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Review

The rich and varied chemistry of group 6 cyclopentadienyl nitrosyl complexes

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Contents

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ABSTRACT

The syntheses and characteristic physical and chemical properties of representative members of important types of cyclopentadienyl nitrosyl complexes of the Group 6 elements are reviewed. These organometallic compounds contain either 14-valence-electron (14e) Cp′M(NO) or 17e Cp′M(NO)$_2$ core fragments [Cp′ = an η^5-cyclopentadienyl ligand, most often η^5-C$_5$H$_5$ (Cp) or η^5-C$_5$Me$_5$ (Cp*); M = Cr, Mo, or W]. All the complexes originate from Cp′M(NO)(CO)$_2$ which can be readily converted into the precursor complexes Cp′M(NO)$_2$X, Cp′M(NO)X$_2$ (M = Mo, W; X = halide) and [Cp′Cr(NO)I]$_2$. The latter compounds are convenient starting materials for the synthesis of [CpCr(NO)$_2$]$_2$ dimer, [CpM(NO)$_2$]$^+$ cations, and neutral compounds such as 17e Cp′Cr(NO)(L)(X) (L = Lewis base; X = halide or alkyl), 18e Cp′M(NO)L$_2$ (L = Lewis base), and 16e or 18e Cp′M(NO)(R)(R′) (M = Mo, W; R, R′ = hydrocarbyl or H). Consideration of the distinctive chemical properties of these compounds has been restricted to transformations in which the Cp′M(NO) and Cp′M(NO)$_2$ scaffolds are retained. The synthetic utility of these types of cyclopentadienyl nitrosyl complexes of the Group 6 elements for mediating specific organic transformations is also highlighted throughout this review.

1. Introduction

Coordination of nitric oxide (NO) to a transition-metal center (M) to form a metal-nitrosyl complex containing a M–NO linkage not only imparts distinctive chemical properties to the metal center but also unique reactivity to the nitrosyl ligand [1]. The chemistry

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of metal nitrosyls continues to attract attention from a diverse array of scientists for several reasons [1]. The first is the important role that NO plays in the environment, having been implicated in the depletion of the ozone layer and the formation of photochemical smog and acid rain [2]. The second is its involvement as a biological signaling molecule with its actions impacting aspects such as blood-pressure control and neuronal communication [3]. In both of these roles, metal ions are known to mediate some of the mentioned processes, and so the establishment of the diagnostic reactivity of bound NO is still the focus of much research worldwide. The third feature of metal-nitrosyl chemistry that continues to be actively investigated is the characteristic chemistry of the metal complexes themselves [4]. Nitric oxide is a strong π-acceptor ligand that stabilizes metals in relatively low oxidation states that result in the metal centers in the nitrosyl complexes exhibiting chemical properties that are often markedly different than those displayed by their isoelectronic and isostructural carbonyl complexes which contain M–CO bonds even though CO is also a relatively strong π-acceptor ligand. All of these aspects of metal-nitrosyl chemistry are strikingly illustrated by the diverse physical and chemical properties of cyclopentadienyl nitrosyl complexes of the Group 6 elements which have been extensively studied in the authors' laboratories. These compounds are the subject of this review article, and they contain 14-valence-electron (14e) Cp′M(NO) or 17e Cp′M(NO)$_2$ [Cp′ = an η^5-cyclopentadienyl ligand, most often η^5-C_5H_5 (Cp) or η^5-C_5Me_5 (Cp*); M = Cr, Mo, or W] core fragments that serve as scaffolds on which the various inorganic and organometallic complexes are constructed.

