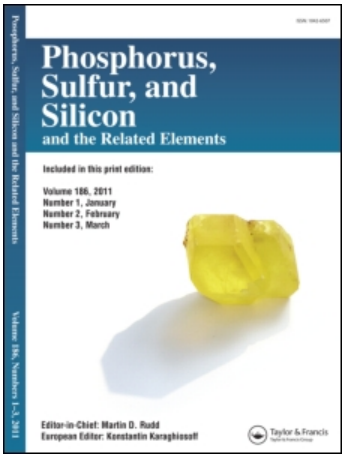

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THE ELECTROCHEMISTRY AND ELECTRONIC STRUCTURE OF HIGH-VALENT MOLYBDENUM AND TUNGSTEN METALLACYCLES

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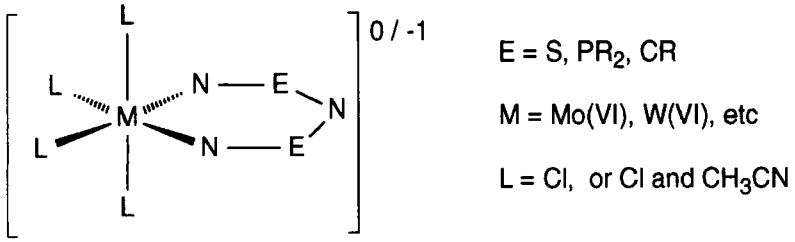
Abstract The metallacycles $[\overline{NPPh_2NPPh_2NMCl_3}]$, M=Mo, W have been studied in CH_2Cl_2 using cyclic voltammetry. The observed redox potentials indicate that the cyclic π-base ligand, $[NPPh_2NPPh_2N]^{3-}$, is capable of stabilising high oxidation states in both molybdenum and tungsten complexes. Empirical MO calculations are presented which rationalize the electronic structure of the metallacycles.

INTRODUCTION

The oxidizing abilities of molybdenum and tungsten compounds in their highest oxidation state are mainly controlled by their ligand environment. Previously we have demonstrated by cyclic voltammetric measurements, that WCl_6 and the hypothetical '$MoCl_6$' are stronger oxidizers than WF_6 and MoF_6.[1] In this connection we were interested in studying the quantitative influence of nitrogen as a ligand on redox potentials in halo complexes such as metallacycles of the general type:



For this purpose we chose to investigate the electrochemical properties of the known metallaphosphazenes $[\overline{NPPh_2NPPh_2NMoCl_3}]$[2] and $[\overline{NPPh_2NPPh_2NWCl_3}]$.[3] In stringently purified CH_2Cl_2 these hybrid ring systems can be studied utilizing the vacuum-tight electrochemical cell described previously.[4]

RESULTS AND DISCUSSION

The cyclic voltammogram of $[\overline{NPPh_2NPPh_2NWCl_3}]$ in CH_2Cl_2 displays two one-electron steps, corresponding to the metal-centred $W^{+6/+5}$ and $W^{+5/+4}$ couples (Figure 1). The first reduction is a fully reversible process at $E_{1/2}$ = -0.38 V vs SCE while the second reduction has been identified as a chemically irreversible but electrochemically quasi-reversible step at $E_{1/2}$ = -1.5 V. No oxidation steps have been observed within the limits of solvent stability. The cv also shows the ferrocene/ferrocenium couple added as internal reference (Figure 1). For $[\overline{NPPh_2NPPh_2NMoCl_3}]$ the first reduction process is reversible at $E_{1/2}$ = +0.26 V and the second reduction is quasi-reversible at $E_{1/2}$ = -0.67 V. The redox potentials obtained in this study are given in Table 1 together with the potentials of the parent tungsten and molybdenum hexachlorides.

