

OXIDATION OF *cis*-BIS(2,2'-BIPYRIDINE)DICARBONYLMOLYBDENUM(0) WITH SILVER(I) SALTS OF COORDINATING ANIONS

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Summary

Oxidation of *cis*-[Mo(CO)₂(bipy)₂] (bipy = 2,2'-bipyridine) by silver(I) salts, AgX (X = NCS, NO₂, NO₃) in acetonitrile solution at room temperature has been found usually to result in the displacement of one bipy ligand by the nucleophile, X. The products have been characterised as *cis*-[Mo(NCS)₂(CO)₂(bipy)(NCMe)], [Mo(η²-NO₃)(CO)₂(bipy)][NO₃] and [Mo(NO₃)(CO)₂(bipy)₂][NO₃] by microanalysis, conductivity measurements and spectroscopy (IR, ¹H NMR, electronic absorption). These results are compared with those for oxidation of *cis*-[Mo(CO)₂(dmpe)₂] (dmpe = ethanediybis(dimethylphosphine)) and can be explained in terms of the basicity of X which increases in the order X = NO₃⁻ < NO₂⁻ < NCS⁻.

Introduction

Previous work on the oxidation of *cis*-[Mo(CO)₂(bipy)₂] has shown that Ag[BF₄] (1 mol) produces red-brown, diamagnetic [Mo₂(CO)₄(bipy)₄][BF₄]₂ which dissociates in acetone solution to form green, paramagnetic *trans*-[Mo(CO)₂(bipy)₂][BF₄]. Either of these molybdenum(I) cations can be oxidised further by Ag[BF₄] (1 mol) in solution to *cis*-[Mo(CO)₂(bipy)₂(solvent)][BF₄]₂ which have been isolated [1]. Oxidation with silver(I) in the presence of a neutral coordinating ligand, L, gives [2] complexes, *cis*-[Mo(CO)₂(bipy)₂L][BF₄]₂ (L = P(OMe)₃, PhC≡CH), some examples of which can also be obtained [3] by substitution in *cis*-[Mo(CO)₂(bipy)₂(solvent)][BF₄]₂.

Investigations of the oxidation of *cis*-[Mo(CO)₂(dmpe)₂] by silver(I) salts have shown that the nature of the anion is important in determining the product of the oxidation [4]. When a coordinating anion such as nitrate or thiocyanate is involved, it is possible to isolate stable seven-coordinate, ionic molybdenum(II) complexes containing the anion coordinated to the metal. When a weakly coordinating anion such as tetrafluoroborate or hexafluorophosphate is used, a stable molybdenum(II) product was not isolated [4].

We report the results of experiments designed to compare the influence of the ligands dmpe and bipy on the products of oxidation reactions involving silver(I) salts of coordinating anions. We show that there are significant differences between the two *cis*-[Mo(CO)₂(L-L)₂] (L-L = bipy or dmpe) complexes which are related to the ease with which L-L is displaced from the metal.

Results

The reaction of *cis*-[Mo(CO)₂(bipy)₂] with silver(I) thiocyanate (2 mol) in acetonitrile is rapid at room temperature, producing a grey precipitate of silver metal and a purple solution from which a purple solid is isolated. The purple solid is a non-electrolyte in acetonitrile solution (λ_{\max} 555 nm). Microanalysis is in agreement with the composition [Mo(NCS)₂(CO)₂(bipy)(NCMe)]. Spectroscopic measurements show that the two CO ligands are *cis* ($\nu(\text{CO})$ 1979s, 1895s cm⁻¹) and that the *N*-bonded thiocyanate ligands are also mutually *cis* ($\nu(\text{CN})$ 2060s, 2040s cm⁻¹). Oxidation has resulted in substitution of the bipy by the thiocyanate ion and, in order to achieve seven-coordination, a molecule of acetonitrile solvent is also coordinated to the metal.

The reaction of *cis*-[Mo(CO)₂(bipy)₂] with silver(I) nitrite (2 mol) in acetonitrile is rapid at room temperature. A grey precipitate of silver metal is formed and a dark green solution from which the product is isolated as orange-yellow crystals (λ_{\max} 490 nm (MeCN)). The complex is a non-electrolyte in acetonitrile solution. The infrared spectrum indicates two *cis* CO ligands ($\nu(\text{CO})$ 2015s, 1930s cm⁻¹). The absence of a strong absorption in the 1335–1250 cm⁻¹ region is consistent with the absence of ionic nitrite. The observations of a strong absorption at 1640 cm⁻¹ and a medium intensity absorption at 1280 cm⁻¹ are consistent with a bridging nitro ($\mu^2, \eta^2(N,O)$ -NO₂) ligand [5]. The presence of an *O*-bonded nitrito ligand is indicated by three strong absorptions (1440, 1063, 810 cm⁻¹). The ¹H NMR spectrum shows a characteristic first-order coupling pattern similar to other bipy complexes we have measured, together with further splitting of each signal which would be consistent with a dimeric structure in which the bipy ligands are inequivalent. This spectroscopic evidence, together with the results of microanalysis indicate that the product is the dimeric, neutral molybdenum(II) complex, [(Mo(ONO)($\mu^2, \eta^2(N,O)$ -NO₂)-(CO)₂(bipy))₂].

