

SUBSTITUTED 2,2'-BIPYRIDINES AS LIGANDS. PREPARATION AND CHARACTERIZATION OF 4,4'-DISUBSTITUTED 2,2'-BIPYRIDINE DERIVATIVES OF THE HEXACARBONYLS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN *

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Summary

The preparation of *cis*-[M(CO)₄(biL)] (M = Cr, Mo, W; biL is 4,4'-X₂-2,2'-bipyridine; X = NMe₂, NH₂, OMe, CMe₃, Me, H, Ph, CH=CHPh, Cl, CO₂H, CO₂Me, NO₂) is reported. The ligands and complexes are characterized by spectroscopy (IR, electronic absorption and emission, NMR (¹H, ¹³C, ¹⁵N, ⁹⁵Mo)) and microanalysis. The variations observed in the spectroscopic properties of these complexes are strongly correlated with electronic substituent parameters of the group X. This is most apparent in the lowest energy (visible) absorption which changes by ca. 0.8 eV between the extremes of donor and of acceptor substituent used.

Introduction

The unsubstituted molecule 2,2'-bipyridine (bpy) was developed as an analytical reagent for iron many years ago [1]. Since that time a large number of complexes have been prepared which contain bpy as a ligand bound to a variety of transition metals in different formal oxidation states [2]. These studies typically take advantage of the improved acceptor character of the bpy ligand compared with a simple chelating aliphatic diamine such as 1,2-diaminoethane. The syntheses of derivatives of bpy substituted at various positions on the ring have been described from time to time, especially by Case [3], but very few of these substituted compounds have been employed as ligands to transition metals until recently, when long chain (surfactant) ester derivatives have received attention [4].

A wealth of information has accumulated about phosphorus donor ligands in recent years [5], and an understanding of the interplay between electronic and steric effects of these ligands in controlling the chemical behaviour of the metals to which

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they are attached has emerged. It is appropriate to enquire whether, in a comparable situation, heterocyclic nitrogen donor ligands can produce similar features of chemical reactivity and whether there are advantages to be gained from the use of these ligands compared to phosphorus donor ligands. A careful choice of nuclear substituent in bpy might be expected to influence either the electronic (4,4'- and 5,5'-substitution) or the steric (3,3'- and 6,6'-substitution) properties of the ligand attached to the metal. When attached to metals in low formal oxidation states, the donor/acceptor character of substituted bpy ligands might be expected to influence the redox properties of the complex in a different way from phosphorus donor ligands, because of the essential contrast between the ($d-\pi^*$) and the ($d-d$) interactions respectively.

We report the characterization, particularly by NMR spectroscopy, of a series of 4,4'-disubstituted 2,2'-bipyridines and the preparation and characterization of some of the complexes which these ligands form with the hexacarbonyls of the Group VI transition metals, particularly molybdenum.

Results

Synthesis

The ligands were prepared by literature methods. We find that when care is taken to prepare and handle Raney nickel in an inert atmosphere (Schlenk apparatus) the ligands 4,4'-X₂-bpy (X = Me [6], CMe₃ [7], C₆H₅ [8]) can be prepared in yields at least as good as those quoted. The distribution of products from the reaction [9] between 4,4'-dinitro-2,2'-bipyridine-1,1'-dioxide and phosphorus trichloride is very sensitive to the conditions. The conditions can be chosen to produce optimum yields of 4,4'-dinitro-, 4-chloro-4'-nitro-, and 4,4'-dichloro-2,2'-bipyridine. 4,4'-Dinitro-2,2'-bipyridine-1,1'-dioxide could not be successfully reduced to 4,4'-dinitro-2,2'-bipyridine with any of the following reagents: triphenylphosphine, tri(*n*-butyl)phosphine, thionyl chloride or ethylisocyanide, even at high temperature in polar solvents (refluxing acetonitrile or dimethylformamide). The use of phosphorus trichloride [9] gives the desired product in very low (< 5%) yield. When the reaction is carried out in acetonitrile solution at room temperature, partial substitution occurs giving 4-chloro-4'-nitro-2,2'-bipyridine in good yield. On raising the temperature (refluxing acetonitrile) further substitution occurs and 4,4'-dichloro-2,2'-bipyridine in equally good yield.

