $RuCl(NO)(PPh_3)_2$, respectively. Allylmagnesium bromide reacts with **77a**, but the exact nature of the product is still uncertain.[204] Addition of carbon monoxide to **77b** does not convert the η^3-allyl ligand to an η^1 configuration, but rather causes the nitrosyl ligand to bend.[205] Cationic rhodium and iridium allyl complexes $[(\eta^3\text{-allyl})M(NO)L_2]^+$ (M = Rh, Ir) have been similarly prepared, and the iridium complex has been a model for the linear ⇌ bent equilibrium of a terminal nitrosyl ligand.[206] Both complexes react with CO to give acrolein oxime (vide infra).

$[(\eta^3\text{-allyl})Fe(NO)_2]_2SnCl_2$

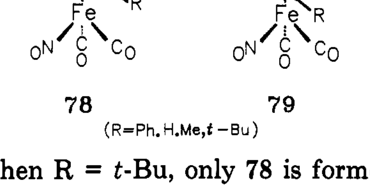
77 a

$(\eta^3\text{-allyl})Ru(NO)(PPh_3)_2$

77 b

A. Cyclopropenyl Complexes

Cyclopropenyl cations react with $[Fe(CO)_3(NO)]^-$ to afford the η^3-cyclopropenyl (**78**) and/or η^3-oxocyclobutenyl (**79**) complexes (R = Ph, H, Me, *t*-Bu).[207]

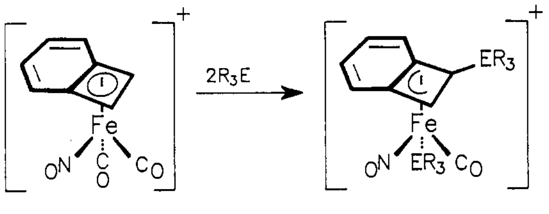


78 79
(R=Ph, H, Me, *t*-Bu)

However, when R = *t*-Bu, only **78** is formed. Phosphines add to **78** with concomitant insertion (migration) of CO into the cyclopropenyl ring to give oxocyclobutenyl complexes analogous to **79**. Again, the complex having R = *t*-Bu is an exception, only undergoing CO substitution when treated with phosphines.[208]

IX. Cyclobutadiene Complexes

Only cyclobutadiene nitrosyl complexes of iron and manganese have been reported in the literature. The iron complex **80** is generated by NO^+ or NO_2^+ attack on the neutral tricarbonyl precursor. Phosphines and arsines, ER_3 (E = P, As), react with **80** to give the addition–substitution product **81**,[209] in which one molecule of ER_3 has effected nucleophilic exo addition to the benzocyclobutadiene ring, and the other ER_3 has effected simple CO substitution. An alternative molecular structure of **81** in which "ER_3" is positioned at a tertiary ring carbon is not ruled out by the presently available data. Other cyclobutadiene ring substituted analogues of **80** have been prepared, and their carbonyl substitution reactions with various σ-donor ligands have been reported.[210] The reactions of anionic nucleophiles X^- (X = Cl, NCO, NO_2, N_3, or NCS) with $[(\eta^4\text{-}C_4Ph_4)Fe(CO)_2(NO)]^+$ result in the loss of CO and the formation of a series of the neutral dimers $[(\eta^4\text{-}C_4Ph_4)Fe(NO)X]_2$.[211]



80 81

(E=P,As)

The manganese complex $(\eta^4\text{-}C_4Ph_4)Mn(CO)_2(NO)$ can be formed (albeit in only 5% yield) by the reaction of $Mn(CO)_4(NO)$ and diphenylacetylene in refluxing toluene. It has been characterized fully by IR and mass spectroscopies and single-crystal X-ray crystallography.[212]