Silver(I) nitrate (2 mol) reacts rapidly with *cis*-[Mo(CO)₂(bipy)₂] in acetonitrile solution at room temperature. A grey precipitate of metallic silver is formed, together with a dark green solution from which two products have been isolated. The major product is a yellow solid (λ_{\max} 420 nm (MeCN)) which is a 1:1 electrolyte in acetonitrile solution. The infrared spectrum of the solid shows absorptions which can be assigned to a unidentate nitrate ligand (1640m, 1440s, 1340m, 1300s, 1008m cm⁻¹) and to anionic nitrate (1380s cm⁻¹), at wavenumbers which are quite close to those in the spectrum [6] of the analogous complex *cis*-[Mo(NO₃)(CO)₂-(dmpe)₂][NO₃]. The $\nu(\text{CO})$ absorption wavenumbers of the bipy complex (2010s, 1923s cm⁻¹) are higher than those of the dmpe complex (1953s, 1892s cm⁻¹) [6]. The well-resolved ¹H NMR spectrum is consistent with the expected diamagnetism ($\delta\text{H}(3)$ 8.39 dq, H(4) 8.12 td, H(5) 7.60 td, H(6) 8.70 dq ppm (MeCN)). This spectroscopic evidence, together with the results of microanalysis show that the major product is *cis*-[Mo(NO₃)(CO)₂(bipy)₂][NO₃]. Once again we wish to draw

attention to the coincidental simplicity of the proton NMR spectrum of a *cis*-bis(bipy) complex of molybdenum [1,7].

The minor product is a green solid (λ_{\max} 435 nm (MeCN)) which is a 1:1 electrolyte in acetonitrile solution, and is relatively less soluble in solvents of lower polarity, such as dichloromethane, than the major product described above. Microanalysis indicates that this complex is the six-coordinate $[\text{Mo}(\eta^2\text{-NO}_3)(\text{CO})_2(\text{bipy})][\text{NO}_3]$. Repeated preparations and analyses of this green salt have failed to provide evidence for the presence of a coordinated acetonitrile solvent ligand. The infrared spectrum of the solid complex establishes the bidentate character of the nitrate ligand (1495s, 1340m, 1250m, 1030m cm^{-1}), and the *cis*-disposition of the CO ligands (1820s, 1720s cm^{-1}). The low values of the $\nu(\text{CO})$ absorption wavenumbers emphasise the enhanced donor/acceptor ratio of both the bidentate nitrate ligand and the bipy ligand in this six-coordinate complex. The observation that the chemical shifts of H(3) and H(6) in this green complex are at significantly lower field than in the yellow $[\text{Mo}(\text{NO}_3)(\text{CO})_2(\text{bipy})_2][\text{NO}_3]$ is consistent with this also.

Discussion

The oxidation reactions of *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2]$ reported here provide an interesting contrast to those of *cis*- $[\text{Mo}(\text{CO})_2(\text{dmpe})_2]$. In general terms, oxidation of the former is usually (but not always) accompanied by substitution of bipy but substitution of dmpe as a result of oxidation of the latter complex is not observed [4]. Oxidation of *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2]$ by $\text{Ag}[\text{NO}_3]$, which contains the weakest of the three nucleophiles considered here, produces *cis*- $[\text{Mo}(\text{NO}_3)(\text{CO})_2(\text{bipy})_2][\text{NO}_3]$, the analogue of *cis*- $[\text{Mo}(\text{NO}_3)(\text{CO})_2(\text{dmpe})_2][\text{NO}_3]$, as the major of two products. The minor product, *cis*- $[\text{Mo}(\eta^2\text{-NO}_3)(\text{CO})_2(\text{bipy})][\text{NO}_3]$, is the result of substitution of bipy by the alternative bidentate nucleophile, nitrate. An increase in the nucleophilicity of the anion from nitrate to nitrite produces only the neutral dimeric, nitro-bridged complex $[\{\text{Mo}(\text{ONO})(\mu^2, \eta^2(N, O)\text{-NO}_2)(\text{CO})_2(\text{bipy})\}_2]$ by oxidation of *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2]$ with $\text{Ag}[\text{NO}_2]$. This is in marked contrast to the oxidation of *cis*- $[\text{Mo}(\text{CO})_2(\text{dmpe})_2]$ by $\text{Ag}[\text{NO}_2]$ which results [4] in the formation of both CO_2 and N_2O as a result of oxidation of CO and reduction of nitrite ion. A pure molybdenum-containing product was not isolated from the reaction [4]. The formation of $[\text{Mo}(\text{ONO})(\text{NO})(\text{CO})(\text{dmpe})_2]$ as a significant intermediate succeeding $[\text{Mo}(\text{NO}_2)(\text{CO})_2(\text{dmpe})_2][\text{NO}_2]$ (or $\text{Mo}(\text{ONO})(\text{CO})_2(\text{dmpe})_2[\text{NO}_2]$) was adduced to explain the observations [4]. In the present instance, no gaseous product is observed. Both nitrite anions are attached to molybdenum(II), one as *O*-bonded nitrito, the other as a bridging η^2 -nitro group, following displacement of bipy.

