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# Ligand Effects on the Electrooxidation of Molybdenum Halide Complexes of the Type $CpMo(CO)_{3-n}(PR_3)_nX$ and $ChMo(CO)_2X$

YAU YI LAU, WILLIAM W. HUCKABEE and STEPHEN L. GIPSON*

*Department of Chemistry, Baylor University, Waco, TX 76798 (U.S.A.)*

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## Abstract

Complexes of the type $CpMo(CO)_{3-n}(PR_3)_nX$ and $ChMo(CO)_2X$, where $Cp = \eta^5\text{-}C_5H_5$, $Ch = \eta^7\text{-}C_7H_7$ and X = halide, can be oxidized electrochemically by one electron in dichloromethane. The potential necessary for oxidation and the rate of decomposition of the resulting cation decrease as *n* increases or as the phosphine becomes a better electron donor. A linear correlation is observed between the highest energy carbonyl stretching frequency and the formal or peak potential for the oxidation. As the halide is changed from chloride to bromide to iodide the oxidation potential increases but the rate of decomposition of the cation decreases. Both of these trends can be traced to the inverse halide order, in which the oxidation potential increases as the electronegativity of the halide ligand decreases. This effect arises from greater metal to halide backbonding in the complexes of the heavier halogens, which decreases electron density on the metal center and thus increases the oxidation potential. However, the added bond order with the heavier halogens apparently also stabilizes those cations toward decomposition.

## Introduction

The electron density on metal centers in transition metal organometallic complexes is sensitive to the ligands to which the metal is bound. Ligands may not only donate electron density to the metal center, through either σ- or π-bonds, but may also withdraw electron density through π-backbonding. Most commonly backbonding ligands, called π-acids, are also σ-donors, and the net electron donation or withdrawal reflects contributions from both types of interaction with the metal. The effects of these types of bonding can be observed by probes of electron density on the metal center. One such probe is electrochemistry. As electron density on the metal increases, the energy of the complex's HOMO (highest occupied molecular orbital) is raised and oxidation, which corresponds to removal of an electron from the HOMO, becomes easier. A direct proportionality between calculated HOMO energy and measured oxidation potential has been observed in the series $Mn(CO)_{6-n}(CNCH_3)_n^+$ [1]. Also, the first ionization energies, which correspond to the HOMO energies, of a series of substituted ferrocenes have been shown to be proportional to their oxidation potentials [2]. As with the HOMO, increasing electron density increases the energy of the LUMO (lowest unoccupied molecular orbital) and so reduction, addition of an electron to the LUMO, should become more difficult. Thus electrochemically measured potentials for oxidation or reduction of a series of complexes can serve as a probe of changes in electron density on the metal center caused by changing σ-basicity and/or π-acidity of the ligands.

In our initial communication of this work [3] we reported on the electrochemical oxidation of a series of molybdenum halide complexes of the general formula $CpMo(CO)_{3-n}(PR_3)_nX$ ($Cp = \eta^5\text{-}C_5H_5$, R = alkyl or aryl, X = halide). We found that these complexes all displayed one-electron oxidations in both dichloromethane and acetonitrile. The potential necessary for oxidation decreased as carbonyl ligands were substituted with increasingly electron-donating phosphines, and at the same time the rate of decomposition of the resulting cation decreased so that the oxidations became more chemically reversible. We now wish to report further information on these oxidations as well as those of the isoelectronic cycloheptatrienyl complexes $ChMo(CO)_2X$ ($Ch = \eta^7\text{-}C_7H_7$), concentrating on the effect of ligand substitution on the formal or peak potential of the oxidations.

## Experimental

Complexes **1** [4], **2**, **3**, **6**, **9** [5], **4**, **7** [6], **5**, **8** [7], **10**, **11**, **12** [8], **13** [9], **14** and **15** [10] were prepared by literature methods and identified by their IR and/or $^1H$ NMR spectra. Compound **11** had not been previously reported but was synthesized by the same method as **10** and **12** and identified by its IR and NMR spectra [IR ($CHCl_3$) $\nu(CO) = 1854\ cm^{-1}$; $^1H$

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*Author to whom correspondence should be addressed.