X. Arene Complexes

Nitrosylation of $(\eta^6\text{-arene})Cr(CO)_3$ or its derivatives may or may not yield cationic arene–metal nitrosyl complexes depending on (i) the reaction conditions, (ii) the solvents employed, and (iii) the nature of the substituents on the arene ring. Although accompanying arene displacement is a common feature of such nitrosylation attempts,[69,213,214] the conversions summarized in eq 30 can be effected under appropriate experimental conditions[215] and the cationic arene nitrosyl product complexes can be isolated. Nucleophiles add to the arene ring of the cationic products to form neutral η^5-pentadienyl complexes.[216,217] Attempts to form a mixed nitrosyl–alkyne–arene complex, by treating $(\eta^6\text{-arene})Cr(CO)_2(PhC{\equiv}CPh)$ with NO^+ (as in eq 30) only resulted instead in protonation of the chromium center due to the solvent used (methanol) and the increased basicity of the chromium center in the starting acetylene complex.[217]

$$\underset{(L=CO,PPh_3)}{(\eta^6\text{-arene})Cr(CO)_2L} \xrightarrow{NO^+} \begin{matrix}[(\eta^6\text{-arene})Cr(CO)(NO)L]^+\\ +\\ [(\eta^6\text{-arene})Cr(CO)_2NO]^+\end{matrix} \qquad (30)$$

Condensation of chromium vapor with nitric oxide, benzene, and boron trifluoride results only a violent explosion of the condensate at ~−30 °C.[218] Hence, the long-sought arene nitrosyl complex $(\eta^6\text{-benzene})Cr(NO)_2$ remains unknown.

XI. Reactivity of Bound NO

Nitric oxide is a well-known atmospheric pollutant, and new ways to convert it into useful chemical compounds such as amines have been the subjects of considerable investigative attention. The existence of a wide variety of transition-metal organometallic nitrosyl complexes has provided the impetus for the study of a series of reactions involving the NO ligands. These reactions range from simple adduct-type interactions with incoming substrates to complete expulsion of the NO ligand from the metal's coordination sphere. These reactions will now be considered in turn.

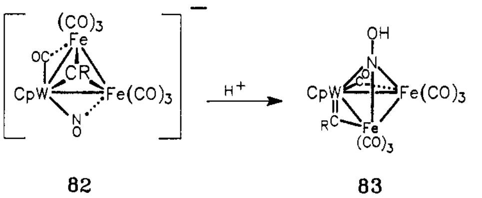
A. Interaction with Lewis Acids

The Lewis basicity of the NO ligand is exemplified in the reactions of $CpCr(NO)_2Cl$ and $CpM(CO)_2(NO)$ (**4**) (M = Cr, Mo, W) with the cyclopentadienyl–lanthanide complexes, R_3Ln (R = Cp, Cp′; Ln = Sm, Er, Yb, Ho, Dy). The ^1H NMR and IR spectral changes that occur upon combination of the reagents are indicative of R_3Ln complexation to the terminal oxygen atoms of the nitrosyl ligands. Specifically, the lowering of the NO stretching frequency by about 30 cm^{-1} evident in the IR spectra is indicative of the weakening of the N–O bond as electrons are donated from the nitrosyl oxygen atom to the lanthanide and the concomitant increase in back-donation of electrons by the group 6 metal into the antibonding π^* orbitals of the complexed NO ligand.[219,220] Other Lewis acids such as $FeCl_3$ form 1:1 adducts with $CpCr(NO)_2Cl$ via the chlorine atom.[222] This feature is not unexpected, since in the chromium complex the chromium–chlorine linkage is best viewed as being highly polar, i.e. $Cr^{\delta+}$–$Cl^{\delta-}$.[44]

The hard Lewis acid tricyclopentadienylsamarium, Cp_3Sm, has been used to investigate the Lewis basicity of bound NO in three kinds of ligation modes, namely, (i) terminal, (ii) two-metal bridging, and (iii) three-metal bridging.[223] The specific complexes used were $CpCr(CO)_2(NO)$, **4** (M = Cr) for terminal NO, $[CpFe(NO)]_2$, **20a** for two-metal bridging NO, and $Cp'_3Mn_3(NO)_4$ for three-metal bridging NO. The results of the study of the IR spectral changes accompanying adduct formation showed that the order of the Lewis basicity of bound NO (toward Cp_3Sm) is terminal NO > μ_2-NO ~ μ_3-NO. In all cases, addition of diethylamine is sufficient to cleave the isonitrosyl linkages, $-NO{\rightarrow}SmCp_3$.