The strongest nucleophile of the three, thiocyanate substitutes bipy at molybdenum(II) to form mononuclear, seven-coordinate *cis*- $[\text{Mo}(\text{NCS})_2(\text{CO})_2(\text{bipy})(\text{NCMe})]$. The involvement of thiocyanate as a bridging ligand is recognised in complexes such as $[\text{Pt}_2\text{Cl}_2(\mu^2, \eta^2(N, S)\text{-SCN})_2(\text{PPr}_3^{\text{n}})_2]$ [8]. The fact that oxidation of *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2]$ by $\text{Ag}[\text{NCS}]$ does not produce a dimer such as $[\{\text{Mo}(\text{NCS})(\eta^2\text{-NCS})(\text{CO})_2(\text{bipy})\}_2]$, containing a bridging thiocyanate ligand, is probably to be explained by the harder acid character of molybdenum(II) which prefers a nitrogen donor ligand (acetonitrile) to sulphur. The influence of the chelating ligand is apparent from the fact that oxidation of *cis*- $[\text{Mo}(\text{CO})_2(\text{dmpe})_2]$ with $\text{Ag}[\text{NCS}]$ gives *cis*- $[\text{Mo}(\text{NCS})(\text{CO})_2(\text{dmpe})_2][\text{NCS}]$ in both dichloromethane

and acetonitrile solution. This indicates the stronger binding of dmpe than bipy to molybdenum(II) so that oxidation simply results in coordination of one anion as a seventh ligand in preference to the solvent. The oxidation with Ag[NCS], in which the anion is a good coordinating nucleophile, is an interesting contrast to the result of oxidation of *cis*-[Mo(CO)₂(bipy)₂] with Ag[BF₄], in which the anion is a much weaker nucleophile with poor coordinating ability, which produces *cis*-[Mo(CO)₂(bipy)₂(NCMe)][BF₄]₂ in acetonitrile solution [1]. The complex *cis*-[Mo(NCS)₂(CO)₂(dppm)₂] (dppm = methanedilylbis(diphenylphosphine)) contains one unidentate and one bidentate di-tertiary phosphine ligand [9].

Previous work has shown [7] that substitution by neutral ligands in *cis*-[Mo(CO)₂(bipy)₂] usually results in displacement of bipy in preference to CO, the only exception being PF₃ which produces *cis*-[Mo(PF₃)₂(bipy)₂] [7]. Substitution by the same neutral ligands in [Mo(CO)₂(bipy)₂(NCMe)][BF₄]₂ results [1,3] in displacement of CO in preference to bipy. In the reactions between anionic ligands and the weakly electrophilic metal complex *cis*-[Mo(CO)₂(bipy)₂] in the presence of an oxidising agent which are reported here, it is unreasonable to suppose that substitution at molybdenum(0) precedes oxidation. There was no reaction observed between *cis*-[Mo(CO)₂(bipy)₂] and either [Et₄N][NCS] or K[NCS] in acetonitrile. Consequently, oxidation to molybdenum(II) must precede a substitution reaction in which the anionic nucleophile displaces bipy from molybdenum(II) in preference to CO.

Experimental

Preparations were all carried out under pre-purified dinitrogen using standard techniques (Schlenk tubes, cannulae, vacuum manifold). All solvents were dried (calcium hydride, sodium, or molecular sieves), deaerated and distilled before use. The preparation of *cis*-[Mo(CO)₂(bipy)₂] has been described in detail [10]. All silver salts (Aldrich) were used as received without further purification. Conductivity measurements were made with a Wayne Kerr bridge B221; the cell constant of the glass conductivity probe was calculated using standardised 0.01 mol dm⁻³ potassium chloride solution. IR spectra were recorded on Perkin-Elmer PE 625 spectrometer. NMR spectra were recorded on a JEOL PS100 spectrometer. Electronic absorption spectra were measured on a Perkin-Elmer PE402 spectrometer. Microanalyses were performed by Mr. A. Fassam.