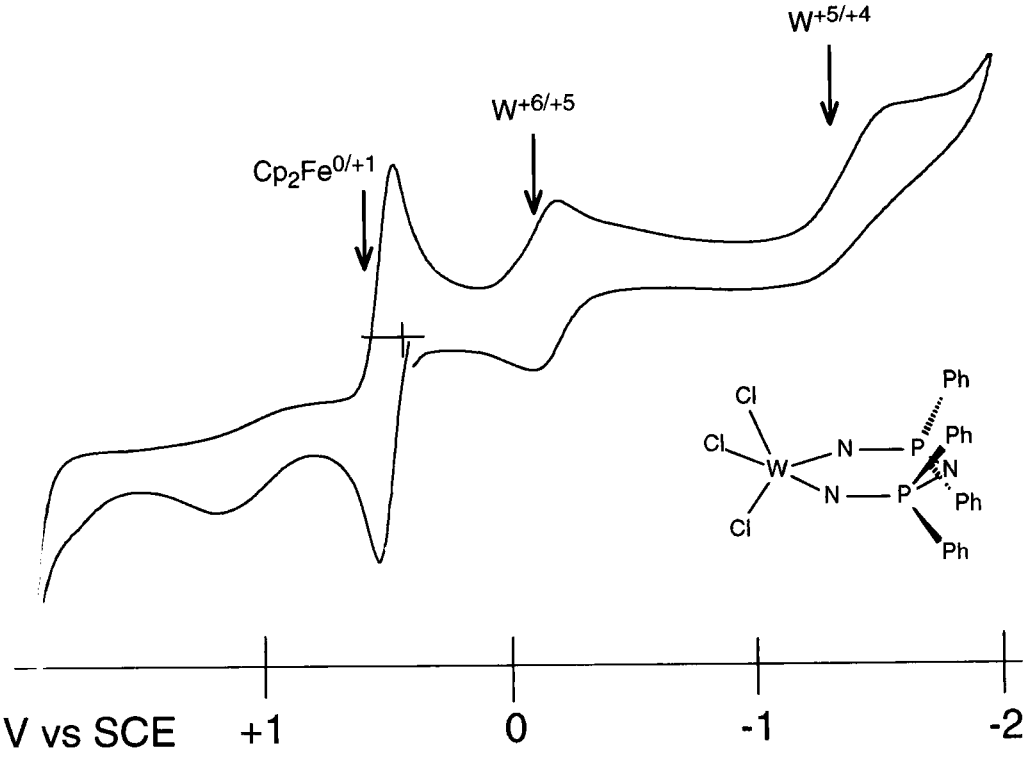


FIGURE 1 Cyclic voltammogram of $[\overline{NPPh_2NPPh_2NWCl_3}]$ scan rate: 100 mV s^{-1} at a Pt-wire electrode in CH_2Cl_2/Bu_4NPF_6 (0.5 M); ferrocene added as an internal reference.

TABLE 1 Half wave potentials of $[\overline{NPPh_2NPPh_2NMCl_3}]^{z/z-1}$ and $[MCl_6]^{z/z-1}$, M=Mo,W couples (*vs.* SCE) in CH_2Cl_2[a]

Compound	$M^{+6/+5}$	$M^{+5/+4}$	Δ[b]
$[\overline{NPPh_2NPPh_2NMoCl_3}]$	+0.26	-0.67	0.93
$[^nBu_4N][MoCl_6]$[c]	+2.20	+1.05	1.15
$[\overline{NPPh_2NPPh_2NWCl_3}]$	-0.38	-1.50	1.12
$[WCl_6]$	+1.59	+0.40	1.19

[a] In Volts; $[FeCp_2]^+/[FeCp_2]$ is observed at +0.48 V *vs.* SCE in CH_2Cl_2

[b] Difference between $M^{+6/+5}$ and $M^{+5/+4}$ redox couples

[c] From Ref. 1

From a comparison of the potentials in Table 1 it is apparent that the phosphazene anion, $[NPPh_2NPPh_2N]^{3-}$, has a remarkable ability to stabilise high oxidation states in the tungsten and molybdenum complexes. The $Mo^{+6/+5}$ redox couple in $[\overline{NPPh_2NPPh_2NMoCl_3}]^{0/-1}$ is 1.94 V more negative than in $[MoCl_6]^{0/-1}$ while in the tungsten case this difference is 1.97 V. In other words: while WCl_6 with an redox potential of the $[WCl_6]^{0/-1}$ couple at $E_{1/2}$ = +1.59 V is a strong oxidizing agent the ring complex $[\overline{NPPh_2NPPh_2NWCl_3}]$ with $[\overline{NPPh_2NPPh_2NWCl_3}]^{0/-1}$ at $E_{1/2}$ = -0.38 V has little or no oxidizing power, although in both complexes tungsten has the oxidation state six. These findings are repeated for the molybdenum complexes. However the redox couples found for the molybdenum complexes are uniformly higher (range from 0.63 to 0.8 V) than their tungsten analogs reflecting an extreme parallelism in the redox potentials for isostructural Mo and W complexes:

