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Molybdenum and Tungsten Complexes with Metallo-ligands Having Sulfur Donor Atoms

DING-XUE KANG, MARIA POOR, ELLIOTT L. BLINN*
Chemistry Department, Bowling Green State University, Bowling Green, OH 43403 (U.S.A.)
and PAUL M. TREICHEL
Department of Chemistry, University of Wisconsin, Madison, WI 53706 (U.S.A.)

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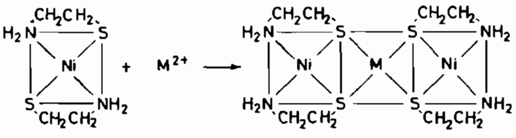
Abstract

The reaction of $Mo(CO)_6$ with 2,3-pentanedione-bis(β-mercaptoethylimino)nickel(II), Nipe, under mild conditions, results in the formation of Nipe-$Mo(CO)_4$, while more forcing conditions give a different product, $[NipeMo(CO)_3]_2$. From an analogous reaction, a tungsten compound of the latter formula was also isolated. The chromium analogue was prepared in a similar manner but lacked the purity necessary to give good analyses. The molybdenum and tungsten complexes were characterized by chemical analyses and solution molecular weight. The magnetic moments of these complexes are anomalous, 2.3–2.4 BM, and suggest that the coordination number of the nickel is greater than four. Electronic spectra support this hypothesis. Cyclic voltammetry data indicate that the $M(CO)_3$ moiety withdraws electron density from the nickel ion in the metallo-ligand. Reactions of $Mo(CO)_6$ and $W(CO)_6$ with bis(2-mercaptoethylamine)nickel(II) ($Ni(MEA)_2$) gave the complexes $Ni(MEA)_2M_2(CO)_{10}$ (M = Mo, W) which were characterized by analyses and infrared and electronic spectra.

Introduction

Hobday and Smith [1] and Mason and coworkers [2] demonstrated that phenolate oxygens, coordinated in a metal complex in which the phenolate is part of a tetradentate Schiff base, are capable of displacing two carbonyl groups from the metal carbonyls. The products are bimetallic complexes having formulas $MLMn(CO)_3Br$ and $NiLM'(CO)_4$ (M′ = Mo, W). A broad scope of this reaction was indicated by the different complexes arising as M, M′ and L were varied; M was chosen to be Ni, Co, Cu, Zn, Pd, Sn, while L is a tetradentate Schiff base and M′ is Mo or W [2].

Metal complexes containing coordinated mercapto groups also act as ligands utilizing a lone pair of electrons on a coordinated sulfur atom. For example, bis(2-mercaptoethylamine)nickel, $Ni(MEA)_2$ (I), is found to react with a variety of metal ions to form polymetallic complexes as represented in the equation below [3–6].



I

II

M = Cd, Ni, Hg

In the organometallic chemistry area, Zanella *et al.* [7] displaced norbornadiene (NBD) from $Mo(CO)_4(NBD)$ with $(Ph_3P)_2Pt(SPh)_2$, the bimetallic complex $(Ph_3P)_2Pt(SPh)_2Mo(CO)_4$ being formed. Dias and Green [8] prepared $Cp_2W(SR)_2M(CO)_4$ (Cp = n-C_5H_5; R = Me; M = Cr, Mo, W); later, complexes of nickel, palladium, platinum, and rhodium [9] and of iron and cobalt [10] containing this metallo-ligand were also reported by these workers. Complexes of titanium metallo-ligands $Cp_2Ti(SR)_2$ (R = Me, Ph) with group (VI) metal carbonyls were reported at about the same time by another group [11]. Recently, Rosenhein *et al.* [12] prepared the complexes $[M(SPh)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co) from $M(SPh)_4{}^{2-}$ and $Mo(CO)_4(NBD)$; an alternative synthesis of these complexes was presented using a reaction between $[Mo(CO)_4(SPh)_2]^{2-}$ and the metal halide, MX_2.

The synthesis of organometallic complexes with metallo-ligands having sulfur donor atoms continues from our earlier work on analogous complexes with oxygen donor atoms [2]. A potential benefit from use of sulfur rather than oxygen as the donor atom was expected since ‘soft’ sulfur atoms are more satisfactory ligands than ‘hard’ oxygen atoms toward ‘soft’ low valent metals.