B. Interaction with Protic Acids

Protonation of an asymmetrically bridging nitrosyl ligand occurs in the complex **82** to generate **83** (eq 31),

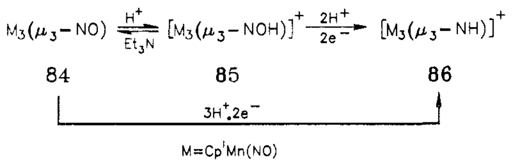


(31)

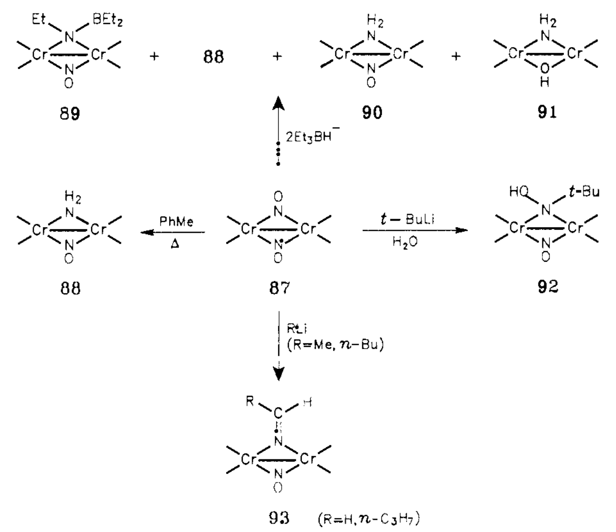
82 83

(R=p-tolyl)

SCHEME XI



SCHEME XII



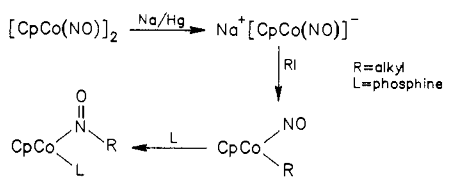
which contains a μ_3-NOH group and exhibits a corresponding broad resonance in its ^{1}H NMR spectrum at δ 10.80 assigned to the hydroxyl proton.[224] The unprecedented sequential transformations in Scheme XI involve the overall formal reduction of a triply bridging nitrosyl ligand.[225] These stepwise proton-induced transformations represent the possible first steps of a process for the reduction of NO to NH_3. The manganese dimer $[Cp'Mn(CO)(NO)]_2$ also undergoes protonation to give $[Cp'_2Mn_2(NO)_2(CO)(NH_2)]^+$ and **86**.[226]

C. Carbanion Reductions

The dinitrosyl dimer $[CpCr(NO)_2]_2$ (**87**) has been used as a model compound with which different kinds of nitrosyl ligand conversions have been effected (see Scheme XII). The known bimetallic compound **88** can be obtained in 15% yield by reflux of **87** in toluene for 24 h.[227] An unusual reactivity pattern of the hydride source, $LiEt_3BH$, is exemplified by its reaction with **87** (in THF solution) as shown in Scheme XII.[228] Compound **89** is isolable in low yield (6%), and its solid-state molecular structure has been determined by X-ray crystallography. Also isolable are the bimetallic complexes **88**, **90**, and **91**, which are the products formed when other hydride sources such as Red-Al or BH_3 react with **87**.[125] Organolithium reagents such as *t*-BuLi, *n*-BuLi, or MeLi react with only one bridging nitrosyl group of **87** to afford, after hydrolysis, either complexes **92** or **93**, depending on whether or not the organolithium reagent contains an α-hydrogen atom.[229]

The carbanion sources RLi (R = Ph, *t*-Bu) also react with $[CpCo(NO)]_2$ at low temperature to yield $Cp_2Co_2(\mu_2\text{-NO})(\mu_2\text{-NHR})$ in a similar manner. More interesting is the fact that the catalytic hydrogenation of the cobalt nitrosyl dimer in the presence of nickel leads first to $Cp_2Co_2(\mu_2\text{-NO})(\mu_2\text{-NH}_2)$, which upon further treatment with H_2 *liberates* NH_3.[230] Similar reactions of RLi with CpNi(NO) at low temperatures[231] lead to the cluster complexes $(CpNi)_3(\mu_3\text{-NR})$ possibly via carbanion (R^-) attack at the coordinated nitrosyl ligand (a feature gaining widespread recognition).[154,232]

