special significance. This anomaly provides strong evidence that the extra proton is attached at O(9), a double linked O(d)-type atom.

Klemperer and Shum[19] studied the NMR spectra of ^{17}O in $[V_{10}O_{28}]^{6-}$ in solution at pH values in the range 4.5–6.0. By indirect reasoning based on peak shifts in the spectra, they concluded that the site of first acid protonation should be at the triply linked O(b). Howarth and Jarrold[20] studied the NMR spectra of ^{51}V over the pH range 2–9 and arrived at the conclusion (arguing against Klemperer and Shum but also by indirect reasoning) that first protonation should take place at the terminal O(g). Our treatment of the Debaerdemaeker et al. structure indicates a doubly linked O(d) site for first protonation. If O(d) is the site of the acid protons in the pyridinium salt crystal, it is quite possible that structure studies of other crystals containing the $[H_2V_{10}O_{28}]^{4-}$ species may reveal the protons to be located at other sites. We clearly are not in a position to predict these protonation sites with confidence. New structure analyses of protonated decavanadate compounds, preferably by neutron diffraction, are needed.

Registry No. $[PV_2Mo_{10}O_{40}]^{5-}$, 58071-93-5; $[PV_3Mo_9O_{40}]^{6-}$, 56188-77-3; $[PW_{12}O_{40}]^{3-}$, 12534-77-9; $[H_2V_{10}O_{28}]^{4-}$, 11117-82-1; $[SiMo_{12}O_{40}]^{4-}$, 50927-64-5.

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Chemical and Electrochemical Reduction of Pentacarbonyl(4-cyanopyridine) Complexes of Chromium(0), Molybdenum(0), and Tungsten(0)

Wolfgang Kaim

Group 6B metal carbonyl complexes having low-lying metal-to-ligand charge-transfer (MLCT) excited states are of current interest in inorganic photochemistry.[1] For a series of pentacarbonyl complexes of molybdenum and tungsten with various pyridines it has been shown that the lowest excited state is of MLCT character only if the pyridine is 4-substituted with a strongly electron-withdrawing substituent such as acyl or cyano, i.e. if there is an easily accessible π^* level of the heterocyclic ligand.[1-3]

The lowest unoccupied molecular orbital (LUMO) in such complexes can be populated through addition of an electron to yield the corresponding radical anion. For a ligand-centered LUMO, persistent π radicals may be expected, especially if the ligand itself already undergoes reversible one-electron reduction. During studies on the redox chemistry of the group 6B metal carbonyl complexes,[4,5] we have examined the reduction of chromium, molybdenum, and tungsten penta-

carbonyl complexes of the heterocyclic ligand 4-cyanopyridine (**1**).

Results

Chemical and electrochemical reductions of the complexes [**1**·M(CO)$_5$] in THF or DMF yield the paramagnetic species [**1**·M(CO)$_5$]$^-$· (Scheme I, route a). For M = W, the one-electron reduction is reversible, while in the case of Cr and Mo it has been found necessary to use additional metal hexacarbonyl in order to shift the dissociation equilibria in the closed reaction systems used to the radical complex side.

The radical complexes [**1**·M(CO)$_5$]$^-$· could also be generated in situ, either by reaction of the 4-cyanopyridine radical anion with hexacarbonylmetal in a replacement of one CO ligand (route b) or by a single electron-transfer reaction of decacarbonyldimetalate with the free ligand (route c). All these reaction pathways indicate the strong tendency for the formation of the radical complexes [**1**·M(CO)$_5$]$^-$·.

The paramagnetic complexes have been characterized by high-resolution electron spin resonance (Figure 1); their formation was studied by cyclic voltammetry. Table I shows reduction potentials and ESR data of the complexes in comparison to the parameters of the free and of the N-methylated 4-cyanopyridine species.

Discussion

Several reaction pathways (Scheme I) lead to the formation of the radical anions of pentacarbonyl(4-cyanopyridine)-chromium, -molybdenum, and -tungsten. Reduction of the neutral complexes occurs at potentials considerably less negative than that of the reduction of the neutral ligand; almost half the effect of methyl quaternization is achieved by pentacarbonylmetal coordination (Table I). The ESR data show that the unpaired electron resides mainly in the ligand π system for all three radical anion complexes investigated; the coordination of M(CO)$_5$ to the radical ligand is, however, evident from the metal isotope splittings in the ESR spectra (Figure 1).

