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Preliminary communication

HOMOLEPTIC PHENYL ISOCYANIDE COMPLEXES OF MOLYBDENUM AND TUNGSTEN: ZEROVALENT SIX-COORDINATE VERSUS DIVALENT SEVEN-COORDINATE

DOUGLAS D. KLENDWORTH, WARREN W. WELTERS III and RICHARD A. WALTON*
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

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Summary

Electrochemical and chemical oxidations of $Mo(CNPh)_6$ and $W(CNPh)_6$ have been shown to yield seven-coordinate $[M(CNPh)_7]^{2+}$. These cations, stabilized as their PF_6^- salts, can be obtained in yields of 80%. The redox and substitution chemistry of these new complexes have been explored. A convenient synthesis of $W(CNPh)_6$ has been devised starting from $W_2(dmhp)_4$ (dmhp is the anion of 2,4-dimethyl-6-hydroxypyrimidine).

Recent work has established that there exist homoleptic isocyanide complexes which are the isoelectronic congeners of mononuclear and dinuclear transition metal carbonyls (e.g. $Mo(CNPh)_6$ versus $Mo(CO)_6$, $Fe_2(CNBu^t)_9$ versus $Fe_2(CO)_9$) [1]. Although CNR and CO are formally isoelectronic, they confer significantly different properties upon the metal center. An especially noteworthy feature is the ability of alkyl and aryl isocyanides to stabilize homoleptic cationic species such as $[Cr(CNR)_7]^{2+}$, $[Cr(CNR)_6]^{2+}$ and $[Mo(CNR)_7]^{2+}$ [2—5] (R = alkyl group), a property not at all prevalent in carbonyl chemistry, with the notable exception of the $[M(CO)_6]^+$ cations (M = Mn, Tc and Re).

In the case of alkyl and aryl isocyanides, changes in the electronic properties of the CN function can be engendered by variations in the nature of the alkyl and aryl substituent. How such systematic changes influence the stabilities of the resulting complexes is a problem of some importance. Thus the molybdenum and tungsten species $[M(CNR)_7]^{2+}$ (R = CH_3, C_6H_{11} or CMe_3) and $M(CNAr)_6$ (Ar = aryl) are known [1a, 4—6], yet the corresponding $[M(CNAr)_7]^{2+}$ and $M(CNR)_6$ have yet to be reported. While there is sufficient evidence to support

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*Address any correspondence to this author.

the notion that aryl isocyanides (ArNC) are better than alkyl isocyanides (RNC) at stabilizing lower oxidation states of the metal, it is by no means clear that this difference is sufficient to preclude the formation of the elusive $[M(CNAr)_7]^{2+}$ and $M(CNR)_6$ species (M = Mo and W). In this communication we address this particular point and report preliminary details of the isolation and characterization of the complexes $[M(CNPh)_7](PF_6)_2$ (M = Mo and W)*.

A major hindrance to the development of the chemistry of aryl isocyanide complexes of tungsten(0), $W(CNAr)_6$, has been the absence of a convenient and reasonably high yield synthetic route [7]. We have found that the reaction between $W_2(dmhp)_4$ (dmhp is the anion of 2,4-dimethyl-6-hydroxypyrimidine) [8] and phenyl isocyanide constitutes an extremely simple method for preparing the dark red monomer $W(CNPh)_6$ in yields (~30%) significantly higher than those reported using other methods. We are working on procedures to increase these yields still further. This synthetic route is an example of an increasing number which involve the reductive or non-reductive cleavage of the multiple metal—metal bonds of suitable dinuclear starting materials [9].

With a ready source of $W(CNPh)_6$ now available, we have explored the chemical and electrochemical oxidations of this complex and that of its molybdenum analog $Mo(CNPh)_6$. In contrast to the well-defined electrochemical processes which characterize the cyclic voltammograms of $Cr(CNAr)_6$ derivatives (corresponding to the redox sequence $[Cr]^{3+} \leftarrow [Cr]^{2+} \leftarrow [Cr]^{+} \leftarrow [Cr]^{0}$) [3], the CV's of $Mo(CNPh)_6$ and $W(CNPh)_6$ are significantly more com-

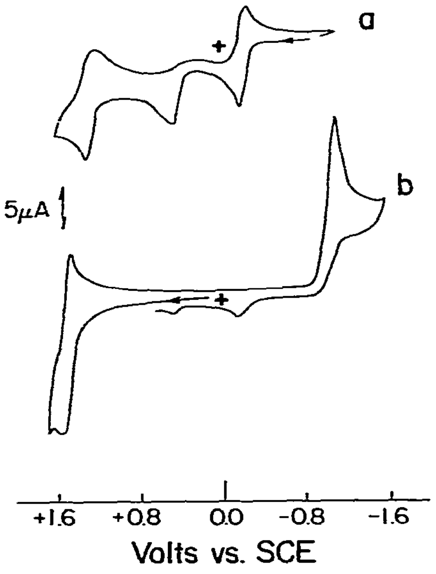

Fig. 1. Cyclic voltammograms in 0.2 *M* tetra-n-butylammonium hexafluorophosphate/dichloromethane of (a) $Mo(CNPh)_6$ and (b) $[Mo(CNPh)_7](PF_6)_2$. Sweep rates for (a) and (b) were 200 mV/s and 300 mV/s, respectively.