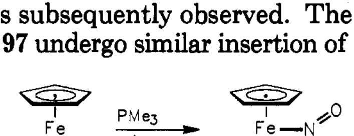
SCHEME XIII



D. Migration of Bound Nitrosyl Ligands

The ability of nitrosyl ligands to adopt different bonding modes toward metals and to react with both electrophiles (such as acids) and nucleophiles (such as carbanions) suggests that under the right experimental conditions it should be possible to effect such reactivity patterns *intramolecularly*. Indeed, migratory insertion reactions of bound NO into metal–carbon bonds are well-known and are fairly well understood processes.[233] For instance, the cobalt complex $Co(Me)_2(PMe_3)_3$ reacts with NO to form diamagnetic $Co(Me)_2(PMe_3)_2(NO)$, which subsequently rearranges with concomitant NO insertion into a Co–Me bond to give the isolable dimer $[CoMe(MeNO)(PMe_3)_2]_2$. This dimeric complex is proposed to be bridged by the nitrosomethane ligands on the basis of its NMR (^{31}P and ^{1}H) and IR spectra.[234] Furthermore, the allyl complexes $[(\eta^3\text{-allyl})Ir(NO)L_2]^+$ (L = PPh_3) and their isoelectronic rhodium analogues react rapidly with CO to give acrolein oxime via intramolecular coupling of the nitrosyl and allyl ligands.[206]

The first detailed mechanistic study of the NO insertion reaction was carried out for the processes outlined in Scheme XIII (R = alkyl, L = PPh_3, PEt_3).[110] The η^1-nitrosoalkane bonding mode in the final product complex was established by X-ray crystallography for the case where R = Et and L = PPh_3. Kinetic studies of the conversion of the nitrosyl alkyl complex to the nitrosoalkane compound (i.e., the last step in Scheme XIII) showed that it followed pseudo-first-order kinetics, a feature consistent with initial NO insertion into the Co–R bond followed by trapping of the resulting 16-electron complex by L. When the nitrosyl alkyl complex CpCo(NO)Me is synthesized in the presence of L = PEt_3, the adduct CpCo(NO)(L)Me, which has bent NO geometry, is formed. Phosphine dissociation from this complex precedes any migratory insertion process subsequently observed. The iron dialkyl complexes **97** undergo similar insertion of NO when R = Me

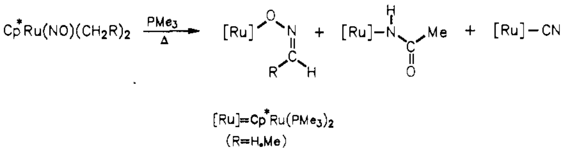


97
(32)

and Cp = Cp[90] or Cp*[86] (eq 32). However, when R = CH_2SPh or CH_2Ph and Cp = Cp*, reductive coupling of the alkyl ligands, instead of NO insertion, is observed (eq 33).[86] An identical reductive coupling of aryl ligands occurs in the thermal decomposition of Cp*Ru-

$$Cp^*Fe(NO)R_2 \xrightarrow[\Delta]{} [Cp^*Fe(NO)]_2 + R{-}R \qquad (33)$$

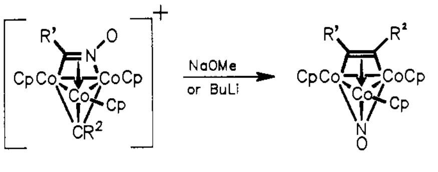
(NO)Ph_2 to give [Cp*Ru(NO)]$_2$ and biphenyl.[92] The alkyl analogues, however, upon treatment with PMe_3 produce isolable organometallic complexes, which are believed to arise from initial migratory insertion of NO into one of the metal–alkyl bonds (eq 34).[95] The cyano complex arises when R = H, and the amide complex is formed when R = Me.



(34)

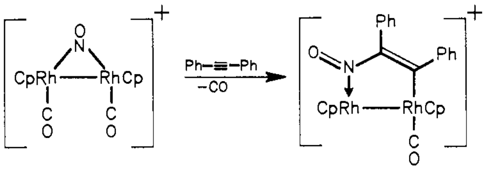
Obviously, the migratory insertion reactions considered here represent new synthetic routes for the formation of carbon–nitrogen bonds. Two other routes, one a nitrosyl–olefin coupling reaction involving cobalt, and the other insertion of NO^+ into a chromium–carbon bond, will be considered in a later section (vide infra).