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*Author to whom correspondence should be addressed.

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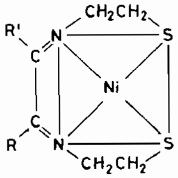
To the best of our knowledge, organometallic complexes with metallo-ligands in which the donor atom is sulfur have contained monodentate sulfur ligands such as S^{2-} or SPh^{1-}. If a mercapto group is part of a bidentate or tetradentate ligand, an additional structural constraint is imposed on the metallo-ligand by the MS_2 bite in the ring system.

With this perspective we have extended our research to the reactions of $Ni(MEA)_2$ (I), 2,3-pentanedione-bis(β-mercaptoethylimino)nickel(II) (Nipe, II), and 2,3-butanedione-bis(β-mercaptoethylimino)nickel(II) (Nibe, III) with group (VI) metal carbonyls.



Nipe; II, R = CH_3, R' = C_2H_5
Nibe; III, R = R' = CH_3

Experimental

All complexes were prepared under an inert atmosphere. The metallo-ligands Nipe and Nibe were prepared as described by Thompson and Busch [13] while $Ni(MEA)_2$ was prepared by the procedure of Jicha and Busch [4]. $Mo(CO)_6$, $W(CO)_6$ and $Cr(CO)_6$ were commercial samples. Solvents were dried using general procedures: CH_3CN was stirred over CaH_2 and distilled from P_4O_{10}, CH_2Cl_2 was distilled from P_4O_{10}, and toluene was predried with $CaCl_2$ and distilled.

Infrared spectra, obtained using 20 DX Nicolet and Perkin-Elmer 1310 infrared spectrometers, are presented in Table 1. A Cary 219 spectrophotometer, for the visible UV range, and a Beckman Acta MIV, for the near infrared range, were used to record electronic spectra (data, see Table 3). Magnetic moments were measured at room temperature using the Faraday method, diamagnetic corrections being made using Pascal constants [14]. Cyclic voltammetry measurements were obtained with a Princeton Applied Research Model 173 three electrode potentiostat, Model 179 digital coulometer, Model 175 Universal programmer, and a Houston Instruments 2000 Recorder. The cell was set up with an SCE reference electrode and a Pt working electrode. Molecular weights were measured at room temperature in CH_2Cl_2 using a Mechrolab vapor pressure osmometer standardized with benzil. Mass spectra were measured using a Kratos MS50 instrument with a fast-atom bombardment ionization source.

Carbon and hydrogen analyses were obtained from Galbraith Microanalytical Laboratories. Nickel analyses were obtained using a Perkin-Elmer Model 603 atomic absorption spectrometer and EDTA titration.

Synthesis of [NipeMo(CO)$_3$]$_2$

A solution of 0.55 g (2.0 mmol) of Nipe dissolved in 50 ml of toluene was placed in a 200 ml two-neck flask fitted with a reflux condenser and a magnetic stirrer. Then, 0.53 g (2.0 mmol) of solid $Mo(CO)_6$ was added. The mixture was heated at reflux for 3 h. (The same product can be obtained by UV irradiation using a GE-HR-SP 100PSP44-4 light source, for three hours.) During this period the color changed from red to green. The reaction mixture was cooled to room temperature and filtered. The solid separated by filtration was washed twice with 30 ml of CH_2Cl_2 and discarded. The washings were added to the toluene filtrate and the solution evaporated to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2 and the solution placed on a silica gel chromatography column (20 × 250 mm). The entire separation procedure was carried out under nitrogen. Using CH_2Cl_2, a light yellow band eluted first. An infrared spectrum indicated that this fraction contained $Mo(CO)_6$. The second fraction, containing the product, was green. The remaining material on the column (red),

TABLE 1. Infrared spectra (ν(CO) (cm^{-1}))[a]

