

Electrophilic O-Methylation of a Terminal Nitrosyl Ligand Attained by an Early–Late Heterobimetallic Effect

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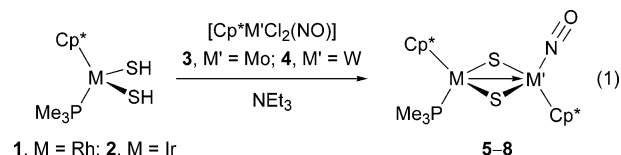
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Summary: The reaction of the group 9 bis(hydrosulfido) complexes $[\text{Cp}^*\text{M}(\text{SH})_2(\text{PMe}_3)]$ ($\text{M} = \text{Rh}, \text{Ir}$) with the group 6 nitrosyl complexes $[\text{Cp}^*\text{M}'\text{Cl}_2(\text{NO})]$ ($\text{M}' = \text{Mo}, \text{W}$) in the presence of NEt_3 affords a series of the bis(sulfido)-bridged early–late heterobimetallic (ELHB) complexes $[\text{Cp}^*\text{M}(\text{PMe}_3)(\mu\text{-S})_2\text{M}'(\text{NO})\text{Cp}^*]$ ($\text{M} = \text{Rh}, \text{Ir}; \text{M}' = \text{Mo}, \text{W}$). Upon treatment of the Rh–W complex **7** with MeOTf , the oxygen atom of the terminal nitrosyl ligand is readily methylated to form the methoxyimido complex $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-S})_2\text{W}(\text{NOMe})\text{Cp}^*]^+$ (**9**⁺), while methylation of the Rh–Mo complex **5** results in S-methylation, giving the methanethiolato complex $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-SMe})(\mu\text{-S})\text{Mo}(\text{NO})\text{Cp}^*]^+$ (**10**⁺).

Cooperation of the metal couples in early–late heterobimetallic (ELHB) complexes¹ has been a major motive for the study of this class of compounds. It still remains a challenge, however, to elicit unique functions from ELHB complexes and to clarify the roles of both early- and late-transition-metal centers.² To cast new light upon such heterobimetallic effects, we have focused our attention on ELHB complexes bearing the nitrosyl ligand, because this ligand exhibits characteristic redox behavior and reactivities depending upon the electronic states of the metal centers,³ even in the homodinuclear complexes, as we have recently demonstrated.⁴ Here we describe the synthesis, structure, and reactivities of sulfido-bridged group 6–group 9 ELHB nitrosyl complexes which feature the extremely electron-rich linear nitrosyl ligand at the group 6 metal center.

The sulfido-bridged ELHB frameworks are successfully prepared by a protocol utilizing the $\text{M}(\text{SH})_2$ functionality.⁵ When the bis(hydrosulfido) complexes of the group 9 metals $[\text{Cp}^*\text{M}(\text{SH})_2(\text{PMe}_3)]$ (**1**, $\text{M} = \text{Rh}$; **2**, $\text{M} = \text{Ir}$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) are

allowed to react with an equimolar amount of the group 6 nitrosyl complexes $[\text{Cp}^*\text{M}'\text{Cl}_2(\text{NO})]$ (**3**, $\text{M}' = \text{Mo}$; **4**, $\text{M}' = \text{W}$) in the presence of 2 equiv of NEt_3 , the bis(sulfido)-bridged ELHB complexes $[\text{Cp}^*\text{M}(\text{PMe}_3)(\mu\text{-S})_2\text{M}'(\text{NO})\text{Cp}^*]$ (**5**, $\text{M} = \text{Rh}$, $\text{M}' = \text{Mo}$; **6**, $\text{M} = \text{Ir}$, $\text{M}' = \text{Mo}$; **7**, $\text{M} = \text{Rh}$, $\text{M}' = \text{W}$; **8**, $\text{M} = \text{Ir}$, $\text{M}' = \text{W}$) are obtained as dark green (**5**–**7**) or violet (**8**) crystals in good to moderate yields (eq 1).⁶ The molybdenum