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TABLE 1. Mo(III/II) formal potentials and carbonyl stretching frequencies for the series $CpMo(CO)_{3-n}(PR_3)_nX$ and $ChMo(CO)_2X$

| Compound | Cp/Ch | $PR_3$[a] | X | $E_f$[b] | $\nu$(CO)[c] |
|---|---|---|---|---|---|
| 1 | Cp | none | Cl | +0.63[d] | 2057, 1985, 1962 |
| 2 | Cp | none | Br | +0.64[d] | 2053, 1982, 1962 |
| 3 | Cp | none | I | +0.68[e] | 2044, 1975, 1961 |
| 4 | Cp | $PPh_3$ | Cl | +0.26 | 1973, 1885 |
| 5 | Cp | $PPh_3$ | Br | +0.28 | 1981, 1896 |
| 6 | Cp | $PPh_3$ | I | +0.30 | 1968, 1890 |
| 7 | Cp | $PBu_3$ | Cl | +0.21 | 1964, 1871 |
| 8 | Cp | $PBu_3$ | Br | +0.22 | 1963, 1872 |
| 9 | Cp | $PBu_3$ | I | +0.24 | 1959, 1872 |
| 10 | Cp | dppe | Cl | −0.25 | 1849 |
| 11 | Cp | dppe | Br | −0.24 | 1854 |
| 12 | Cp | dppe | I | −0.23 | 1853 |
| 13 | Ch | none | Cl | +0.43[f] | 2027, 1981 |
| 14 | Ch | none | Br | +0.44[g] | 2027, 1982 |
| 15 | Ch | none | I | +0.46 | 2023, 1979 |

[a] Ph = phenyl, Bu = n-butyl, dppe = $\eta^2$-bis(diphenylphosphino)ethane ($n$ = 2). [b] Average of anodic and cathodic peak potentials measured at a Pt disc electrode in $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$ at 200 mV/s and referenced to $Fc^+/Fc$ internal standard. [c] Solvent = $CCl_4$ (1–3) or $CHCl_3$ (4–15). [d] Anodic peak potential of irreversible oxidation. [e] $\nu$ = 5 V/s. [f] $\nu$ = 50 V/s. [g] $\nu$ = 10 V/s.

NMR ($CDCl_3$, 90 MHz, 300 K) $\delta$ 7.9–7.2 (m, Ph), 4.46 (s, Cp), 3.0–0.8 (m, $CH_2$)]. Solvents were high purity (Burdick and Jackson distilled in glass or Fisher optima) and were distilled under nitrogen before use: tetrahydrofuran from Na/benzophenone and dichloromethane from calcium hydride. All other chemicals were reagent grade or better and were used as received.

Procedures for electrochemical measurements have been reported previously [3]. As recommended by IUPAC [11], all potentials are expressed relative to the formal potential of the ferrocenium/ferrocene couple ($Fc^+/Fc$), which we measure as +0.50 V versus Ag/AgCl.

## Results and Discussion

Table 1 lists the formal potentials obtained by cyclic voltammetry in dichloromethane and the carbonyl stretching frequencies of the compounds studied. Several interesting trends can be noted. The most obvious trend is the decrease in formal potential as phosphines are substituted for carbonyl ligands. Replacement of a $\pi$-bonding CO ligand with a strong $\sigma$-donating phosphine would be expected to increase the electron density on the metal center. This increased electron density should be reflected in two parameters: the formal potential of the Mo(III/II) couple; and the carbonyl stretching frequency(ies). This is indeed the case. As we reported previously, substitution of one CO ligand with triphenylphosphine lowers the oxidation potential by 300 to 500 mV. Substitution with the more powerful electron donor tri-n-butylphosphine decreases the Mo(III/II) potential by about another 60 mV, and 1,2-bis(diphenylphosphino)ethane gives complexes with Mo(III/II) formal potentials about 900 mV less positive than those of the tricarbonyl complexes.