Tricarbonyls					
$[NipeMo(CO)_3]_2$	2030(s)	2002(vs)	1910(vs)	1865(vs)	
$[NipeW(CO)_3]_2$	2030(s)	2002(vs)	1925(vs)	1855(vs)	1820(vs)
$[NipeCr(CO)_3]_2$	2050(s)	1975(s)	1920(vs)	1855(vs)	1835(w)
Tetracarbonyls					
$NipeMo(CO)_4$	2005(m)	1950(sh)	1900(vs)	1820(m)	
$NibeMo(CO)_4$	1995(m)	1950(sh)	1870(vs)	1815(m)	
Pentacarbonyls					
$Ni(MEA)_2Mo_2(CO)_{10}$	2066.7(s)	1982.2(s)	1939.8(vs)	1902.1(w)	
$Ni(MEA)_2W_2(CO)_{10}$	2063.4(s)	1971.9(m)	1930.5(vs)	1899.0(m)	

[a] Solution spectra in CH_2Cl_2

believed to be Nipe, could be eluted with CH_3OH. The green solution, the second fraction to elute, was evaporated to dryness at room temperature leaving a black solid, the product, which was dried under vacuum over P_4O_{10}. *Anal.* Calc. for [Nipe-Mo(CO)$_3$]$_2$: C, 31.68; H, 3.53; Ni, 12.91. Found: C, 31.97; H, 3.52; Ni, 12.50%. Molecular weight: calc. 909; found 855.

An unsuccessful attempt was made to confirm the molecular weight of this compound by mass spectrometry. The parent peak conformed to monomeric NipeMo(CO)$_3$; a cluster of peaks (there are 7 stable isotopes of molybdenum) is found around m/e 456. Another cluster is found at m/e 428 which fits NipeMo(CO)$_2$, and peaks around m/e 275 and 123 correspond to the Nipe and Mo(CO) groups, respectively.

Preparation of [NipeW(CO)$_3$]$_2$

The method used to prepare black [NipeW(CO)$_3$]$_2$ was the same as that used for [NipeMo(CO)$_3$]$_2$ except 0.704 g (2.0 mmol) of W(CO)$_6$ was used and the reaction time was 6 h. *Anal.* Calc. for [Nipe-W(CO)$_3$]$_2$: C, 26.55; H, 2.97; Ni, 10.81. Found: C, 26.04; H, 2.75; Ni, 10.53%. Molecular weight: calc. 1085; found 1231.

Reaction of Cr(CO)$_6$ with Nipe

This reaction was carried out in the same manner except 0.44 g (2.0 mmol) of Cr(CO)$_6$ was used and the reaction time was 2 h. A black product was obtained in small yield. Chemical analysis on this sample gave poor results; however, the infrared spectrum of this substance (Table 1) was similar to those for [NipeMo(CO)$_3$]$_2$ and [NipeW(CO)$_3$]$_2$.

Preparation of NipeMo(CO)$_4$

To 200 ml of toluene was added 1.02 g (3.8 mmol) of Nipe and 0.993 g (3.8 mmol) of Mo(CO)$_6$. This mixture was heated at reflux for 1.5 h. The solution was allowed to cool to room temperature and then filtered. The precipitate was dissolved in CH_2Cl_2 and Skelly B was added to the solution. The mixture was cooled in a refrigerator overnight; a dark colored precipitate formed which was separated by filtration and dried under vacuum. *Anal.* Calc. for NipeMo(CO)$_4$: C, 32.32; H, 3.32; N, 5.80. Found: C, 31.39; H, 3.38; N, 5.64%.

Reaction of Mo(CO)$_6$ and Nibe

Mo(CO)$_6$ (0.405 g, 1.53 mmol) was dissolved in 100 ml of toluene and Nibe (0.400 g, 1.53 mmol) was added. The red–purple solution was refluxed for 90 min and then stirred at room temperature for an additional 2 h. A precipitate was separated by filtration. No additional product was obtained from the colored filtrate upon evaporation. The solid was recrystallized using CH_2Cl_2 and then dried *in vacuo* over P_4O_{10}. Its infrared spectrum (Table 1) was similar to that for NipeMo(CO)$_4$.

