

TRIS-BIPYRIDINE COMPLEXES OF MOLYBDENUM(II) AND RELATED COMPOUNDS *

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Summary

Reaction of *cis*-[Mo(CO)₂(bipy)₂(NCMe)][BF₄]₂ (bipy = 2,2'-bipyridine) with 4,4'-X₂-2,2'-bipyridine (biL) (X = NMe₂, CMe₃, H, Cl) in acetonitrile solution or with pyridine (pyr) produces the six-coordinate, 16-valence electron complexes [Mo(bipy)₂(biL)][BF₄]₂ and [Mo(bipy)₂(pyr)₂][BF₄]₂. [Mo(CO)(bipy)₂(biL)][BF₄]₂ is an unstable intermediate in these reactions. The products have been characterised by microanalysis and spectroscopic measurements (¹H, ¹³C NMR, electronic absorption and IR).

Introduction

The influence of substituents at the 4- and 4'-positions of 2,2'-bipyridine (bipy) on the properties of group 6 metal carbonyl complexes of the type *cis*-[M(CO)₄(biL)] (M = Mo, W) has been shown to be significant [1–3]. An interesting reaction occurs when the molybdenum(II) salt [Mo(CO)₂(bipy)₂(NCMe)][BF₄]₂ reacts with bipy in acetonitrile [4]. The product is the 16-valence electron complex [Mo(bipy)₃][BF₄]₂. We were interested to compare the influence of pyridine ring substituents on the properties of these six-coordinate molybdenum(II) dications with that in the neutral tetracarbonylmolybdenum(0) analogues.

Results

Synthesis

The reaction between *cis*-[Mo(CO)₂(bipy)₂(NCMe)][BF₄]₂ and various biL in acetonitrile solution at 300–310 K produces a deep purple solution from which air-sensitive purple-black crystals of [Mo(bipy)₂(biL)][BF₄]₂ can be isolated. Higher temperatures (reflux) can be used to hasten the reaction but then the yields of

* Dedicated to Professor G.E. Coates on his 70th birthday.

product are lower. The purple solutions of these complexes immediately turn green on exposure to air. Monitoring the synthesis reactions in solution at room temperature by infrared spectroscopy shows a common pattern of behaviour. The $\nu(\text{CO})$ absorptions of the dicarbonyl complex (1985, 1908 cm^{-1}) are replaced by a single absorption at ca. 1860 cm^{-1} produced by $[\text{Mo}(\text{CO})(\text{bipy})_2(\text{biL})][\text{BF}_4]_2$. When this monocarbonyl complex is warmed gently (320–330 K) in acetonitrile solution, the CO absorption at ca. 1860 cm^{-1} disappears and the $[\text{Mo}(\text{bipy})_2(\text{biL})][\text{BF}_4]_2$ product can be isolated.

Stirring a solution of *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2(\text{NCMe})][\text{BF}_4]_2$ (1 mol) in acetonitrile with pyridine (2 mol) at room temperature produces a deep purple solution from which crystals of $[\text{Mo}(\text{CO})(\text{bipy})_2(\text{pyr})_2][\text{BF}_4]_2$ were isolated. The CO stretching frequency of this complex is 1860 cm^{-1} . When the complex is heated in solution, the CO absorption disappears and $[\text{Mo}(\text{bipy})_2(\text{pyr})_2][\text{BF}_4]_2$ can be isolated.

Spectra

Assignment of the apparently complex proton NMR spectra was quite straightforward in the light of our previous work on bipy and biL complexes of molybdenum(0) and molybdenum(II) [1,5]. The proton NMR spectra of the $[\text{Mo}(\text{bipy})_2(\text{biL})][\text{BF}_4]_2$ complexes (Table 1) indicate the following general conclusions. The bipy ring protons are generally sensitive to the influence of the biL ligand and shift to lower field as the substituent X on biL becomes a better acceptor. The influence of X is not great (ca. 0.1 ppm for H(4) and H(6); ca. 0.5 ppm for H(3) and H(5), for X changing from NMe_2 to Cl) but it is significant. The proton resonances of the biL ligand shift to lower field as the substituent X becomes a poorer donor/better acceptor [1], but the shift is generally rather smaller in the case of $[\text{Mo}(\text{bipy})_2(\text{biL})]^{2+}$ than of either $[\text{Mo}(\text{CO})_4(\text{biL})]$ or the free biL. The coordination shift, Δ defined as $(\delta(\text{complex}) - \delta(\text{free ligand}))$ is generally greater for any ring proton of biL or pyr attached to molybdenum(II) in $[\text{Mo}(\text{bipy})_2(\text{biL})]^{2+}$ and $[\text{Mo}(\text{bipy})_2(\text{pyr})_2]^{2+}$, than when these ligands are attached to molybdenum(0) in $[\text{Mo}(\text{CO})_4(\text{biL})]$ and $[\text{Mo}(\text{CO})_4(\text{pyr})_2]$. The electron donor/acceptor character of the substituent X of biL has no consistent influence on the coordination shift of the biL proton in $[\text{Mo}(\text{bipy})_2(\text{biL})]^{2+}$ complexes. Although the chemical shifts of these protons are sensitive to the nature of X, the coordination shift is independent of the