$$M(VI) \rightleftharpoons M(V) \rightleftharpoons M(IV)$$

Empirical MO calculations have been performed which rationalize the electronic structure of the metallacycles. Figure 2 presents the orbital interaction diagram for $[\overline{NPH_2NPH_2NMoCl_4}]^{2-}$ for two fragments $[MoCl_4]^{2+}$ and $[NPH_2NPH_2N]^{3-}$. The results of the calculations are in good accord with their physical and spectroscopic properties.

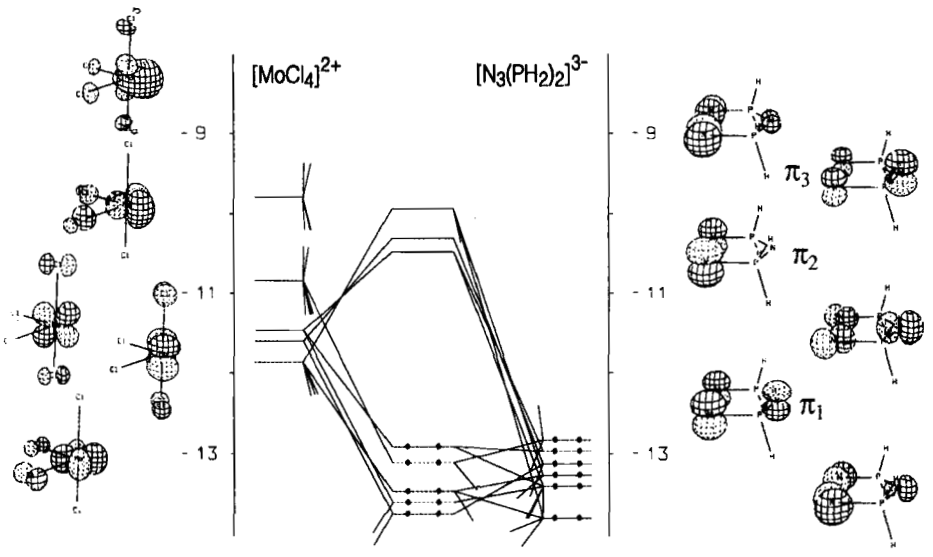


FIGURE 2 Molecular orbital interaction diagram for the model compound $[NPH_2NPH_2NMoCl_4]^{2-}$

A larger study including also the metalladithiatriazines $[Ph_4As][Cl_4MN_3S_2]$, M = Mo, W as well as other halo complexes such as $[MOCl_5]^-$ and $[MNCl_4]^-$, M = Mo, W will be published elsewhere.[5]

ACKNOWLEDGEMENTS

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REFERENCES

1. G.A. Heath, K.H. Moock, D.W.A. Sharp and L.J. Yellowlees, J. Chem. Soc., Chem. Commun., 1503 (1985).
2. H.W. Roesky, K.V. Katti, U. Seseke, H.-G. Schmidt, E. Egert, R. Herbst and G.M. Sheldrick, J. Chem. Soc.,Dalton Trans., 847 (1987).
3. H.W. Roesky, K.V. Katti, U. Seseke, M. Witt, E. Egert, R. Herbst and G.M. Sheldrick, Angew. Chem., 98, 447 (1986); Angew. Chem., Int. Ed. Engl., 25, 477 (1986).
4. K.H. Moock and M.H. Rock, J. Chem. Soc., Dalton Trans., 2459 (1993).
5. K.H. Moock and R.T. Boeré, manuscript in preparation.