complexes **5** and **6** show one strong IR absorption assignable to the NO stretching around 1520 cm^{-1} , while the tungsten congeners **7** and **8** show an absorption at 1490 cm^{-1} . These $\nu(\text{NO})$ values, lying in the lowest edge for a terminal nitrosyl ligand, manifest the strong $\text{M}' \rightarrow \text{NO}$ back-bonding.⁷ Particularly noteworthy is the large red shift from the mononuclear thiolato complexes $[\text{Cp}^*\text{M}'(\text{NO})(\text{SPh})_2]$ ($\nu(\text{NO})$ 1631 ($\text{M}' = \text{Mo}$), 1609 cm^{-1} ($\text{M}' = \text{W}$)),⁸ which mimic the coordination environment of **5**–**8** except for the neighboring late transition metal. We thus attribute the strong π back-bonding to the influx of electrons to the group 6 metal center through the $\text{M}(\text{III}) \rightarrow \text{M}'(\text{II})$ dative bond, which has been indicated by the short Rh–W separation (2.91 \AA , mean) and the acute Rh–S–W angles (75.9° , mean) in the crystal structure of **7** (Figure 1).⁹ Enhancement of the π donation of the bridging sulfur atoms by the rhodium atom is not evident, because the W–S distances in **7** (2.33 \AA) are comparable with those in the related polysulfido complex $[\text{Cp}^*\text{W}(\text{NO})(\text{S}_5)]$ (2.33 \AA).¹⁰ The increased electron density, in

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(9) Crystallographic data for **7**: $\text{C}_{23}\text{H}_{39}\text{NOPRhS}_2\text{W}$, FW = 727.42, monoclinic, space group $P2_1/n$, $a = 17.008(2)\text{ \AA}$, $b = 18.843(2)\text{ \AA}$, $c = 17.127(2)\text{ \AA}$, $\beta = 97.121(8)^\circ$, $V = 5446(1)\text{ \AA}^3$, $Z = 8$, $T = 293\text{ K}$, $\rho_{\text{calcd}} = 1.774\text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 50.57\text{ cm}^{-1}$, 12 486 unique reflections, $R(R_w) = 0.037(0.038)$ for 620 variables and 8566 reflections ($I > 3\sigma(I)$), GOF = 1.012.

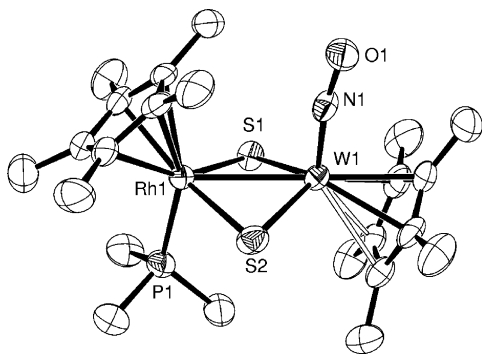


Figure 1. Molecular structure of **7**. One of the two crystallographically independent components in the crystal is shown. Thermal ellipsoids are shown at the 50% probability level.

combination with the trans influence of the nitrosyl ligand,¹¹ also results in the displacement of the Cp* ligand on the tungsten atom from the symmetrical η^5 coordination:¹² the two W–C bonds trans to the nitrosyl ligand (2.53–2.55 Å) are meaningfully longer than the other three W–C bonds (2.34–2.37 Å), although the Cp* protons are indistinguishable in the ¹H NMR spectrum, even at –90 °C. Despite the strong π interaction the structure of the W–N–O moiety is not exceptional as a linear nitrosyl ligand.