Preparation of Ni(MEA)$_2$Mo$_2$(CO)$_{10}$

To a two-neck 250 ml flask containing 140 ml of methanol and equipped with a reflux condenser and nitrogen inlet was added 0.84 g (4.0 mmol) of Ni(MEA)$_2$ and 2.11 g (8.0 mmol) of Mo(CO)$_6$. The minimum heat necessary to cause reflux was maintained until the reactants dissolved and the solution turned brown (about 2 h). After being allowed to cool to room temperature, the solution was evaporated to dryness under vacuum. The solid remaining was extracted with two 70 ml portions of CH_2Cl_2 and silica gel column chromatography was carried out with CH_2Cl_2 as the elutant. The first fraction off the column was yellow and the second was brown. The brown solution was evaporated to dryness at room temperature, and the solid residue, the product, was dried in vacuum over P_4O_{10} overnight. The product is a black powder. *Anal.* Calc. for Ni(MEA)$_2$Mo$_2$(CO)$_{10}$: C, 24.60; H, 1.76; Ni, 8.60. Found: C, 25.13; H, 2.18; Ni, 8.52%.

Preparation of Ni(MEA)$_2$W$_2$(CO)$_{10}$

The procedure for the preparation of Ni(MEA)$_2$-W$_2$(CO)$_{10}$ was the same as that used to prepare Ni(MEA)$_2$Mo$_2$(CO)$_{10}$ except 2.8 g (8.0 mmol) of W(CO)$_6$ was used and the reaction time was 10 h. The product is a black powder. *Anal.* Calc. for Ni(MEA)$_2$W$_2$(CO)$_{10}$: C, 19.00; H, 1.41; Ni, 6.84. Found: C, 19.33; H, 1.58; Ni, 6.72%.

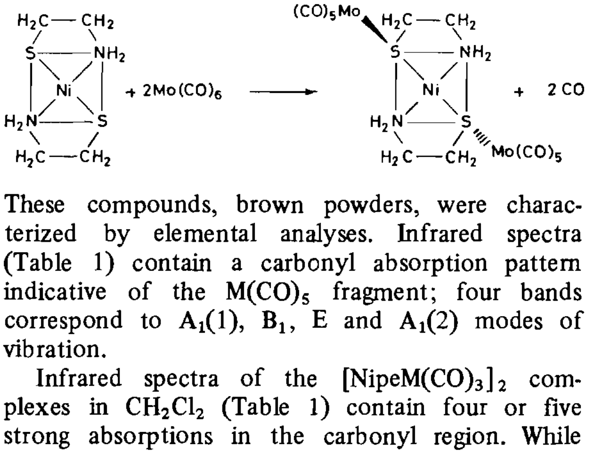
Results and Discussion

Refluxing a solution of Nipe or Nibe with Mo(CO)$_6$ in toluene for $1\frac{1}{2}$ h led to the formation of NipeMo(CO)$_4$ or NibeMo(CO)$_4$ respectively. However, when a mixture of Nipe and Mo(CO)$_6$ in toluene was allowed to reflux for 3 h a compound was isolated that has the empirical composition Nipe-Mo(CO)$_3$. Osmometric measurements in CH_2Cl_2 determined that this complex is a dimer, [Nipe-Mo(CO)$_3$]$_2$. Heating of solutions of these reagents for longer period of times led to the formation of an uncharacterized solid without carbonyl bands in its infrared spectrum. No reaction occurs when a mixture of Nipe or Nibe and Mo(CO)$_6$ was heated at reflux for 6 h in CH_2Cl_2, whereas in boiling DMF total decarbonylation of the metal carbonyl occurred. Clearly, formation of the product in these reactions is dependent on the temperature and duration of the reaction.

The reaction of W(CO)$_6$ with Nipe in toluene required 6 h to reach completion with formation of the product, [NipeW(CO)$_3$]$_2$. No attempt was made to isolate the presumed intermediate in this reaction, NipeW(CO)$_4$, at shorter reaction times. In a similar reaction between Cr(CO)$_6$ and Nipe only a low yield of impure compound was obtained; this was believed to be [NipeCr(CO)$_3$]$_2$ since its infrared spectrum closely matched infrared spectra of similar Mo and W complexes.