In closing this section, we present in eq 35 and 36 two unusual deinsertion and insertion reactions of bound NO.[235] As shown in eq 35, complex **94** [resulting from the first observed NO^+ insertion into the metal cluster–carbon bond of the precursor $(CpCo)_3(\mu_3\text{-}CR_2)$] reacts with deprotonating reagents to give the unexpected product **95**, in which carbyne coupling has occurred *with simultaneous deinsertion* of *NO*.[236] In the chemical transformation summarized in eq 36, an unprecedented insertion of an alkyne into a metal–nitrosyl bond occurs.[111] Attempts to obtain crystals of **96** suitable for X-ray diffraction failed, but its formulation is adequately supported by conventional characterization data. Moreover, precedents for similar insertions of an alkyne into M–CO links do exist.



(35)

94 **95**



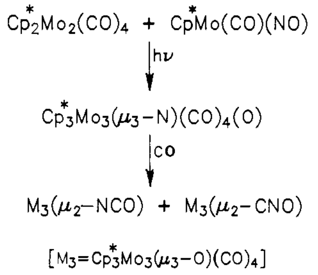
(36)

96

E. Displacement of Bound Nitrosyl Ligands

The chromium complex $CpCr(NO)_2Cl$ reacts with a wide range of strong donor ligands (L) such as pyridine, PPh_3, and NCR (R = cyclohexyl) to effect substitution of a nitrosyl group by L, 17-electron CpCr(NO)(L)Cl complexes being the final products.[237] During a recent study of the photolytic behavior of the coordination compounds $Rh(NO)(CO)(PPh_3)$ and $Ir(NO)(CO)Cl(PPh_3)_2$ in the presence of PPh_3,[238] it was demonstrated that the nitrosyl ligand (rather than carbonyl!) is preferentially expelled from the metal's coordination sphere. Such a process of selective nitrosyl ligand displacement has not, to the best of our knowledge, been detected during the photolysis of organometallic nitrosyl complexes.

SCHEME XIV



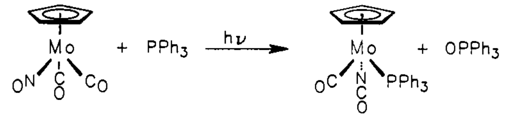
F. Nitrosyl Group as an Oxygen Atom Source

The thermal decomposition of dinitrosyl complexes to produce N_2, NO, and N_2O and the closely related catalytic disproportionation of nitric oxide into N_2 and O_2 have been detailed.[239] In addition, triphenylphosphine has been oxidized by bound nitric oxide (with rigorous exclusion of oxygen) as outlined in eq 37.[240] The indicated products are obtained in low yields, and in air the molybdenum complex rapidly decomposes to the oxo complex, $MoOCl_3(PPh_3O)_2$.

$$[M(NO)Cl_3]_n + \text{excess } PPh_3 \longrightarrow M(NO)Cl_3(OPPh_3)_2 \qquad (37)$$

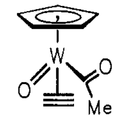
(M=Mo,W)

The photochemical reaction of $CpMo(CO)_2(NO)$ and PPh_3 in benzene solution results both in simple substitution of the carbonyl ligands (vide supra) and in the novel combination of NO and CO to form the isocyanate ligand as shown in eq 38.[25] Control reactions are consistent with the initial formation of organometallic nitrene species that capture CO to form the NCO group. The isocyanate complex shown in eq 38 has been structurally characterized by X-ray diffraction. Matrix isolation studies of the reaction of the tungsten congener, $CpW(CO)_2(NO)$, with PPh_3 provided definitive evidence for such CO capture by a nitrene group. Isotopic labeling studies established that the CO component of the isocyanate ligand does indeed originate from the CO ligand.[241] Isocyanate ligand formation has also been observed in the photolytic condensation reaction outlined in Scheme XIV.[242] The isostructural isocyanate (NCO) and fulminate (CNO) clusters were cocrystallized from the product mixtue. The reaction sequence in the scheme parallels that proposed for the formation of the NCO ligand in eq 38. In this case, however, the nitrosyl ligand splits into N and O atoms which are *held together in the same complex molecule* to give an oxo nitride complex which then adds CO.