Perturbation effects of the coordinated metal pentacarbonyl groups on the ESR parameters are as expected;[4,5] this includes a marked increase of the pyridine ^{14}N coupling constant as well as a high g value for the tungsten complex (large spin–orbit coupling constant of tungsten). Particularly revealing is the behavior of the two hydrogen coupling constants $a_{H(2,6)}$ and $a_{H(3,5)}$, whose relation is reversed in the sequence of Table I. The chromium radical complex takes a special position in that it exhibits identical values for all the proton hyperfine coupling, thereby indicating that the acceptor function of the C–CN moiety is exactly matched by the effect of the N–Cr(CO)$_5$ group. For both the molybdenum and the tungsten derivatives, the electron-acceptor strength of the N-organometallic group seems to be greater than that of the cyano substituent at C(4). Nevertheless, despite the difference between the Mo and W species vs. the Cr radical complex the ESR and electrochemical results suggest a low-lying ligand-centered LUMO and low-energy MLCT transitions not only for molybdenum[3] and tungsten[1,2] but also for pentacarbonyl(pyridine)chromium complexes.

Preliminary studies in the 4-acylpyridine complex series[1-3] have shown that comparable reductions to persistent radicals take place.[6] Complete characterization of these radical complexes by ESR spectroscopy is impaired by their low symmetry due to the restricted $C(4)–C_{acyl}$ rotation on the ESR time scale.[7]

In summation, the ESR results derived from one-electron reduction of these complexes prove the ligand character of their

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Table I. Reduction Potentials, $E_{1/2}$ (V vs. SCE), of 4-Cyanopyridine and Its Complexes in DMF and ESR Parameters of the One-Electron Reduction Products in THF (Coupling Constants a_X in μT)

radical	$E_{1/2}$	$a_{H(2,6)}$	$a_{H(3,5)}$	$a_{N(1)}$	$a_N{}^{CN}$	a_M	g
1⁻· [a]	−1.73	154	249	569	238		2.0029
[1·Cr(CO)₅]⁻·	−1.23[c]	196	196	715	218	60[d]	2.0029
[1·Mo(CO)₅]⁻·	−1.23[c]	225	166	762	220	123[e]	2.0031
[1·W(CO)₅]⁻·	−1.20	225	165	668	220	210[f]	2.0041
[1·CH₃]·[b]	−0.60	401	25	640	195		not reported

[a] For ESR parameters in DMF cf.: Rieger, P. H.; Bernal, I.; Reinmuth, W. H.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 683. [b] Grossi, L.; Minisci, F.; Pedulli, G. F. *J. Chem. Soc., Perkin Trans. 2* **1977**, 943. [c] E_{pc}, irreversible reduction in DMF. [d] ⁵³Cr, $I = {}^3/_2$, 9.5% natural abundance. [e] ⁹⁵,⁹⁷Mo, $I = {}^5/_2$, 25.4% natural abundance. [f] ¹⁸³W, $I = {}^1/_2$, 14.3% natural abundance.

Scheme I

M = Cr, Mo, W
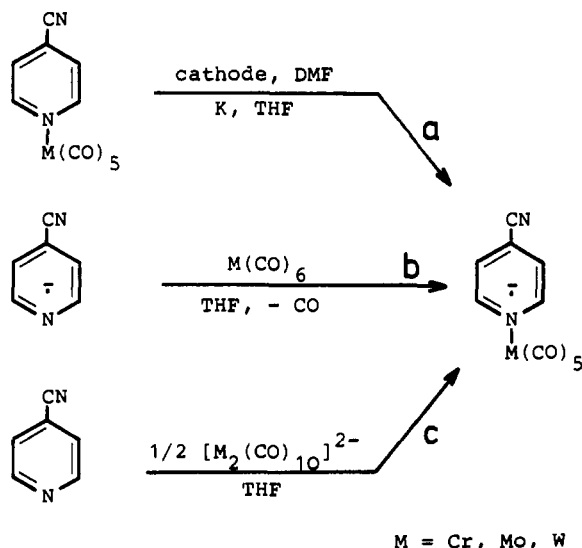
LUMO, thus confirming the interpretation of the lowest excited state as due to a metal (d) to ligand (π^*) charge transfer.[1-3]