Carbonyl stretching frequencies are known to be indicative of electron density on the metal center of carbonyl complexes. Since formal potentials of oxidations are similarly related to the metal's electron density, one would expect a correlation between formal potential and $\nu$(CO). Others have observed such correlations between redox potentials and force constants [12, 13], single stretching frequencies of monocarbonyl complexes [14–16], or highest energy stretching frequencies for polycarbonyls [17]. Figure 1 shows a plot of Mo(III/II) formal potential versus $\nu$(CO) of the highest energy carbonyl stretch for each of the complexes studied. A linear relationship is seen between the two parameters with a slope of $4.31 \times 10^{-3}$ V/cm$^{-1}$, an intercept of −8.23 V and a correlation coefficient of 0.993. Interestingly, the cycloheptatrienyl complexes fit well into the correlation with the cyclopentadienyl complexes. The effect of expanding the capping ring and thus replacing a carbonyl ligand by a ring olefin produces a smaller decrease in formal potential and $\nu$(CO) than adding a phosphine, but the proportionality between the two effects is the same as for phosphine substitution.

Much smaller changes in potential occur when the halide is changed, but in each series of complexes the same trend holds: the oxidation potential increases as the halide is changed from chloride to bromide to

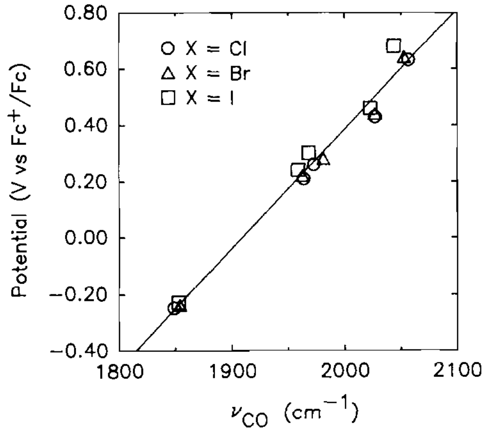

Fig. 1. Plot of Mo(III/II) formal potential in dichloromethane vs. highest energy $\nu$(CO) for the series $CpMo(CO)_{3-n}(PR_3)_nX$ and $ChMo(CO)_2X$.

iodide. This is the inverse of the order expected on the basis of simple halide electronegativities. Since electronegativity decreases from chloride to iodide, one would expect the electron density on the metal to increase and thus the oxidation potential to decrease. The opposite trend, called the 'inverse halide order', IHO, was first described by Zietlow *et al.* [18] and attributed to metal–d to halide–d backbonding.

In addition to the systems cited in ref. 18 ($Mo_2(PR_3)_4X_4$ and $Tc(L{-}L)_2X_2^+$ [19], L–L = chelating diphosphine and/or -arsine), many other cases of the IHO can be found in the literature for both oxidations and reductions. Some of the different series of complexes displaying the IHO include $Cr(CO)_5X^-$ [20], $Ch_2Mo_2(\mu\text{-}X)_3$ [10], $CpMo(NO)X_2$ [21], $Cp^*Mo(NO)X_2$ [21], *mer*-$Mn(CO)_3(L{-}L)X$ [22], $Mn(PhNC)_5X$ [23], $Re(dmpe)_2X_2^+$ [24], $CpFe(CO)_2X$ [25], CpFe(dppe)X [23], $Rh(CO)(PPh_3)_2X$ [26] and $Ir(CO)(PPh_3)_2X$ (reduction) [26]. Of course, there are exceptions. The series *mer*-$Re(CO)_3(pmt)_2X$ [27], $Fe(4\text{-}CH_3C_6H_4NC)_2(PPh(OEt)_2)_3X^+$ [28] and $Ir(CO)(PPh_3)_2X$ (oxidation) [29] do not follow the IHO.

While the formal potentials of complexes displaying the IHO may not follow the order expected from simple electronegativities, their order does agree with other measures of electronegativity. Vaska and Peone [30] developed a 'total electronegativity' for various anionic ligands based upon the carbonyl stretching frequencies of the complexes $M(CO)(PPh_3)_2A$, where M is Rh or Ir and A is an anionic ligand. Vaska's total electronegativity takes into account both the classical $\sigma$-electronegativity as well as the $\pi$-electronegativity, $\pi$-acidity, of the anion. On this electronegativity scale the halides are ordered Cl < Br < I.