(38)

Other examples of oxo complex formation from nitrosyl compounds include the thermal decomposition reaction of $Cp_2V(NO)I$ to give $\{Cp_2VI\}_2[CpV(NO)]_2(\mu\text{-}O)_4$, whose solid-state molecular structure has been determined.[5] Disproportionation reactions involving nitric oxide have also been observed in its reactions with Cp_2VCl to give N_2O and $Cp_3V_2O_2Cl_2$ and with Cp_2Cr to give $CpCr(NO)_2(NO_2)$. The oxo ligand in **104** derives from the nitrosyl oxygen of NO during its reaction with the carbonyl precursor **48**.[148]



104

The ability of bound NO to lose oxygen is perhaps best exemplified by the electrochemical reduction of the $CpM(CO)_2(NO)$ (M = Mo, W) complexes (**4**). One-electron reductions afford the $[CpM(CO)_2NO]^{\bullet-}$ radicals, which on the basis of their ESR spectra are formulated as having the extra electron localized on the M–NO fragment, a localization that causes bending of the nitrosyl ligand.[243] This observation, together with the X-ray and PES studies of the related $CpM(NO)_2Cl$ complexes, which indicate significant electron density transfer to the oxygen atoms of the nitrosyl ligands (vide supra), may well account for the ability of the NO ligands in these species to function as sources of atomic oxygen.

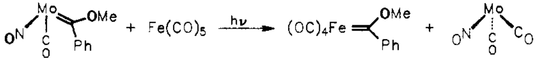
XII. Applications

The application and transition-metal nitrosyl coordination complexes in organic synthesis and in pollution control has been reviewed.[244] This section highlights some applications of organometallic nitrosyl complexes that have been developed primarily from the organometallic point of view. For clarity, this last section is subdivided into applications involving the metal center, the nitrosyl ligand, or π-bound organic ligands.

A. Involving the Metal Center

The cationic complex $[CpW(NO)_2]^+$ rapidly isomerizes 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene and dimerizes 1,1-diphenylethylene to the head-to-tail cyclic dimer, 1,1,3-triphenyl-3-methylindan.[37] Some olefins such as allylbenzene do not, however, react with this electrophilic cation. This is somewhat surprising since $[CpW(NO)_2]^+$ is sufficiently electrophilic to abstract Ph^- from $NaBPh_4$. It has been proposed that incipient carbocations are generated during its reactions with olefins. Similar results have been obtained with $[M(NO)_2(CH_3CN)_4]^{2+}$ (M = Mo, W), $[Rh(NO)(CH_3CN)_4]^{2+}$, and $[Fe(NO)_2(solv)_n]^+$.[245]

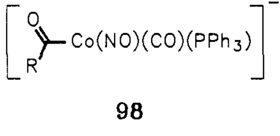
The 18-electron carbene complex **35** (M = Mo) has been shown[246] to be a good carbene-transfer agent to both $Fe(CO)_5$ (eq 39) and to $Ni(CO)_4$. In the latter case, $[(OC)Ni{=}C(OMe)Ph]_3$ is the putative product.[134]



(39)

35

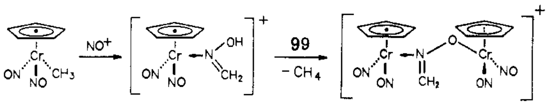
The cobalt acylate complexes **98** (R = alkyl, aryl) are generated by R^- attack on $Co(NO)(CO)_2(PPh_3)$. These thermally unstable complexes readily transfer the acyl functionality to allylic halides, conjugated ketones, and quinones to form β,γ-unsaturated ketones, 1,4-dicarbonyl compounds, and 4-acylcyclohexadienones, respectively.[166]



98

(R=alkyl,aryl)

The dinitrosyl dimer $[CpCr(NO)_2]_2$ (**7**) selectively abstracts halogens from *vic*-dihaloalkanes to produce the corresponding alkenes.[247] Furthermore, the dinitrosyl compound **99** inserts NO^+ as shown in eq 40



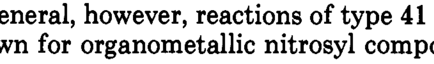
(40)

99 100 101

to give the noval formaldoxime complex **100**, in which the intramolecular dimensions of the formaldoxime ligand resemble those of free formaldoxime.[248] Complex **100** reacts in the presence of excess **99** to give the bimetallic oximato dimer **101**.[249] The initial NO^+ insertion reaction shown in eq 40 is without precedent and should provide new ways of carbon–nitrogen bond formation (vide supra).