Experimental Section

Physical Measurements. Cyclic voltammetry was performed with the Princeton Applied Research 173/175 System using a glassy-carbon working electrode and a saturated calomel electrode (SCE) as reference. A solution of 0.1 M tetrabutylammonium perchlorate in dimethylformamide (DMF) served as electrolyte. Cyclic voltammograms were recorded with 100 mV/s scan rate; besides the reduction waves for the complexes there were signals from dissociation products[8] following the electron uptake by the complex. Electron spin resonance measurements were carried out with a Varian E 9 spectrometer in the X-band mode. Coupling constants and g values were determined relative to the perylene radical anion in DME.[9]

Materials. All manipulations were carried out under an atmosphere of dry argon or under high vacuum. The solvents DMF and THF (Merck, p.A.) were rigorously dried with potassium (THF) or 4-Å molecular sieves (DMF) and freshly distilled before use. 4-Cyanopyridine (Aldrich) and metal hexacarbonyls (Alfa-Ventron) were used as purchased. The complexes were prepared from photolytically generated THF·M(CO)₅ solutions and the ligand in THF.[1-3] The solvent and starting materials were removed under vacuum, and the complexes were recrystallized from benzene/hexane mixtures.

Chemical Radical Generation. For ESR measurements, the reactions were carried out in sealed glass apparatus under high vacuum.

Route a. The complexes [1·M(CO)₅] were dissolved in THF and reacted with freshly distilled potassium. In the case of M = Cr and Mo the addition of the appropriate metal hexacarbonyl leads to an increase in the radical concentration.

Route b. 4-Cyanopyridine radical anion, generated by potassium reduction in THF, was reacted with a metal hexacarbonyl slurry in THF. Slow evolution of CO was observed, together with the formation of the radical complexes.
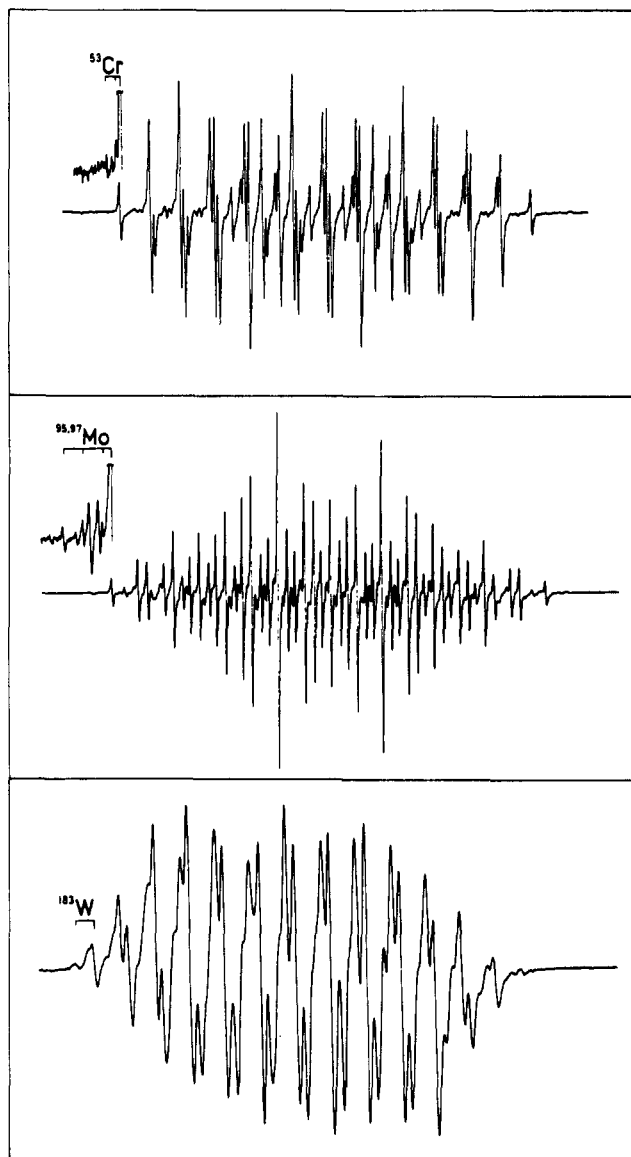
(8) Cf.: Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1976**, 749.
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Figure 1. ESR spectra of the radical complexes [1·M(CO)₅]⁻·, M = Cr, Mo, W, at room temperature in THF. Metal isotope hyperfine structure (cf. Table I) is indicated at the low-field wings of the spectra.