The complexes *cis*-[M(CO)₄(4,4'-X₂-bpy)] (M = Cr, Mo, W) were prepared either by direct thermal reaction [10] between [M(CO)₆] and 4,4'-X₂-bpy (X = Me, M = Cr, Mo, W; X = CMe₃, M = Mo) or by substitution in *cis*-[M(CO)₄(η^2, η^2 -bicyclo[2.2.1]hepta-2,4-diene)] with 4,4'-X₂-bpy (X = Me, CO₂Me; M = Cr, Mo, W; X = NMe₂, NH₂, OMe, CH=CHPh, CO₂H, Cl, NO₂; M = Mo) or 4-Cl,4'-NO₂-bpy in tetrahydrofuran solution. Using the latter method, the molybdenum complexes form on stirring the mixture at room temperature for 10–20 h (overnight). The use of these mild conditions was particularly important to ensure that the ligand did not suffer any transmutation of its functional groups during the synthesis of the complex. The chromium and tungsten complexes required heat (reflux) to drive the syntheses to completion. The complex *cis*-[Mo(CO)₄(4,4'-(NO₂)₂-bpy)] was also prepared by heating Mo(CO)₆ with 4,4'-dinitro-2,2'-bipyridine-1,1'-dioxide in either THF or acetonitrile, a reaction reminiscent of the decarbonylation/substitution

procedure which makes use of trimethylamine *N*-oxide [11].

Many of the *cis*-[M(CO)₄(biL)] complexes form large, intensely coloured crystals from THF or dichloromethane/petroleum ether mixtures, while some others (for example, biL = 4,4'-X₂-bpy, X = NMe₂, CO₂H) are poorly soluble and attempts at recrystallisation from various polar solvent mixtures produced only powdery solids.

Spectra

As expected, there are no absorptions in the visible region ($\lambda_{\max} \geq 350$ nm) of the spectra of the ligands. The spectra of the complexes *cis*-[M(CO)₄(biL)] in solution usually show two, fairly symmetric absorptions of medium intensity ($3500 \leq \epsilon \leq 8000$) in the visible region. The lower energy absorption is particularly sensitive to the nature of the substituent X on the bpy rings. This is apparent from the colour of the solutions: for example, in acetonitrile solution the complex (X = NMe₂) is yellow and the complex (X = NO₂) is deep blue. The assignment of these absorptions is ambiguous: clearly they possess a major metal-to-ligand charge transfer (MLCT) component together with some metal localised *d* → *d* (ligand field) character [12]. An electron donor substituent tends to increase the energy of the excited state so that the lowest MLCT absorption moves to higher energy, whereas an electron attracting substituent causes the same MLCT absorption to move to lower energy. A plot of $\lambda_{\max}$ (MLCT) vs. the Hammett substituent σ_p for X (which is a measure of inductive interaction) is linear (correlation coefficient, $c = 0.96$). The influence of the metal on the value of $\lambda_{\max}$ (MLCT) in *cis*-[M(CO)₄(biL)] (M = Cr, Mo, W) is not significant. The emission spectra of the complexes were observed in solid 2-methyltetrahydrofuran glass matrices at 77 K. The complexes are all weak emitters. The intensity of the emission decreases as the substituent group X becomes more electron withdraw-

TABLE I

ABSORPTION MAXIMUM OF LOWEST ENERGY MLCT BAND AND EMISSION MAXIMUM IN COMPLEXES *cis*-[Mo(CO)₄(4,4'-X₂-bpy)]

X	$\lambda_{\max}$ (absorption) ^a (nm)	$\lambda_{\max}$ (emission) ^b (nm)
NMe ₂	430	565 (406) ^c
NH ₂	427	
OMe	453	590 (425) ^c
CMe ₃	467	595 (468) ^c
CH ₃	464	605 (477) ^c
H	474	
C ₆ H ₅	492	
styryl	509	
CO ₂ H	529	
Cl	502	677 (484) ^c
CO ₂ Me	536	700 (483) ^c
Cl/NO ₂	569	
NO ₂	594	

^a THF solution, room temperature. ^b MTHF glass, 77 K. ^c Excitation maximum recorded by irradiating at the emission maximum with the analyser beam and sweeping the source beam.

ing; emission could not be observed for *cis*-[Mo(CO)₄(4,4'-(NO₂)₂-bpy)]. The emission maxima follow the same general trend as the lowest energy MLCT absorption maxima, and can be correlated with the Hammett substituent parameter σ_p^+ , which is a measure of conjugative interaction. The energy difference between the maxima (Table 1) is approximately constant (0.81 ± 0.02 eV) and independent of the substituent X. The solvent dependence of the electronic spectra will be discussed in detail elsewhere [13].

The infrared spectra of *cis*-[M(CO)₄(biL)] in the solid state show bands characteristic of the substituted bpy ligand in the region 1600, 1000 and 850–700 cm⁻¹ which are only slightly shifted from their values in the free ligand but substantially diminished in intensity. The values of $\nu(\text{CO})$ in the complexes demonstrate the electronic influence of the substituent in the bipyridine ring. As the substituent becomes a better acceptor the values of $\nu(\text{CO})$ increase (Table 2). Force constant calculations using the simple force field model proposed by Cotton and Kraihanzel [14] show that both k_1 (equatorial CO ligands) and k_2 (axial CO ligands) increase with the electron acceptor character of the substituent group, X. The metal has only a marginal effect on the values of $\nu(\text{CO})$ in the complexes *cis*-[M(CO)₄(biL)] (M = Cr, Mo, W) as noted in other systems [15].