B. Involving Nitrosyl Ligands

The ability of nitrosyl ligands in metal complexes to catalyze the air oxidation of organic substrates is probably due to the occurrence of their reaction with oxygen as summarized in eq 41.[250] The latter step



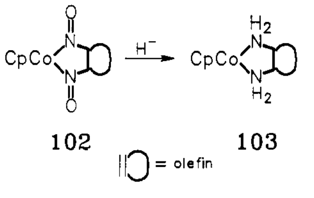
$$M{-}NO + 1/2O_2 \longrightarrow M{-}NO_2 \xrightarrow{S} M{-}NO + SO \qquad (41)$$

M=metal complex
S=organic substrate

involving O-atom transfer[251] has been extensively studied for a bimetallic Co–Pd system in which concomitant NO exchange between the metals also occurs.[252] In a similar manner, $(P_2)Fe(NO)_2$ (P_2 = chelating phosphine) catalyzes the air oxidation of chelating phosphines probably via a nitro intermediate.[253] In general, however, reactions of type **41** are not well-known for organometallic nitrosyl compounds.

C. Involving Nitrosyl and Other Ligands

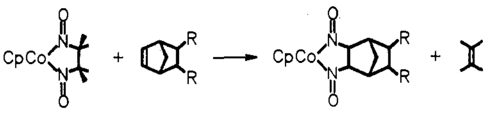
A well-studied transformation of the condensation of a nitrosyl compound with an olefin involves the cobalt dimer $[CpCo(NO)]_2$. When this dimer is reacted with NO and olefin, complexes of the type **102** result. The initial studies[254] employed norbornene as the olefin, but this chemistry has been subsequently extended to encompass a range of simple olefins.[255] Hydride reduction of complexes **102** yields diamine complexes **103** from which the diamines can be liberated. These sequential reactions represent the first general method for the direct transformation of various olefins to their primary 1,2-diamines. Complexes **102** also undergo exchange reactions, a particular example being illustrated in eq



(42)

102 103

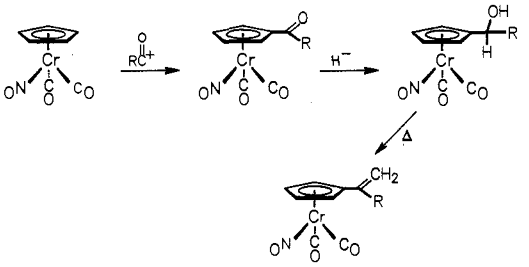
43.[256] Kinetic and mechanistic studies of these exchange reactions show that they occur by initial dissociation of olefin from complexes **102**. The initial condensation reaction to form **102** is believed to involve $CpCo(NO)_2$ formation, though this has not yet been confirmed.



(43)

D. Involving π-Bound Organic Ligands

A bound η^5-cyclopentadienyl ring has been derivatized in the stepwise fashion shown in eq **44**.[221]



(44)

Various ring-substituted cyclopentadienyl nitrosyl complexes are obtainable by this method. This fact is of fundamental importance since many of these complexes are not accessible by conventional synthetic routes.

Nucleophilic addition to the organic ring in $[(\eta^5\text{-hexadienyl})Mn(CO)_2(NO)]^+$ cations to form the neutral η^4-diene derivatives has been the subject of several studies.[185,257,258]

Finally, the "selective binding and activation of one aldehyde enantioface" has been achieved recently by employing the chiral cation $[CpRe(NO)(PPh_3)]^+$ (**14**).[259]

It is likely that future research efforts will focus even more on developing new synthetic and material applications of organometallic nitrosyl complexes.

XIII. Acknowledgment.

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