Route c. 4-Cyanopyridine was treated in excess with a solution of potassium decacarbonyldimetalate, prepared from M(CO)₆ and potassium in THF.

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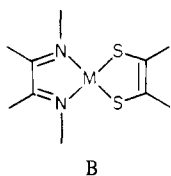## Mixed-Ligand 1,2-Diimine Ethylene-1,2-dithiolate Complexes of Nickel, Palladium, and Platinum

Arnd Vogler,* Horst Kunkely, Joachim Hlavatsch,
and Andreas Merz[1]

The discussion of mixed-valence (MV) or intervalence (IT) transition-metal complexes has been largely restricted to systems containing a reducing and an oxidizing metal center.[2-4] If the metal–metal interaction is weak, definite oxidation states can be assigned to the metals and charge-transfer (CT) or IT electronic transitions from the reduced to the oxidized metal occur at relatively low energies. Mononuclear metal complexes in which a ligand occurs in different oxidation states ($L_{red}ML_{ox}$) are also MV compounds.[5,6] However, in the electronic spectra of complexes containing catecholate and *o*-semiquinone as MV ligands, IT absorptions were not detected.[6] MV ligands seem also to be present in the 1,2-dithiolene complexes of Ni(II), Pd(II), and Pt(II)[7] (A). The

A
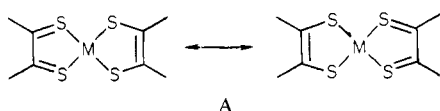
electronic structure is described by two equivalent resonance forms.[8] The highest occupied ($2b_{1u}$) and the lowest unoccupied ($3b_{2g}$) ligand orbitals are equally delocalized over both ligands.[8-10] The $2b_{1u} \rightarrow 3b_{2g}$ electronic transition has then no CT contribution. However, one of both resonance forms may prevail in the ground state if the complex becomes unsymmetric by the proper choice of substituents at the ligands.[11] The ground state is represented almost exclusively by one of both mesomeric forms, when the 1,2-dithioketone is replaced by 1,2-diimine as oxidizing ligand[12] (B). The $2b_{1u} \rightarrow 3b_{2g}$

B

(in D_{2h} symmetry) transition becomes now a CT or IT transition from the reducing 1,2-ethylenedithiolate to the oxidizing 1,2-diimine ligand.[12,13] The present investigation was undertaken to gain more insight into the electronic structure of these ligand-based MV complexes with particular reference to the influence of the metal.

Results and Discussion

Synthesis. Six complexes of the type M(1,2-diimine)-(ethylene-1,2-dithiolate) (III) were prepared with nickel,

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Table I. Electrochemical Data for (1,2-Diimine)(ethylene-1,2-dithiolate)metal(II) Complexes[a]

complex	redn		oxidn	
	$E_0'(1)^b$	$E_{p/2}(2)^c$	$E_{p/2}(1)$	$E_{p/2}(2)^g$
Ni(BABA)(MNT)	−0.70	−1.50	+0.8^d	
Pd(BABA)(MNT)	−0.78	−1.50	+1.18^e	
Pt(BAB)(MNT)	−0.78	−1.42	+1.20^f	
Ni(BABA)(TT)	−1.00	−1.66	+0.48^d	
Pd(BABA)(TT)	−0.98	−1.66	+0.58^d	+1.20
Pt(BABA)(TT)	−0.94	−1.66	+0.64^b	+1.20, +1.34