The ¹H NMR spectra of both the substituted ligands and the complexes show a simple first-order pattern which enables the identification of the bpy ring protons to be made easily in these systems (Table 3). The coupling constants of the bpy ring protons change very little as a result of coordination. Least-squares analysis of the correlation between the proton resonances of the free ligands, 4,4'-X₂-bpy, and of their complexes *cis*-[Mo(CO)₄(4,4'-X₂-bpy)] with the Hammett parameter, $\sigma_p(X)$, of the substituent group X shows that this is significant in each case. For H(3) and H(6) the coordination shift (Δ) is sensitive to the nature of the substituent group, indicating that the chemical shift of these protons is more dependent on the nature of X than in the free ligand. For example, δ (H(6) complex) is given by $(8.97 + 0.91 \sigma_p(X))$ ppm whereas δ (H(6) free ligand) is given by $(8.67 + 0.63 \sigma_p(X))$ ppm. The correlations also show that the separation $|\delta \text{ (H(6) complex)} - \delta \text{ (H(3) complex)}|$

TABLE 2

CARBONYL LIGAND STRETCHING FREQUENCIES, OF *cis*-[Mo(CO)₄(4,4'-X₂-bpy)] IN ACETONITRILE SOLUTION

X	$\nu(\text{CO}) (\text{cm}^{-1})$			
Nme ₂	2010s	1889vs	1865sh	1814s
NH ₂	2010s	1871sh	1823vs	1764sh
OMe	2016s	1898sh	1871sh	1827s
CMe ₃	2014s	1901vs	1875sh	1830s
CH ₃	2019s	1900vs	1868s	1820s
H	2020s	1904vs	1880sh	1828s
C ₆ H ₅	2017s	1902vs	1878sh	1824s
styryl	2014s	1901vs	1875sh	1822s
CO ₂ H	2018s	1909vs	1885sh	1830s
CO ₂ Me	2017s	1907vs	1887sh	1831s
Cl	2018s	1906vs	1882sh	1828s
Cl/NO ₂	2016s	1924vs	1879sh	1828s
NO ₂	2023s	1924s	1900vs	1846vs

TABLE 3

¹H NMR CHEMICAL SHIFTS (δ(ppm)) OF 4,4'-X₂-bpy (A) AND *cis*-[Mo(CO)₄(4,4'-X₂-bpy)](B) IN DMSO-*d*₆ SOLUTION

X	H(3)		H(5)		H(6)		other	
	A	B	A	B	A	B	A	B
NMe ₂	7.83	7.55	6.73	6.78	8.31	8.32	3.15	3.14
NH ₂	7.56	7.23	6.46	6.63	8.03	8.22	5.97	6.84
OMe	7.93	8.22	7.03	7.23	8.50	8.72	3.91	3.91
CMe ₃	8.40	8.62	7.47	7.63	8.61	8.86	1.34	1.42
CH ₃	8.23	8.52	7.27	7.47	8.54	8.79	2.34	2.44
H	8.35	8.65	7.20	7.64	8.53	8.98	7.79	8.19
C ₆ H ₅	8.72	9.12	7.82	7.98	8.80	9.02	7.62, 8.03	7.45, 8.06
Cl	8.48	9.00	7.78	7.90	8.81	9.09	—	—
CO ₂ Me	8.86	9.03	7.96	8.05	8.96	9.32	3.92	3.95
NO ₂	8.95	9.37	8.28	8.30	9.13	9.69	—	—

Least-squares analysis $\delta(H(n))$ (ppm) = X + Y σ_p

<i>n</i>	X	Y	<i>c</i> ^a
3A	8.40	0.87	0.92
3B	8.63	1.33	0.93
5A	7.48	1.12	0.94
5B	7.64	1.09	0.95
6A	8.67	0.63	0.93
6B	8.97	0.91	0.99

^a *c* is the correlation coefficient.

increases more rapidly in the complexes than in the free ligands as the electron donor character of the group X increases. Although $\delta(H(5))$ is sensitive to the nature of X, the coordination shift is independent of the substituent. The influence of the metal atom is not significant.