2. Preparation and properties of Cp′M(NO)- and Cp′M(NO)$_2$-containing complexes

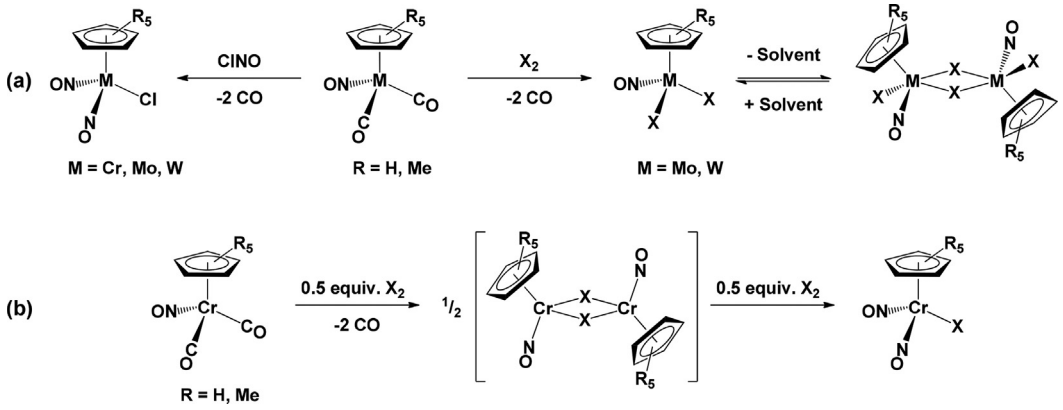
As summarized in Scheme 1, these complexes all originate from the precursor Cp′M(NO)(CO)$_2$ compounds which can be readily synthesized on a large scale by sequential treatment of M(CO)$_6$ with NaCp′ and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in THF [5]. In the special case of Cr(CO)$_6$, its similar treatment with NaCp and 1/3 $S_3N_3Cl_3$ produces the analogous thionitrosyl complex, CpCr(NS)(CO)$_2$, whose infrared spectrum indicates that NS is a stronger π-acid ligand than NO [6]. Reaction of the Cp′M(NO)(CO)$_2$ compounds with ClNO in CH_2Cl_2 affords the precursor complexes Cp′M(NO)$_2$Cl [7,8] which undergo metathesis reactions with a wide range of reagents to form other Cp′M(NO)$_2$R derivatives (R = H, alkyl, aryl, etc.) [9,10]. Similarly, treatment of the molybdenum and tungsten Cp′M(NO)(CO)$_2$ compounds with a source of X_2 (X = halogen) converts the reactants into Cp′M(NO)X_2 species [11,12] that are the precursors to a whole host of Cp′M(NO)R_2 (M = Mo, W) complexes [14,15]. However, the chromium analogues exhibit different reactivity when exposed to halogens (Scheme 1). Thus, treatment of CpCr(NO)(CO)$_2$ with I_2 in a 2:1 molar ratio in CH_2Cl_2 affords excellent yields of [CpCr(NO)I]$_2$. This dimer does not appear to contain a conventional two-center, two-electron Cr–Cr bond since it is moderately paramagnetic both in solution and in the solid state. It reacts further with excess I_2 to produce CpCr(NO)$_2$I as the final nitrosyl-containing product [16]. In contrast, CpCr(NO)(CO)$_2$ is rapidly converted into CpCr(NO)$_2$X (X = Cl, Br) in the presence of $C1_2$ and Br_2, respectively, in CH_2Cl_2, with no intermediate species being detectable spectroscopically. In other words, unlike for Mo and W, no CpCr(NO)X_2 compounds are isolable from analogous halogenation reactions of CpCr(NO)(CO)$_2$. The reactivity of Cp*Cr(NO)(CO)$_2$ toward I_2 and Br_2 generally resembles that exhibited by its Cp analogue, the presence of the Cp* ligand not imparting any enhanced stability to the intermediate complexes.

All the monometallic complexes shown in Scheme 1 have three-legged piano-stool molecular structures in solutions with M–NO linkages that are essentially linear. In addition, the oxygen atoms of the nitrosyl ligands are relatively strong Lewis bases [17]. The distinctive physical and chemical properties of representative members of important types of complexes derived from Cp′M(NO)$_2$X and Cp′M(NO)X_2 are highlighted in the following sections of this article with illustrative chemical reactions being restricted to transformations in which the Cp′M(NO) and Cp′M(NO)$_2$ scaffolds remain intact. Reactions which result in cleavage of the nitrosyl N–O bonds have been previously summarized [18].

3. Cp′M(NO)$_2$-containing compounds

3.1. [CpCr(NO)$_2$]$_2$ dimer

Reduction of green CpCr(NO)$_2$Cl with either zinc in THF or sodium in benzene affords good yields of purple [CpCr(NO)$_2$]$_2$, the isoelectronic and isostructural analogue of the well-known carbonyl dimer, [CpFe(CO)$_2$]$_2$ [19]. The molecular structure of the chromium complex contains two terminal and two bridging NO ligands whose presence is confirmed by the IR spectrum of the compound in CH_2Cl_2 that exhibits υ_{NO} at 1667 (s) and 1512 (m) cm^{-1}. Unlike its carbonyl analogue, the chromium nitrosyl dimer exhibits a propensity to abstract halogen atoms from inorganic, organometallic, and organic molecules [19]. For instance, as illustrated in Scheme 2, [CpCr(NO)$_2$]$_2$ is a useful reagent for the selective debromination of organic substrates to obtain the indicated olefin products in >75% yields [20]. The organometallic product in each of these latter reactions is CpCr(NO)$_2$X (X = Cl, Br).



Scheme 1. (a) Preparation of Cp′M(NO)$_2$- and Cp′M(NO)-containing complexes. (b) Reactions of Cp′Cr(NO)(CO)$_2$ with X_2 (X = halogen).