[a] Cyclic voltammograms at a Pt-disk electrode in 0.1 M *n*-BuNClO$_4$/CH$_3$CN; potentials in V vs. SCE. [b] Pure Nernstian waves for $v = 0.5$–20 V s^{-1}. [c] Quasi-reversible waves; potentials given for $v = 0.2$ V s^{-1}. [d] Chemically irreversible waves with peak heights corresponding to two-electron oxidations. [e] Beginning reversibility at $v > 20$ V s^{-1}. [f] Nernstian behavior at $v \geqslant 2$ V s^{-1}; E_0 given. [g] Irreversible waves; potentials given for $v = 0.2$ V s^{-1}.
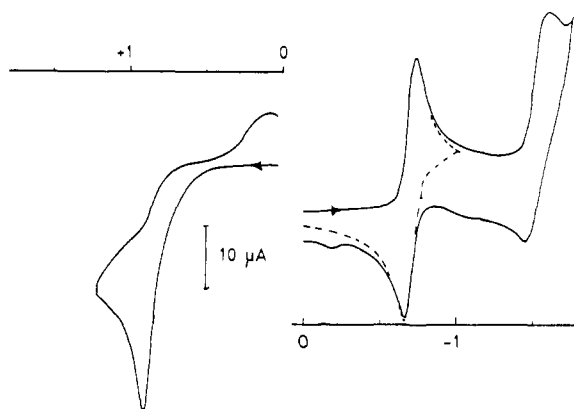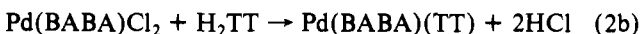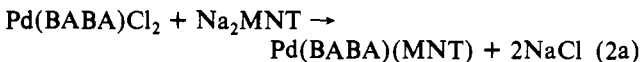
Figure 1. Cyclic voltammetric oxidation and reduction of Ni-(BABA)(MNT) (1 mM in 0.1 M TBAP/CH$_3$CN) at a 2-mm o.d. Pt disk (scan rate 0.2 V s^{-1}; potentials vs. SCE).

palladium, and platinum as central metal, biacetyl bis(anil) (BABA) as diimine, and disulfidomaleonitrile (MNT^{2-}) and 3,4-toluenedithiolate (TT^{2-}) as dithiolate ligands. The complex Ni(BABA)(MNT) was synthesized according to a procedure by Miller and Dance.[12] The compound Ni(BABA)(TT) was obtained by a similar method (eq 1). For the palladium

$$Ni(BABA)_2Cl_2 + H_2TT \rightarrow$$
$$Ni(BABA)(TT) + BABA + 2HCl \quad (1)$$
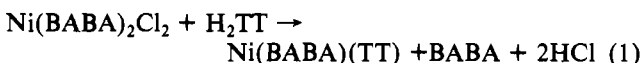
complexes Pd(benzonitrile)$_2$Cl$_2$ was used as starting material. It reacted with BABA to yield Pd(BABA)Cl$_2$. It was not necessary to isolate this compound. Upon addition of Na$_2$MNT or H$_2$TT the desired complexes were obtained (eq 2). A different route was employed for the synthesis of the

$$Pd(BABA)Cl_2 + Na_2MNT \rightarrow$$
$$Pd(BABA)(MNT) + 2NaCl \quad (2a)$$

$$Pd(BABA)Cl_2 + H_2TT \rightarrow Pd(BABA)(TT) + 2HCl \quad (2b)$$

platinum complexes. In solution it was apparently not possible to achieve a coordination of BABA to platinum. However, finely ground Na$_2$PtCl$_4$ reacted in a melt of BABA at 170 °C. The stoichiometry of the Pt(BABA) complex formed in this reaction was not established. In analogy to other diimine (bipyridyl and *o*-phenanthroline) complexes of platinum, Pt-(BABA)Cl$_2$ was most likely formed. An isolation of this compound was not required. The crude product reacted with Na$_2$MNT or H$_2$TT (see eq 2) to yield Pt(BABA)(MNT) and Pt(BABA)(TT). All six complexes crystallize as dark blue to deep purple solids.

Electrochemistry. Cyclic voltammetric data are presented in Table I and Figure 1. All six complexes undergo a