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Bipyridinedicarbonitrile complexes of molybdenum and tungsten *

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Abstract

The preparation of *cis*-[$Mo(CO)_4$(biL)] (biL denotes 2,2′-bipyridine-x,x'-dicarbonitrile, $x,x' = 4,5$) is reported. Reaction of these complexes with [$W(CO)_5$(THF)] produces [$MoW_2(CO)_{14}$(biL)]. The synthesis of [$W_2CO)_{10}$(biL)] (biL, $x,x' = 5$) is also reported. The ligands and complexes have been characterised by spectroscopy (IR, electronic absorption, NMR) and microanalysis. The synthesis of biL is significantly assisted by ultrasonication.

Introduction

Previous studies on metal complexes of substituted heterocyclic nitrogen donor ligands have shown that the electronic influence of the substituent is enhanced as a consequence of coordination and that it is transmitted to other ligands attached to the metal atom [1]. The solvent polarity significantly influences the properties of these complexes in solution [2,3]. The substituents investigated (halide, OR, NR_2, CR_3, CO_2R) were limited in the nature of their interaction with the heterocyclic ring. Therefore, we have undertaken a wide-ranging study of cyano-substituted derivatives of 2,2′-bipyridine. There has been a lot of interest in recent years in the metal complexes formed by pyridinecarbonitriles [4], but the use of the potentially more interesting bipyridinedicarbonitriles as coordinating ligands has not been reported. We have explored the complexes formed by 2,2′-bipyridine-x,x'-dicarbonitriles ($x,x' = 3$–6) as ligands to various metals. To restrict the scope of the present report, we shall confine our attention to some Group 6 metal complexes in which the substituents are either in direct conjugation with the metal ($x,x' = 4$) or with one another ($x,x' = 5$).

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Results and discussion

The synthesis of 2,2′-bipyridine-5,5′-dicarbonitrile (**1**) has been described [5]; the overall yield from 5,5′-dimethyl-2,2′-bipyridine was low (25%). We have improved this significantly by using ultrasonication of the reaction mixture in which the poorly soluble diamide precursor is dehydrated by trichlorooxophosphorus(V). The overall yield of 2,2′-bipyridine-5,5-dicarbonitrile from 5,5′-dimethyl-2,2′-bipyridine is 54%. The same technique has been applied to the synthesis of 2,2′-bipyridine-4,4′-dicarbonitrile (**2**), which is recorded for the first time.

The ligands **1** and **2** react with [$Mo(CO)_4$\{η^2,η^2-bicyclo[2.2.1]hepta-2,4-diene\}] in tetrahydrofuran to form the dark blue (L = **1**) and purple (L = **2**) complexes [$Mo(CO)_4$L] (**3** and **4**, respectively), which are isolated as well-shaped, analytically pure needles from dichloromethane and petroleum ether or THF/petroleum ether. The characterisation of the complexes is straightforward and consistent with patterns observed earlier [1]. The influence of solvent on the electronic absorption spectrum of the complex **3** of the 5,5′-disubstituted ligand is significant. In a solvent of low polarity (benzene, chloroform), the lowest energy MLCT absorption in the visible region is at markedly (50 nm) lower energy than in the 4,4 -disubstituted derivative, implying that, contrary to expectation, the nitrile substituents in the complex **3** are exerting a greater electron-withdrawing effect upon the metal than in the isomeric complex **4**.

The complexes [$Mo(CO)_4$L] (L = **1**, **2**) react with [$W(CO)_5$(THF)] in tetrahydrofuran solution at ambient temperature to produce the trimetallic complexes [$MoW_2(CO)_{14}$L] as dark brown crystals **5**, **6** which have been characterised by microanalysis and spectroscopy. The stability of the complex **6** of the 4,4′-substituted ligand **2** in solution at ambient temperature is lower than that of the 5,5′-disubstituted ligand in [$MoW_2(CO)_{14}$(**1**)] (**5**)

The ligand **1** reacts with two molar equivalents of [$W(CO)_5$(THF)] in tetrahydrofuran to produce [$W_2(CO)_{10}$(**1**)], which has been isolated as orange crystals **7** and has been characterised by microanalysis and spectroscopy. Whereas the mononuclear complex [$Mo(CO)_4$(**1**)] (**3**) shows two well-separated absorptions in the visible region of the electronic spectrum, the lower energy absorption (at 592 nm in THF) is not present in the electronic absorption spectra of either of the tungsten complexes, [$W_2(CO)_{10}$(**1**)] (**7**) and [$MoW_2(CO)_{14}$(**1**)] (**5**). These spectra appear to show that the pentacarbonyltungsten substituents are the major influence on the low energy CT transitions in the trimetallic complex.

