

Preliminary communication

REDOX AND ISOCYANIDE SUBSTITUTION CHEMISTRY OF BIS(2,2'-BIPYRIDINE) DERIVATIVES OF MOLYBDENUM AND TUNGSTEN CARBONYL

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Summary

Redox reactions of *cis*-[Mo(CO)₂(bpy)₂] (bpy is 2,2'-bipyridine) produce [Mo(CO)₂(bpy)₂]^z (z = ±1, +2), which react with isocyanides to substitute CO or bpy or both of these, depending on the charge, z.

Studies of the reactions of complexes of the general type [MoQ₂(biL)₂] (Q = CO, CNR, C₂H₄, N₂) have been limited for the most part to those cases in which biL is a ditertiary phosphine [1]. An important distinction in reactivity between complexes of aryl- and alkyl-phosphines has been established [2]. Depending on Q, the reactions of the neutral complexes may result in substitution [3], or conversion [4] of Q, or in the oxidation of the metal [5], but biL is not displaced. The consequences of a more profound change in the nature of biL can be observed by the use of 2,2'-bipyridine (bpy) ligands, the donor/acceptor properties of which can be controlled by substitution at the rings.

Cyclic voltammetry of the photosensitive, deep purple complex [6] *cis*-[Mo(CO)₂(bpy)₂] (I) (δ(¹H) in CD₃CN: 7.50 (H5), 8.01 (H4), 8.44 (H3), 8.66 (H6) ppm) shows a reversible one-electron reduction wave (E_{1/2} - 1.64 V vs. SCE) and two one-electron oxidation waves (E_{1/2} - 0.54 V, reversible; +0.30 V, irreversible) in acetonitrile solution. Reduction of I with either sodium amalgam or sodium naphthalenide produces dark brown, paramagnetic *cis*-[Mo(CO)₂(bpy)₂]⁻ ion (ν(CO) 1770, 1680 cm⁻¹, g_{av} 1.981) in dimethoxyethane solution. Oxidation of I with AgBF₄ (1 mol) in methyl cyanide, or with AlCl₃ in dichloromethane [7] followed by NaBF₄, at room temperature produces the diamagnetic binuclear [{Mo(CO)₂(bpy)₂]₂][BF₄]₂ (II) (ν(CO)

1910, 1763 cm^{-1}). Warming an acetone solution of II gives paramagnetic mononuclear *trans*-[Mo(CO)₂(bpy)₂][BF₄] (III) ($\nu(\text{CO})$ 1860 cm^{-1} ; g_{av} 1.98; M^+ 551 [8]). Both II and III react with AgBF₄ (1 mol) in methyl cyanide at room temperature to form the same dark red-brown seven coordinate molybdenum(II) product [Mo(CO)₂(bpy)₂(NCMe)][BF₄]₂ (IV) ($\nu(\text{CO})$ 1976, 1896 cm^{-1} ; $\delta(^1\text{H})$ in CD₃CN: 2.00 (CH₃) 7.66 (H5), 8.37 (H4), 8.62 (H6), 8.75 (H3) ppm; M^+ 679 [8]). Reduction of IV with sodium naphthalenide in tetrahydrofuran/methyl cyanide occurs under mild conditions and proceeds stepwise via III to I. Oxidation of I with AgBF₄ (2 mol) in water produces the yellow aquo-cation, *cis*-[Mo(CO)₂(bpy)₂(OH₂)]₂[BF₄]₂ (V) ($\nu(\text{OH})$ 3260 cm^{-1}) which is converted to IV immediately on dissolution in methyl cyanide.

Although I reacts rapidly with *p*-tolyl isocyanide in methyl cyanide solution at room temperature to give *cis*-[Mo(CO)₂(CNR)₄] (R = *p*-tolyl) exclusively, the reaction between I and excess ethyl isocyanide at room temperature produces *cis,cis*-[Mo(CO)₂(CNEt)₂(bpy)]. No further substitution occurs, even on prolonged heating in pure ethyl isocyanide. The salt IV reacts with ethyl isocyanide (3 mol) at room temperature to give violet [Mo(bpy)₂(CNEt)₃][BF₄]₂ ($\delta(^1\text{H})$ in CD₃CN: 1.34 (CH₃) 4.04 (CH₂), 7.52 (H5), 8.13 (H4), 8.20 (H3), 8.55 (H6) ppm, $\nu(\text{CN})$ 2150s, 2110s cm^{-1}). Addition of 5 mol or excess ethyl isocyanide to IV produces dark purple [Mo(bpy)(CNEt)₅][BF₄]₂ ($\delta(^1\text{H})$ in CD₃CN: 1.37 (CH₃), 3.95 (CH₂), 7.74 (H5), 8.26 (H4), 8.57 (H3), 9.00 (H6) ppm, $\nu(\text{CN})$ 2215(sh), 2187(sh), 2130s cm^{-1}). It was not possible to achieve complete substitution of the ligands in IV by EtCN; however, the desired orange-yellow complex [Mo(CNEt)₇][BF₄] was formed in high yield in the reaction between ethyl isocyanide and [Mo(CO)₄Cl₂]₂ [9] in chloroform solution followed by anion exchange with NaBF₄ [10]. The structures of this series of seven coordinate cations will be the subject of a separate paper. The addition of ethyl isocyanide to the molybdenum(I) dimer II, causes a redox disproportionation reaction and [Mo(bpy)₂(CNEt)₃][BF₄]₂ can be isolated. Reactions of the complexes [Mo(CO)₂(bpy)₂]^z with other classes of nucleophiles have been carried out and will be reported in detail. The tungsten analogues of the redox series [W(CO)₂(bpy)₂]^z have also been prepared. In general, we find that the tungsten complexes in a particular oxidation state are more susceptible to substitution than their molybdenum analogues.

The availability of a redox series of isolable complexes [M(CO)₂(bpy)₂]^z (M = Mo, W; z = 0, ±1, +2) in which modification of the bpy ligands can influence significantly the redox reactivity of the complexes formed [11], provides a route for the preparation of other [MQ₂(bpy)₂] and the prospect of a strict comparison with the isoelectronic ruthenium(II) and osmium(II) complexes such as [Os(NCMe)₂(bpy)₂][PF₆]₂ [12].

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