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*As regards homoleptic alkyl isocyanide complexes of Mo^0 and W^0, we have recently learned of two independent and successful attempts to synthesize $Mo(CNBu^t)_6$ (private communications from Professor G. Wilkinson (Imperial College) and Dr. M. Green (University of Bristol); see also, D.E. Berry, Ph.D. Thesis, University of Bristol, 1977).

plex. The latter are strikingly similar, that of a dichloromethane solution of $Mo(CNPh)_6$ being shown in Fig. 1(a). With 0.2 *M* Bu_4NPF_6 as supporting electrolyte, solutions of $Mo(CNPh)_6$ exhibit a reversible one-electron oxidation at $E_{1/2}$ = —0.21 V vs. SCE. A second oxidation at $E_{p,a}$ = +0.50 V vs. SCE is irreversible and is followed by a chemical step in which an unidentified product ($E_{1/2}$ = +1.28 V vs. SCE) is formed (i.e. by an EEC mechanism). In the case of $W(CNPh)_6$ the corresponding oxidations are at $E_{1/2}$ = —0.16 V and $E_{p,a}$ = +0.46 V. Bulk electrolysis of the $Mo(CNPh)_6$ solution at +0.6V (i.e. anionic of the irreversible oxidation) produced a lemon yellow solution whose CV displayed an oxidation wave at $E_{1/2}$ ~ +1.42 V and an irreversible reduction at $E_{p,c}$ ~ —1.1V. Since this CV resembled those of the seven-coordinate homoleptic alkyl isocyanide complexes $[Mo(CNR)_7](PF_6)_2$ [6], we have explored the possibility that $[Mo(CNPh)_7]^{2+}$ is a product of the oxidation of $Mo(CNPh)_6$. This has been shown to be the case.

When $NOPF_6$ is added to a stirred solution of $Mo(CNPh)_6$ in tetrahydrofuran there is an immediate color change from bright red to dark purple. Addition of hexane to the solution precipitates dark purple $[Mo(NO)(CNPh)_5]$-PF_6 (I) in 90% yield (Anal. Found: C, 53.11; H, 3.45; N, 10.78. Calcd: C, 53.44; H, 3.21; N, 10.69%. IR spectrum (nujol mull): ν (CN) 1992w, 2140vs (br), 2195w; ν(NO) 1676s cm^{-1}). Work-up of the filtrate afforded yellow needles of $[Mo(CNPh)_7](PF_6)_2$ (II) in 7% yield (Anal. Found: C, 53.32; H, 3.41; N, 8.59. Calcd.: C, 53.12; H, 3.19; N, 8.85%. IR spectrum (nujol mull): ν(CN) 2140vs (br) cm^{-1}). Solutions of the diamagnetic seven coordinate complex III in acetone-d_6 exhibit phenyl resonances at δ 7.79 and 7.67 ppm in the ^1H NMR spectrum.

To optimize the yield of $[Mo(CNPh)_7](PF_6)_2$ through oxidation of $Mo(CNPh)_6$, both a mild oxidant and the presence of an excess of phenyl isocyanide are needed. An acetone solution of $Mo(CNPh)_6$ was treated with $AgNO_3$, KPF_6 and a slight excess of PhNC. The reaction mixture was stirred for 4 h, filtered, and the filtrate reduced to low volume under a stream of N_2. When diethyl ether was added and the mixture cooled to 0° C, yellow crystals of II were obtained in 80% yield (Anal. Found: C, 53.32; H, 3.32; N, 8.78%). Work-up of the filtrate gave a small crop (<10%) of I, presumably formed by a competitive reaction involving reduction of the excess nitrate ion which is present.

A comparison of the CV of a dichloromethane solution of an authentic sample of $[Mo(CNPh)_7](PF_6)_2$ (Fig. 1b) with the CV's of the solutions which are formed following the exhaustive electrolysis (at +0.6 V) of $Mo(CNPh)_6$ confirmed that II is indeed present as a major product following the electrochemical oxidation of $Mo(CNPh)_6$. In addition to the one-electron oxidation $[Mo(CNPh)_7]^{2+} \rightarrow [Mo(CNPh)_7]^{3+} + e$ (at +1.42 V), there is an irreversible two-electron reduction at $E_{p,c}$ = —1.06 V in the CV of II. The wave at $E_{p,a}$ = —0.18 V (Fig. 1b) is due to the formation of $Mo(CNPh)_6$ following this reduction. The quantitative conversion of II to $Mo(CNPh)_6$ can be accomplished chemically in tetrahydrofuran solution using Mg metal as the reductant.

Corresponding studies on the chemical oxidations of $W(CNPh)_6$ have shown that $[W(NO)(CNPh)_5]$ PF_6 (III) and $[W(CNPh)_7](PF_6)_2$ (IV) can be produced in high yields (>70%). The complexes III and IV possess very similar properties to their molybdenum analogs. For example, the CV of a dichloromethane solution of IV shows a reversible one-electron oxidation at $E_{1/2} = +1.32$ V vs. SCE and an irreversible two-electron reduction at $E_{p,c} = -1.02$ V vs. SCE. This reduction leads to the formation of $W(CNPh)_6$.

Both II and IV appear to exhibit a rich substitution chemistry. Reactions with monodentate phosphines yield the yellow, crystalline disubstitution products $[M(CNPh)_5(PR_3)_2](PF_6)_2$ ($PR_3 = PEt_3, P(OEt)_3, PPr^n_3, PEt_2Ph$ or $PEtPh_2$) or $[M(CNPh)_6(PPh_3)](PF_6)_2$ in yields of 60—80%. These studies are continuing and will be reported in detail when complete.

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