The electron-rich nature of the group 6 metal centers in **5–8** is further evidenced by the cyclic voltammetry measurements. Complexes **5–8** undergo reversible single-electron oxidations: the molybdenum complexes **5** and **6** are oxidized at 0.22–0.24 V (vs SCE), whereas the tungsten complexes **7** and **8** are oxidized at 0.12–0.13 V. We reasoned that the oxidation takes place at the group 6 metal center, since the potentials are dependent upon the group 6 metals, regardless of the group 9 metals. On the other hand, no notable reduction waves are observed in the range up to –1.5 V. These results make a striking contrast with the redox behavior of the parent mononuclear group 6 nitrosyl complexes [Cp*M'X₂(NO)] (M' = Mo, X = Cl, Br, I; M' = W, X = I), for which a reversible single-electron reduction at –0.3 to –0.5 V has been observed.¹³

The strong π back-bonding to the nitrosyl ligand in **5–8** prompted us to examine their reactions with an electrophile. Treatment of the Rh–W complex **7** with 1 equiv of MeOTf (OTf = OSO₂CF₃) in CH₂Cl₂ cleanly affords a dark red solid, which is characterized by the absence of IR absorptions ascribable to the NO multiple bond and a new ¹H NMR resonance for OMe protons at δ 4.06. These spectroscopic data suggest that electrophilic O-methylation of the nitrosyl ligand takes place to give the Rh(III)–W(VI) methoxyimido complex

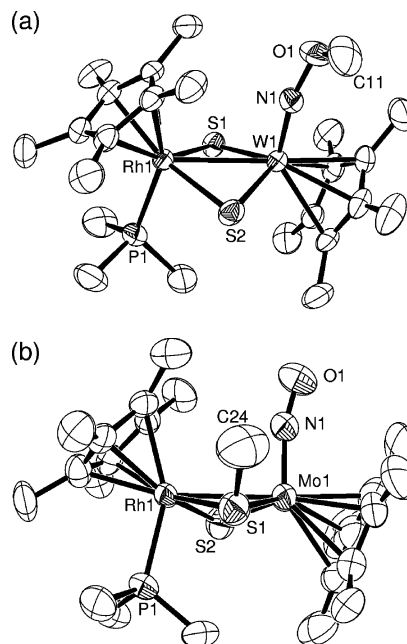
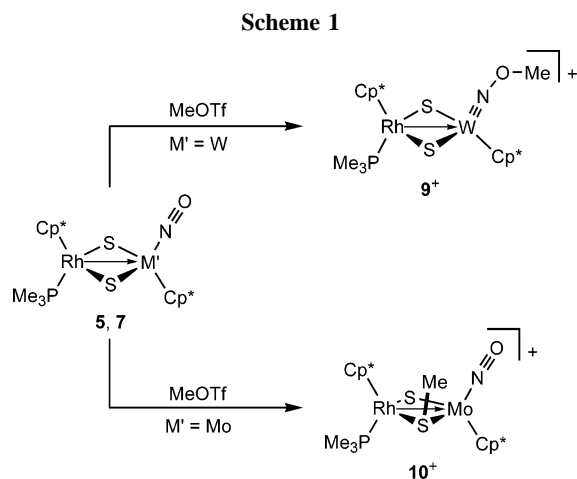


Figure 2. Molecular structures of the cationic parts of (a) **9**⁺PF₆[–] and (b) **10**⁺BPh₄[–]. For **10**⁺BPh₄[–], one of the two crystallographically independent components in the crystal is shown. Thermal ellipsoids are shown at the 50% probability level.