Preparations

Bis-(N-thiocyanato)2,2'-bipyridinedicarbonylacetonitrilemolybdenum(II)

Solid silver(I) thiocyanate (0.61 g, 3.66 mmol) was slowly added to a stirred solution/slurry of *cis*-[Mo(CO)₂(bipy)₂] (0.85 g, 1.83 mmol) in acetonitrile (40 cm³). The mixture rapidly changed colour (to purple) and a metallic grey precipitate of silver was formed. After 0.3 h the mixture was filtered through Celite to remove the silver precipitate. The filtrate was concentrated by evaporation under reduced pressure. Addition of petroleum ether (40–60°C boiling fraction) to the concentrate and cooling (273 K) produced a purple solid which was isolated by filtration, washed and dried in vacuo (0.43 g, 51% yield). (Found: C, 43.4; H, 2.5; N, 15.1; S, 14.1. C₁₆H₁₁MoN₅O₂S₂ calcd.: C, 41.3; H, 2.3; N, 15.1; S, 13.8%). ¹H NMR (CD₃CN): δ 7.95 (td, H(5)), 8.16 (td, H(4)), 8.48 (d, H(3)), 8.72 (d, H(6)) ppm.

Nitrito(nitro)2,2'-bipyridinedicarbonylmolybdenum(II) dimer

A solution of silver(I) nitrite (0.79 g, 4.14 mmol) in acetonitrile (10 cm³) was slowly added to a rapidly stirred slurry of *cis*-[Mo(CO)₂(bipy)₂] (0.95 g, 2.07 mmol) in acetonitrile (30 cm³). The reaction mixture rapidly changed colour to dark green and a metallic grey precipitate of silver was formed. After 0.3 h the mixture was filtered through Celite to remove the silver precipitate. The filtrate was evaporated to dryness under reduced pressure giving a green solid. The green solid was extracted with dichloromethane (3 × 10 cm³), the extracts were filtered, concentrated and then covered with a layer of petroleum ether (40–60°C boiling fraction) and stored. The yellow crystalline solid, which was deposited from the solution, was isolated by filtration, washed with diethyl ether and dried in vacuo (0.48 g, 58% yield). (Found: C, 35.9; H, 2.2; N, 13.8. C₁₂H₈MoN₄O₆ calcd.: C, 36.0; H, 2.0; N, 14.0%). ¹H NMR (CD₃CN); δ 7.70 (td, H(5)), 8.18 (td, H(4)), 8.44 (d, H(3)), 8.83 (d, H(6)) ppm.

Reaction of cis-[Mo(CO)₂(bipy)₂] with silver(I) nitrate

A solution of silver(I) nitrate (1.31 g, 6.72 mmol) in acetonitrile (30 cm³) was slowly added to a rapidly stirred slurry of *cis*-[Mo(CO)₂(bipy)₂] (1.56 g, 3.36 mmol) in acetonitrile (30 cm³). The reaction mixture rapidly changed colour to dark green and a metallic grey precipitate of silver was formed. After 0.5 h the mixture was filtered through Celite to remove the silver precipitate. The filtrate was evaporated to dryness under reduced pressure giving a dark green solid. The green solid was extracted with dichloromethane (3 × 10 cm³), the extracts were filtered, concentrated and then covered with a layer of petroleum ether (40–60°C boiling fraction) and stored. The yellow crystalline material which was deposited from the solution was isolated by filtration, washed with a small volume of diethyl ether and dried in vacuo to give crystals of [Mo(NO₃)(CO)₂(bipy)₂][NO₃] (0.95 g, 48% yield). (Found: C, 44.9; H, 2.9; N, 13.7. C₂₂H₁₆MoN₆O₈ calcd.: C, 44.9; H, 2.7; N, 14.2%). Conductivity, Λ 156 S cm² mol⁻¹ (10⁻³ mol dm⁻³ in MeCN). Following extraction of the green solid with dichloromethane, the residue was dissolved in acetone, filtered and then carefully covered with a layer of diethyl ether and stored. The green solid was isolated by filtration, washed with diethyl ether and dried in vacuo to give [Mo(NO₃)(CO)₂(bipy)][NO₃] (0.23 g, 13% yield). (Found: C, 33.1; H, 1.8; N, 12.2. C₁₂H₈MoN₄O₈ calcd.: C, 33.3; H, 1.9; N, 12.9%). Conductivity, Λ 147 S cm² mol⁻¹ (10⁻³ mol dm⁻³ in MeCN). ¹H NMR (CD₃CN); δ 7.42 (td, H(5)), 8.17 (td, H(4)), 8.49 (d, H(3)), 9.05 (d, H(6)) ppm.

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