TABLE 1

PROTON NMR CHEMICAL SHIFTS (δ (ppm)) OF $[\text{Mo}(\text{bipy})_2(\text{biL})][\text{BF}_4]_2$ COMPLEXES IN CD_3CN SOLUTION

biL	X		H(3)	H(4)	H(5)	H(6)
4,4'-X ₂ -bipy	NMe_2	bipy	8.50d	8.19td	7.37td	8.79d
		biL	8.33d	(3.28s)	7.05dd	8.77dd
	CMe_3	bipy	8.66d	8.28td	7.82td	8.88d
		biL	8.44d	(1.50s)	7.73dd	8.82d
	Cl	bipy	8.86d	8.32td	7.93td	8.93d
		biL	8.57d	–	8.08dd	9.15dd
(pyr) ₂	–	bipy	8.82d	8.34td	7.73td	9.13d
		pyr	–	7.37m	8.57t	8.80d

substituent. For the complexes $[\text{Mo}(\text{CO})_4(\text{biL})]$, the coordination shifts of both H(3) and H(6), but not H(5), are sensitive to the nature of X [1]. The proton decoupled carbon NMR spectra of the $[\text{Mo}(\text{bipy})_2(\text{biL})][\text{BF}_4]_2$ complexes have been recorded. Attempts to assign these spectra indicated the need for partially coupled spectra, but our attempts to record these spectra have been hampered by the rather poor solubility of the complexes.

The infrared spectra of $[\text{Mo}(\text{bipy})_2(\text{biL})][\text{BF}_4]_2$ and $[\text{Mo}(\text{bipy})_2(\text{pyr})_2][\text{BF}_4]_2$ as solid mulls all show several absorptions of weak to medium intensity in the region $1650\text{--}1500\text{ cm}^{-1}$. This is in contrast to the observation of a single absorption in the infrared spectra of *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2]$ (1578 cm^{-1}) and *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2\text{-}(\text{NCMe})][\text{BF}_4]_2$ (1610 cm^{-1}) in the same region.

The electronic spectra of the $[\text{Mo}(\text{bipy})_2(\text{biL})][\text{BF}_4]_2$ complexes in acetonitrile solution all show a broad, featureless absorption of moderate intensity ($\log \epsilon > 3.0$) centered at ca. 575 nm. The nature of the substituent, X, in biL has no significant influence on the energy of this absorption maximum. This is in contrast to the absorption spectra of $[\text{Mo}(\text{CO})_4(\text{biL})]$ complexes in which the substituent X exerts a very marked influence on the lowest energy charge transfer absorption [1]. The visible absorption spectrum of $[\text{Mo}(\text{bipy})_2(\text{pyr})_2][\text{BF}_4]_2$ in acetonitrile solution shows a broad band centered at 545 nm, at higher energy than the analogous complexes containing biL. This difference is reminiscent of that which is observed [2] between $[\text{Mo}(\text{CO})_4(\text{pyr})_2]$ and $[\text{Mo}(\text{CO})_4(\text{biL})]$ and emphasises the influence of conjugation in bipy and biL on the properties of their complexes.

Conclusions

The six-coordinate molybdenum(II), $[\text{Mo}(\text{bipy})_2(\text{biL})]^{2+}$ complexes reported in this paper enable a useful comparison to be made with the six-coordinate molybdenum(0) $[\text{Mo}(\text{CO})_4(\text{biL})]$ complexes reported earlier [1]. The molybdenum(II) salts are all very much more sensitive to aerial oxidation in solution than the neutral molybdenum(0) complexes. The proton NMR spectra show clearly that the higher donor/acceptor ratio of bipy compared to CO results in an attenuation in the influence of the substituent X in biL. The formation of $[\text{Mo}(\text{bipy})_2(\text{biL})]^{2+}$ and $[\text{Mo}(\text{bipy})_2(\text{pyr})_2]^{2+}$ in preference to the seven-coordinate monocarbonyl complex is remarkable, given that all the ligands attached to molybdenum(II) are neutral. That this is a metastable condition is demonstrated by the rapid reaction with an alkyl isocyanide which results in formation of $[\text{Mo}(\text{bipy})_2(\text{CNR})_3][\text{BF}_4]_2$; however, trimethylphosphite neither substitutes nor adds to $[\text{Mo}(\text{bipy})_3][\text{BF}_4]_2$ at ambient temperature.