If stored under vacuum as solids, [NipeM(CO)$_3$]$_2$ complexes (M = Mo, W) are relatively stable but partial decomposition is observed after about three months, as evident from diminished intensity of the carbonyl stretches in infrared spectra. The complexes are soluble in CH_2Cl_2, $CHCl_3$, acetone and THF. Under nitrogen, solutions remain green for only two to three hours, after which a developing red color (from Nipe) is evident. In air, green solutions of these complexes turn red within a few minutes; the UV–Vis spectra of these solutions indicate the presence of free Nipe and infrared spectra lack carbonyl stretches, confirming the absence of metal carbonyl groups. The tungsten compound, [NipeW(CO)$_3$]$_2$, persists for a somewhat longer time in solution in CH_2Cl_2 than does [NipeMo(CO)$_3$]$_2$. The limited stability of these complexes in solution contributed to a lack of success in growing single crystals suitable for X-ray diffraction studies.

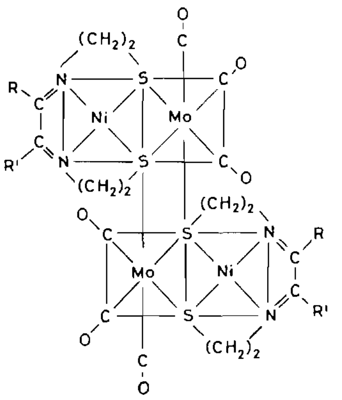
Reactions of Mo(CO)$_6$ or W(CO)$_6$ with Ni(MEA)$_2$, result in products of the formula Ni(MEA)$_2$M$_2$(CO)$_{10}$ for which a likely structure is shown below. Retaining its *trans* geometry, this metallo-ligand cannot chelate a single metal.



These compounds, brown powders, were characterized by elemental analyses. Infrared spectra (Table 1) contain a carbonyl absorption pattern indicative of the M(CO)$_5$ fragment; four bands correspond to A$_1$(1), B$_1$, E and A$_1$(2) modes of vibration.

Infrared spectra of the [NipeM(CO)$_3$]$_2$ complexes in CH_2Cl_2 (Table 1) contain four or five strong absorptions in the carbonyl region. While two or three bands are typically seen in the carbonyl region for monomeric M(CO)$_3$L$_3$ systems, the infrared carbonyl pattern for oligomers is generally more complex. For example, Finnimore *et al.* [15] observed six bands in the carbonyl region for the *cis*-bridged dimeric complex [Mn(CO)$_3${μ-S(CMe)(=NMe)}]$_2$.

A possible structure for [NipeM(CO)$_3$]$_2$, based on the known structure of [Mn(CO)$_3${μ-S(CMe)(=NMe)}]$_2$, is shown below. This structure accommodates the dimeric formulation and allows the low-valent metal to achieve an 18 electron configuration. A possible argument against this structure is the coordination of two of the sulfurs to four groups (the R group and three metals). Compounds with this structural feature are rare, but not unknown [16, 17].



The donor strength of these sulfur donor metallo-ligands can be evaluated from infrared data (Table 2). The average values for the four carbonyl stretches for NipeMo(CO)$_4$ and NibeMo(CO)$_4$ (around 1910 cm^{-1}) are approximately the same as the calculated average value for Mo(CO)$_4$(bipy) [18] (bipy = 2,2-bipyridine), from which it may be concluded that these metallo-ligands and bipyridine have roughly the same donor characteristics.

Other comparisons of infrared data are compromised somewhat since the systems being compared are not fully analogous. Nipe and Nibe appear to be somewhat poorer acceptors than traditional sulfide ligands; for example, higher average carbonyl values are recorded for (RSC$_2$H$_4$SR)Mo(CO)$_4$ (R = Me, 1930 cm^{-1} and R = Ph, 1933 cm^{-1}) [19, 20]. A comparison of sorts can be made with complexes of other metallo-ligands with sulfur donors. The average ν(CO) values for NipeMo(CO)$_4$ and NibeMo(CO)$_4$ are lower than those for Cp$_2$Ti(SPh)$_2$Mo(CO)$_4$ (1944 cm^{-1}). In the latter system, there is crystallographic evidence of a metal–metal bond; electron donation from molybdenum to titanium is postulated, lowering electron density on the