The greater $\pi$-acidity of the halogens is supported by other studies. Schlodder *et al.* [31] examined the $\pi$-donor ability of anionic ligands by measuring IR intensities of CO and CN stretching modes in Rh, Ir and Pt complexes. They found that the relative $\pi$-acceptor ability of the halogens increases in the order Cl < Br < I. In addition to IR spectroscopy, $^{13}C$ NMR chemical shifts can also give information about electron density. The chemical shift of the carbonyl ligand *trans* to halide in the series $CpMo(CO)_3X$, $CpMo(CO)_2(PPh_3)X$ and $ChMo(CO)_2X$ moves upfield on changing the halide from chloride to bromide to iodide [32]. This upfield shift, indicating more shielding of the carbonyl carbon, is caused by decreased backbonding to the carbonyl ligand, arising from lower electron density on the metal center. Thus, $^{13}C$ NMR demonstrates that electron density on molybdenum in these series decreases on going from chloride to bromide to iodide, in agreement with Vaska's total electronegativity and the increasing redox potentials which we observe.

The crystal structures of $ChMo(CO)_2Cl$ and $ChMo(CO)_2Br$ also provide evidence of greater backbonding between the heavier halogen and the metal [33]. Both atomic and covalent radii predict an increase in M–X bond length of 15 pm on changing from chloride to bromide, but the observed increase is only 3.1 pm. Thus, the Mo–Br bond is relatively shorter than the Mo–Cl bond. This shorter than expected bond length has been attributed to a greater degree of multiple bonding between Mo and Br arising from better metal to halide backbonding. The added bond order indicated by these crystal structures may help explain our observation of higher stability in the cations containing heavier halogens despite their higher oxidation potentials.

Another, related, trend which we have observed in the redox potentials of our structurally similar cyclopentadienyl complexes is a decreased effect of halide substitution as additional, or better-donating, phosphines are added. On changing from chloride to iodide the formal, or peak, potential increases by 50 mV in the $CpMo(CO)_3X$ series, 40 mV in the $CpMo(CO)_2(PPh_3)X$ series, 30 mV in the $CpMo(CO)_2(PBu_3)X$ series and 20 mV in the CpMo(CO)(dppe)X series. The decreasing carbonyl stretching frequencies demonstrate that the metal center is becoming more electron rich in this order, and so at first thought one might expect an increasing effect of halide substitution. As the metal becomes more electron rich from replacement of carbonyl ligands with phosphines, it should backbond better to the halide. The greater backbonding might be expected to magnify the differences between the halides and result in larger potential differences for the more electron rich complexes.

However, on second thoughts the observed decrease in the effect seems reasonable. Complexes with a low electron density on the metal will have contracted metal d-orbitals which will overlap poorly with the small d-orbitals of chloride, better with the larger d-orbitals of bromide, and best with the even larger d-orbitals of iodide. As the electron density on the metal center increases, the metal's d-orbitals will expand and overlap better with the halide's. This increase in overlap will be more noticeable for chloride than for iodide (or bromide) since chloride began with such poor overlap. Thus, as the electron density of the metal increases the difference in overlap of its d-orbitals with the different halogens will decrease and the observed difference in oxidation potential will decrease. Among previously reported series of halide complexes, this trend is also followed in the oxidations of $Mo_2(PMe_3)_4X_4$ versus $Mo_2(PEt_3)_4X_4$ [18], but not in their reductions or in the reductions of $Tc(dppe)_2X_2^+$ versus $Tc(dmpe)_2X$ [19, 24] or $CpMo(NO)X_2$ versus $Cp^*Mo(NO)X_2$ [21].

In summary, we have shown that changes in ligand produce changes in electron density on the metal center in the molybdenum complexes studied, and that these changes in electron density can be probed by electrochemistry and IR spectroscopy. Substitution of electron withdrawing carbonyl ligands with electron donating phosphines increases electron density on the metal center, lowers both oxidation potential and carbonyl stretching frequencies, and stabilizes oxidation products. In contrast, both the oxidation potential and cation stability increase as the halide is changed from chloride to bromide to iodide. These trends can be explained by greater backbonding to the heavier halogens. Increased backbonding removes more electron density from the metal center and thus increases oxidation potential, but because of the multiple bond character imparted by the backbonding the oxidized species are stabilized.

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