Experimental

Preparations were all carried out under pre-purified dinitrogen using standard techniques. All solvents were dried, deaerated and distilled before use. The preparation of $[\text{Mo}(\text{CO})_2(\text{bipy})_2(\text{NCMe})][\text{BF}_4]_2$ has been described in detail [5]. The ligands biL were prepared in the usual way [1]. IR spectra were recorded on a Perkin-Elmer PE402 spectrometer. Microanalyses were performed by Mr. A. Fassam.

Preparations

4,4'-Dichloro-2,2'-bipyridinebis(2,2'-bipyridine)molybdenum(II) bis(tetrafluoroborate)

4,4'-Dichloro-2,2'-bipyridine (0.295 g, 1.31 mmol) was added to *cis*-[Mo(CO)₂(bipy)₂(NCMe)][BF₄]₂ (0.89 g, 1.31 mmol) in acetonitrile (20 cm³). The resulting solution was heated at gentle reflux for 2 h, during which the colour changed to deep purple. The mixture was then evaporated to dryness. The residue was dissolved in acetone, filtered, and then the filtrate was allowed to mix with diethyl ether by slow diffusion. Purple-black crystals grew from the solution over a period of 4 d. These crystals were isolated by filtration, washed with diethyl ether and dried (0.35 g, 37% yield). (Found: C, 44.7; H, 2.9; N, 10.5. C₃₀H₂₂B₂Cl₂F₈MoN₆ calc: C, 44.6; H, 2.7; N, 10.4%); δ(¹³C NMR, CD₃CN solution) 153.83, 153.10, 151.04, 150.07, 148.25, 145.34, 129.32, 128.10, 126.65, 125.92 p.p.m. IR (Nujol) ν 1600m, 1585w, 1570w, 1530w, 1319w, 1280w, 1060br, 760m, 720m cm⁻¹. Using the same procedure with 4,4'-bis(dimethylamino)-2,2'-bipyridine gave a deep purple complex. (Found: C, 48.9; H, 3.9; N, 14.0. C₃₄H₃₄B₂F₈MoN₈ calc: C, 49.5; H, 4.1; N, 13.6%). δ(¹³C NMR, CD₃CN solution) 156.74, 153.00, 152.38, 150.50, 149.58, 143.03, 127.62, 123.85, 108.57, 105.29 ppm. IR (Nujol) ν 1620s, 1540w, 1319w, 1275m, 1205w, 1060br, 760m, 720w cm⁻¹. With 4,4'-bis(*t*-butyl)-2,2'-bipyridine a deep purple complex was also obtained. (Found: C, 52.9; H, 4.9; N, 9.4. C₃₈H₄₀B₂F₈MoN₆ calc: C, 53.6; H, 4.9; N, 9.9%). δ(¹³C NMR, CD₃CN solution) 155.09, 152.98, 138.06, 127.74, 127.01, 126.77, 113.29 ppm. IR (Nujol) ν 1625w, 1600m, 1580w, 1530w, 1410m, 1319w, 1250m, 1200w, 1060br, 760m cm⁻¹.

Bis-(2,2'-bipyridine)monocarbonylbis(pyridine)molybdenum(II) bis(tetrafluoroborate)

Pyridine (0.21 g, 2.68 mmol) was added to [Mo(CO)₂(bipy)₂(NCMe)][BF₄]₂ (0.91 g, 1.34 mmol) in acetonitrile (20 cm³). The mixture was stirred at ambient temperature overnight and was then carefully evaporated to dryness under reduced pressure. The purple solid residue was washed with diethyl ether and dried in vacuum (0.62 g, 60% yield). (Found: C, 48.6; H, 3.1; N, 11.1. C₃₁H₂₆B₂F₈MoN₆O calc: C, 48.4; H, 3.4; N, 10.9%.) IR (Nujol) ν 1860s, 1600m, 1440s, 1319m, 1260m, 1065br, 960w, 760s cm⁻¹. After this solid is redissolved in acetonitrile and the solution is then heated at reflux for an hour, another purple solid can be isolated by evaporation of the solvent. Found: C, 48.2; H, 3.4; N, 11.3. C₃₀H₂₆B₂F₈MoN₆ calc: C, 48.6; H, 3.5; N, 11.3%. δ(¹³C NMR, CD₃CN solution) 153.70, 149.50, 140.48, 138.20, 126.28, 125.6, 124.82 ppm. IR(Nujol) ν 1620w 1600m, 1585m, 1560w, 1495w, 1420w, 1315m, 1272w, 1050br, 755s 725s cm⁻¹.

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