Experimental

3-Methyl- and 4-methyl-pyridine were purchased from Aldrich and coupled (Raney nickel [6]) to give the corresponding x,x'-dimethyl-2,2′-bipyridine ($x,x' = 5, 4$). The dimethyl compound was converted into the x,x'-bis(carboxamide) by way of the bis(carboxylic acid) and the bis(acyl chloride) by standard methods. 2,2′-Bipyridine-4-4′-bis(carboxamide) (0.168 g, 0.694 mmol) was added to trichlorooxophosphorus(V) (6.58 g, 43 mmol) and the mixture in a flask fitted with a condenser and drying tube ($CaCl_2$) was placed in an ultrasonic bath which contained water at room temperature and sonicated (50 kHz) until the suspension

had disappeared (61 h). The temperature of the water in the bath rose to 45°C during this time. 2,2′-Bipyridine-4,4′-dicarbonitrile was isolated from the reaction mixture following hydrolysis (of $POCl_3$), neutralisation (aq. NaOH) and extraction ($CHCl_3$). The solid product was purified by sublimation (150°C, 0.05 torr) and recrystallised from acetonitrile as colourless needles, m.p. 247–248°C. Yield 88%. Analysis: Found C, 69.6; H, 2.8; N, 26.9. $C_{12}H_6N_4$ calcd.: C, 69.9; H, 3.0; N, 27.2%. 2,2′-Bipyridine-5,5′-dicarbonitrile (**1**) was prepared in a similar manner (Yield 86%, m.p. 284–285°C; lit. [5] m.p. 269–271°C). Physical data **1**: ^{1}H NMR δ 8.45 (H(4), $^3J_{34}$ 8.6, $^4J_{46}$ 2.2 Hz), 8.71 (H(3), $^3J_{34}$ 8.3, $^5J_{36}$ 0.9 Hz), 9.13 (H(6), $^5J_{36}$ 0.8, $^4J_{46}$ 2.2 Hz) ppm (acetone-d_6). ^{13}C NMR: δ 110.78 (C(5)), 116.46 (*C*N), 121.66 (C(3)), 140.48 (C(4)), 152.10 (C(6)), 156.97 (C(2)) ppm ($CDCl_3$). IR (Nujol): 2242 vs, 1595 vs, 1538s, 1465 vs, 1375s, 1241s, 1033s, 952m, 852 vs, 740s, 658m cm^{-1}. **2**: ^{1}H NMR δ 7.92 (H(5), $^4J_{35}$ 1.6, $^3J_{56}$ 4.9 Hz), 8.74 (H(3), $^4J_{35}$ 1.6, $^5J_{36}$ 0.9 Hz), 9.01 (H(6), $^5J_{36}$ 0.8, $^3J_{56}$ 4.9 Hz) ppm (acetone-d_6). ^{13}C NMR δ 116.35 (*C*N), 121.89 (C(4)), 123.14 (C(3)), 125.85 (C(5)), 150.34 (C(6)), 155.53 (C(2)) ppm ($CDCl_3$). IR (Nujol): 3099 m, 3075 ms, 2251 ms, 2242 m, 1590 vs, 1549 vs, 1460 vs, 1370 vs, 1256 ms, 1234 ms, 1106 s, 993 s, 908 s, 860 vs, 801 s, 588 s cm^{-1}.