TABLE 2. Infrared data on Mo(CO)$_4$(L)$_2$ compounds

Complex	ν(CO)$_{av}$ (cm^{-1})
NipeMo(CO)$_4$	1919
NibeMo(CO)$_4$	1908
bipyMo(CO)$_4$ [18]	1909
MeSC$_2$H$_4$SMeMo(CO)$_4$ [19, 20]	1930
PhSC$_2$H$_4$SPhMo(CO)$_4$ [20]	1933
(Ph$_3$P)$_2$Pt(SPh)$_2$Mo(CO)$_4$ [7]	1921
Cp$_2$W(SPh)$_2$Mo(CO)$_4$ [8]	1881
Cp$_2$Ti(SPh)$_2$Mo(CO)$_4$ [11]	1944

TABLE 3. Electronic spectra in CH_2Cl_2

Complex	Wavelength (nm) (extinction coefficient (m^{-1} cm^{-1}))			
$[NipeMo(CO)_3]_2$	780(5820)	473(9450)	316(14500)	268(30200)
$[NipeW(CO)_3]_2$	810(9160)	462(12500)	315(31300)	266(high)
$[NipeCr(CO)_3]_2$	515(8220)	388(7330)		
$Ni(MEA)_2Mo_2(CO)_{10}$	455(5050)	385(7560)	365sh(6670)	
$Ni(MEA)_2W_2(CO)_{10}$	480(4950)	390(6290)	322(6000)	

molybdenum(0) center [21]. In the apparently similar tungsten(IV) complex $Cp_2W(SPh)_2Mo(CO)_4$, a greater donation of electronic charge from sulfur to molybdenum occurs (relative to the Ni and Ti complexes) as judged by the lower average ν(CO) value of 1881 cm^{-1} [20]. Here we might assume that the interaction of filled d orbitals on tungsten (a d^2 system) destabilizes the d electrons of molybdenum(0) leading to higher pi donation from the latter metal to the carbonyl groups.

A comparison of values of carbonyl stretching frequencies in $Ni(MEA)_2M_2(CO)_{10}$ with similar data for various $Mo(CO)_5(L)$ compounds also leads to the conclusion that the metallo-ligand is a fairly strong donor and a poor acceptor relative to traditional ligands. The carbonyl stretching frequencies in these compounds are comparable, for example, to values in the complexes $M(CO)_5(L)$ (L = amines, ethers) [22].

Dilute solutions of $[NipeMo(CO)_3]_2$ and $[NipeW(CO)_3]_2$ in CH_2Cl_2 are green, in contrast to the red color of Nipe in the same solvent. Electronic spectra reflect this difference (Table 3); whereas Nipe has one absorption band at 536 nm, $[NipeM(CO)_3]_2$ complexes have visible absorptions at 473 (M = Mo) and 462 (M = W) nm. Molybdenum and tungsten carbonyl complexes have electronic transitions in this region of the spectrum only when the energy absorption is associated with an electronic transition in the ligand [23]. Thus, it is likely that an absorption in the visible region for both compounds is due to the nickel(II) chromophore, the shift from the value found for the free metallo-ligand (536 nm) to higher energy resulting from coordination to the low-valent metal. The high values for the extinction coefficients for the visible bands in these complexes further suggest that some charge transfer is occurring. A further absorption for $[NipeMo(CO)_3]_2$ and $[NipeW(CO)_3]_2$, not seen for Nipe, occurs in the near infrared region at 790 and 810 nm respectively. A near infrared band can indicate a coordination number for nickel(II) greater than four [24]. An expanded coordination number for nickel(II) could arise if a carbonyl group acts as a bidentate ligand, bonding to the molybdenum(0) or tungsten(0) in the usual manner and to the nickel(II) in a sideways fashion, utilizing pi electron density of the CO group. While infrared bands in the 1700 to 1650 cm^{-1} range reflecting this mode of bonding were not seen, such bands are often weak and not detected.