[Cp*Rh(PMe₃)(μ -S)₂W(NOMe)Cp*](OTf) (**9**⁺OTf[–]), as shown in Scheme 1. The detailed structure of **9**⁺ has been determined by an X-ray crystallographic study of **9**⁺PF₆[–], which is obtained by the anion metathesis of **9**⁺OTf[–] with Bu₄NPF₆ (Figure 2a).¹⁴ The metrical parameters of the alkoxyimido ligand in **9**⁺ closely resemble those in [CpNbCl₂(NOBu')], derived from an *O*-*tert*-butylhydroxylamine salt.¹⁵ It should be emphasized that electrophilic methylation of a genuine terminal nitrosyl ligand is unprecedented. The closest example to the present reaction is the methylation of the anionic nitrosyl complex [Cp*MoMe₃(NO)Li(thf)₂], giving the methoxyimido complex [Cp*MoMe₃(NOMe)].¹⁶ The Mo–N–O–Li array in the starting lithiated complex, however, is best described as a bridging oxo–imido ligand on the basis of X-ray crystallography and IR spectroscopy. On the other hand, the more reduced μ -NO ligands are more likely to undergo electrophilic methylation.¹⁷ We also note

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(14) Crystallographic data for **9**⁺PF₆[–]: C₂₄H₄₂F₆NOP₂RhS₂W, FW = 887.42, monoclinic, space group P2₁/c, *a* = 8.714(3) Å, *b* = 24.849(4) Å, *c* = 14.533(2) Å, β = 91.52(2)°, *V* = 3145(1) Å³, *Z* = 4, *T* = 293 K, ρ_{calcd} = 1.874 g cm^{–3}, $\mu(\text{Mo K}\alpha)$ = 50.57 cm^{–1}, 7231 unique reflections, *R* (*R*_w) = 0.030 (0.031) for 422 variables and 6041 reflections (*I* > 3 σ (*I*)), GOF = 1.018.

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several examples of protonation of a terminal nitrosyl ligand as a related transformation: N-protonation has been reported mainly for late-transition-metal nitrosyls,¹⁸ whereas O-protonation to a (nitrosyl)tungsten complex has emerged only recently.¹⁹

In contrast to the O-methylation of **7**, treatment of the Rh–Mo complex **5** with MeOTf followed by anion metathesis with NaBPh₄ results in selective formation of the methane-thiolato complex [Cp*Rh(PMe₃)(μ-SMe)(μ-S)Mo(NO)Cp*]-(BPh₄) (**10**⁺BPh₄⁻). The complex **10**⁺BPh₄⁻ exhibits a ν(NO) band at 1573 cm⁻¹ in the IR spectrum and a singlet at δ 2.58 attributable to an SMe group. The S-methylation has further been confirmed by an X-ray analysis (Figure 2b).²⁰ Obviously, the more electron-rich tungsten center, which is inferred from the IR spectroscopy, is the second prerequisite for the methylation of the nitrosyl ligand.

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(20) Crystallographic data for **10**⁺BPh₄⁻: C₄₈H₆₂BMoNOPRhS₂, FW = 973.77, triclinic, space group *P*1, *a* = 10.204(1) Å, *b* = 18.072(3) Å, *c* = 27.000(5) Å, α = 75.05(1)°, β = 88.46(1)°, γ = 82.92(1)°, *V* = 4773(1) Å³, *Z* = 4, *T* = 293 K, ρ_{calcd} = 1.355 g cm⁻³, μ(Mo Kα) = 7.62 cm⁻¹, 21 897 unique reflections, *R* (*R*_w) = 0.053 (0.054) for 1133 variables and 8584 reflections (*I* > 3σ(*I*)), GOF = 1.014.

In conclusion, we have demonstrated that the late metal in the appropriately designed ELHB complexes increases the electron density on the neighboring early metal by strong electron donation from the late to the early transition metal. The extraordinarily electron-rich character of the terminal nitrosyl ligand endowed by this ELHB effect enables the electrophilic O-methylation of the ligand. Further study of electrophilic functionalization of the nitrosyl ligand and other small molecules on the ELHB platform is currently under way.

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Supporting Information Available: Text, tables, and figures giving experimental procedures, spectroscopic and electrochemical properties, and selected bond lengths and angles for complexes **7**, **9**⁺PF₆⁻, and **10**⁺BPh₄⁻ and CIF files giving crystallographic data, including associated tables, for complexes **7**, **9**⁺PF₆⁻, and **10**⁺BPh₄⁻. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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