Preparations involving metal carbonyl complexes were carried out under pre-purified dinitrogen by standard techniques. All solvents were dried, deaerated, and distilled before use. IR spectra were observed on a Perkin–Elmer PE 683 spectrometer. NMR spectra were recorded on a JEOL GX 270 spectrometer and electronic spectra were measured with a Shimadzu UV-240 spectrophotometer. Microanalyses were performed by Mr. A.J. Fassam in this Laboratory. The metal carbonyl precursors [$Mo(CO)_4(\eta^2,\eta^2$-$C_7H_8)$] [7] and [$W(CO)_5$(THF)] [8] were prepared by standard methods. (2,2′-Bipyridine-5,5′-dicarbonitrile)tetracarbonylmolybdenum(0) was prepared from the reaction between 2,2′-bipyridine-5,5′-dicarbonitrile (**1**) (0.334 g, 1.62 mmol) and [$Mo(CO)_4(\eta^2,\eta^2$-$C_7H_8)$] (0.487 g, 1.62 mmol) in tetrahydrofuran solution. The product was isolated as a purple/black free-flowing powder after removal of solvent under vacuum, washing with chloroform (20 cm^3), and drying under vacuum (0.641 g, 1.55 mmol). Recrystallisation from dichloromethane/light petroleum or THF/light petroleum yields permanganate-coloured needles. Analysis: Found: C, 46.7, H, 1.3; N, 13.3. $C_{16}H_6MoN_4O_4$ calcd.: C, 46.4; H, 1.5; N, 13.5%. ^{1}H NMR: δ 8.66 (H(4), $^3J_{34}$ 8.5, $^4J_{46}$ 1.9 Hz), 8.94 (H(3), $^3J_{34}$ 8.5, $^5J_{36}$ 0.8 Hz), 9.54 (H(6), $^5J_{36}$ 0.6, $^4J_{46}$ 1.9 Hz) ppm (acetone'-d_6). ^{13}C NMR δ 113.22 (C(5)), 115.89 (*C*N), 125.48 (C(3)), 142.23 (C(4)), 156.22 (C(5)), 157.16 (C(2)), 206.39 (CO, *trans* to L), 222.72 (CO, *cis* to L) ppm ($CDCl_3$). IR: 2245 w, 2025 s, 1918 vs, 1895 sh, 1847 s cm^{-1} (CH_2Cl_2); λ_{max} 647, 385 (C_6H_6); 663, 383 ($CHCl_3$); 592, 378 (THF); 624, 380 (CH_2Cl_2); 565, 373 (Me_2CO); 552, 365 (MeCN); 545, 368 (DMSO) nm. The product of the reaction between 2,2′-bipyridine-4,4′-dicarbonitrile (**2**) (0.094 g 0.456 mmol) and [$Mo(CO)_4(\eta^2,\eta^2$-$C_7H_8)$] (0.137 g, 0.456 mmol) in tetrahydrofuran solution was isolated in a similar manner as a purple/black powder (0.142 g, 0.344 mmol). Recrystallisation from dichloromethane/light petroleum produced permanganate-coloured needles. Analysis: Found: C, 46.2; H, 1.4; N, 13.5. $C_{16}H_6MoN_4O_4$ calcd.: C, 46.4; H, 1.5; N, 13.5%. ^{1}H NMR δ 8.07 (H(5), $^4J_{35}$ 1.7, $^3J_{56}$ 5.8 Hz), 9.16 (H(3), $^4J_{35}$ 1.7, $^5J_{36}$ 0.8 Hz), 9.43 (H(6), $^5J_{36}$ 0.8, $^3J_{56}$ 5.8 Hz) ppm (acetone-d_6). ^{13}C NMR: δ 116.61 (*C*N), 122.36 (C(4)), 127.11 (C(3)), 128.49 (C(5)), 154.51 (C(6), 155.84 (C(2)), 205.30 (CO, *trans* to L), 223.20 (CO, *cis* to L) ppm ($CDCl_3$). IR: 2245 w, 2025 s, 1920 vs, 1895 sh, 1850 s cm^{-1} (CH_2Cl_2). λ_{max} 591,

428 (C_6H_6); 610, **441** ($CHCl_3$); 560, 392 (THF); 586, 425 (CH_2Cl_2); 540, 385 (Me_2CO): 534, 381 (MeCN); 522, 378 (DMSO) nm.

(2,2′-Bipyridine-5,5′-dicarbonitrile)tetradecacarbonylmolybdenumditungsten

A solution of freshly prepared [$W(CO)_5$(THF)] (0.11 g, 0.28 mmol) in tetrahydrofuran was added to a stirred solution containing [$Mo(CO)_4$(**1**)] (0.0575 g, 0.14 mmol) in tetrahydrofuran. The colour of the solution darkened slowly. After a total of 24 h stirring in the dark, the usual work-up gave a dark brown free flowing powder (0.121 g, 0.114 mmol). Recrystallisation from tetrahydrofuran/light petroleum produced dark brown flaky needles. Analysis: Found: C, 30.3; H, 0.9; N, 5.2. $C_{26}H_6MoN_4O_{14}W_2$ calcd.: C, 29.4; H, 0.6; N, 5.3%. IR: 2238 vw, 2078 ms, 2012 m, 1973 m, 1943 vs, 1920 s, 1895 sh, 1850 m cm^{-1} (CH_2Cl_2). λ_{max} 515, 420, 375, 305 (CH_2Cl_2); 450, 420, 380, 300 nm (THF).

μ-(2,2′-Bipyridine-5,5′-dicarbonitrile)bis(pentacarbonyltungsten)

A freshly prepared solution of [$W(CO)_5$(THF)] (0.291 g, 0.735 mmol) in tetrahydrofuran was added to a stirred solution of 2,2′-bipyridine-5,5′-dicarbonitrile (0.074 g, 0.359 mmol) in tetrahydrofuran (60 cm^3). The golden colour of the tungsten-containing solution darkened slowly. After a total of 24 h stirring in the dark, the usual work-up gave orange/yellow crystals of the product (0.0976 g, 0.114 mmol). Analysis: Found: C, 30.6; H, 0.6; N, 6.5. $C_{22}H_6N_4O_{10}W_2$ calcd.: C, 30.9; H, 0.7; N, 6.6%. IR: 2080 m, 1975 w.sh, 1945 vs. 1910 ms cm^{-1} (CH_2Cl_2). λ_{max} 410, 390, 305, 290 nm (THF).

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