Electronic spectra of the $Ni(MEA)_2M_2(CO)_{10}$ complexes in CH_2Cl_2 contain absorptions at 455 and 385 nm (M = Mo) and 480 and 390 nm (M = W). The uncomplexed metallo-ligand has absorptions at 536 and 460 nm in methanol. Shifts to higher energy on coordination parallel the shifts seen in the $[NipeM(CO)_3]_2$ complexes.

The magnetic moments at room temperature for $[NipeMo(CO)_3]_2$ and $[NipeW(CO)_3]_2$ are 2.39 and 2.31 BM respectively. The magnetic moment of $Ni(MEA)_2Mo_2(CO)_{10}$ is 2.19 BM, while for $Ni(MEA)_2W_2(CO)_{10}$ it is 1.98 BM. Assuming that molybdenum and tungsten have 18 electron configurations (reasonable based on the values of ν(CO)), this is an anomalous value for a nickel(II) ion. Square planar nickel(II) complexes are diamagnetic while six-coordinate nickel(II) complexes usually have magnetic moments between 2.8 and 3.4 BM [25]. A singlet–triplet spin state equilibrium for the nickel(II) ion could explain the low magnetic moment values. For a spin equilibrium to occur, the nickel(II) ion must be tetragonally distorted from a square planar configuration; this further supports the suggestion that a carbonyl group is interacting with nickel(II). A less attractive explanation for the anomalous magnetic properties of the above complexes involves electron transfer between the metals with an interaction between unpaired spins over several metal atoms.

Cyclic voltammetry indicates that $[NipeMo(CO)_3]_2$ reduces at −1.25 V while $[NipeW(CO)_3]_2$ reduces at −1.10 V. An associated oxidation peak was observed for both complexes at −0.95 V. In contrast, a reduction wave for Nipe occurs at −1.5 V. Coulometric measurements indicate that the reduction processes for both systems involve two electrons. These reduction processes are likely associated with the nickel centers since most Mo(0) and W(0) carbonyl compounds typically require more negative voltages for reduction [24–28]. Since Nipe is reduced a more negative potential than either of the $[NipeM(CO)_3]_2$ complexes, it can be concluded that the interaction of the $Mo(CO)_3$ and $W(CO)_3$

moieties with terminal sulfurs on Nipe results in the withdrawal of electron density from the nickel(II) center. The higher the net positive charge on nickel(II), the lower the energy of its LUMO and the easier it is to carry out this reduction.

Samples of $[NipeMo(CO)_3]_2$ and $[NipeW(CO)_3]_2$ are irreversibly oxidized, at 0.52 and 0.43 V respectively. Nipe is irreversibly oxidized at 0.87 V. Since donation from Nipe to $Mo(CO)_3$ or $W(CO)_3$ would make the nickel(II) more difficult to oxidize, these oxidations are presumably at the zerovalent metal center. It is known that $M(CO)_3(L)_3$ oxidize at similar potentials [29, 30].

In constant voltage electrolysis experiments (at 0.9 V) on $[NipeMo(CO)_3]_2$ and $[NipeW(CO)_3]_2$, the solutions turned from green to red, indicating decomposition of these complexes to Nipe.

Cyclic voltammetry on $Ni(MEA)_2Mo_2(CO)_{10}$ in CH_2Cl_2 showed no reduction waves up to -2 V; however an irreversible reduction was observed at -1.75 V for $Ni(MEA)_2W_2(CO)_{10}$. An irreversible oxidation occurs at 0.7 V for both $Ni(MEA)_2Mo_2(CO)_{10}$ and $Ni(MEA)_2W_2(CO)_{10}$.

Conclusions

In summary, electrochemical, infrared and electronic spectral data indicate that metallo-ligands with donor mercapto-groups are good donors of electronic charge when coordinated to a $M(CO)_3$ or $M(CO)_4$ moiety. The electrochemical data show a reduction response at lower potential for the bimetallic complexes than the metallo-ligand indicating transfer of electron density from the metallo-ligand center to the low valent metal center. The blue shift observed on attaching an organometallic moiety to the metallo-ligand is consistent with the lowering of the energy of the bonding molecular orbitals centered on the metallo-ligand. Finally, the relatively low average carbonyl stretching frequencies for the bimetallic complexes indicate an accumulation of electron density at the metal carbonyl center.

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