Solubility problems and the need for long accumulation times conspired to restrict the range of complexes for which ¹³C NMR spectra were recorded. The results (Table 4) show that both C(3) and C(5) are deshielded on coordination by a similar amount (average value 1.70 (C(3)), 1.79 (C(5)) ppm) but that C(6) is significantly more (average value 3.44 ppm) shifted to lower field. In contrast, C(2) is generally shielded on coordination (average value -1.11 ppm) which may be seen as the consequence of a distortion of the ring current in the *syn*-1,4-diazabutadiene fragment of the ligand. The chemical shift $\delta(C(4))$ appears to vary in a random manner: this is probably due to anisotropic effects produced by the substituent attached to this carbon atom. The ¹³C resonances of the CO ligands are rather insensitive to the substituent on the bpy ring.

The ¹⁵N NMR spectrum (recorded at 40 MHz) for the complex *cis*-[Mo(CO)₄(4,4'-(Me₃C)₂-bpy)] and the 4,4'-(Me₃C)₂-bpy ligand show clearly that the nitrogen atoms in the complex ($\delta(^{15}\text{N}) - 154.7$ ppm relative to Me¹⁵NO₂) are more shielded than in the free ligand ($\delta - 116.0$ ppm). Quadrupole broadening prevented the determination of the ¹⁴N NMR spectrum of the complex. The ⁹⁵Mo

TABLE 4

 ^{13}C NMR CHEMICAL SHIFTS ($\delta(\text{ppm})$) OF 4,4'-X₂-bpy (A) AND *cis*-[Mo(CO)₄(4,4'-X₂-bpy)] (B) IN CDCl₃ SOLUTION

X		C(2)	C(3)	C(4)	C(5)	C(6)	other	CO(<i>cis</i>)	CO(<i>trans</i>)
CMe ₃	A	161.11	120.80	156.80	118.38	149.19	35.04	30.65	
	B	161.85	123.65	154.68	123.14	152.48	35.04	30.14	205.2
CH ₃	A	156.68	125.07	148.56	122.29	149.43	21.31		
	B	155.14	126.75	150.31	123.31	152.95	21.53	223.20	205.82
H	A	156.75	124.15	137.40	121.34	149.65			
	B	155.51	125.80	138.01	122.73	153.68			
Cl	A	156.50	124.46	145.38	121.82	150.14			
	B	154.97	126.14	145.05	122.99	153.65		222.09	204.75
COOMe	A	156.72	123.43	138.87	120.80	150.29	165.80	52.82	
	B	154.53	124.10	138.25	121.42	153.16	163.80	53.10	204.30

NMR spectrum (recorded at 28.88 MHz) in the same complex shows $\delta(^{95}\text{Mo}) - 1172.7$ ppm (relative to $\text{Na}_2^{95}\text{MoO}_4$) which is towards the more positive end of the range of values found for ^{95}Mo resonances in molybdenum(0) complexes so far [16]. This is consistent with the donor properties of the ligand acting to decrease the energy gap.

Discussion

The spectroscopic properties of the complexes whose synthesis and characterisation are reported show that the substituents in the 4,4'-disubstituted-2,2'-bipyridine ligands exercise a significant influence. This is most apparent from the colour of the complexes in solution. The energy of the lowest energy absorption changes by 0.77 eV between the extremes of electron donor (NMe_2) and acceptor (NO_2) substituent which we have investigated. The results of infrared and various NMR spectroscopic measurements concur in showing that the electronic influence of the substituent is enhanced as a consequence of coordination and that it is transmitted to the other ligands attached to the metal atom. The nature of the metal atom has no significant influence on the spectroscopic properties which are reported here; however, we expect that the emission spectra and related properties such as excited state lifetimes and photochemistry will be more sensitive to the metal. This has been observed for analogous complexes of ruthenium(II) and osmium(II) [17]. Apart from comparison of wavenumber values of $\nu(\text{CO})$ in di-tertiary phosphine complexes, *cis*- $[\text{M}(\text{CO})_4(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)]$ ($\text{R} = \text{Me}, \text{Ph}$) [18], and di-secondary sulphide complexes *cis*- $[\text{M}(\text{CO})_4(\text{RSCH}_2\text{CH}_2\text{SR})]$ ($\text{R} = 4\text{-YC}_6\text{H}_4$, $\text{Y} = \text{NMe}_2, \text{OMe}, \text{Me}, \text{H}, \text{Cl}, \text{NO}_2$) [19], there is very little information, in detail comparable to that reported here, which shows how remote substituents in bidentate ligand molecules can be employed to exercise precise control of the electronic properties of the metals to which these ligands are attached. The use of this control in the chemistry of other complexes of Group VI metals containing substituted bpy ligands will be the subject of future publications.

Experimental

Materials

2,2'-Bipyridine was purchased from Aldrich and was either recrystallised from hot 60/80 petroleum ether or resublimed (80–100°C/0.05 mmHg) in vacuo before use. 4,4'-Bis(dimethylamino)-2,2'-bipyridine was a generous gift from I.C.I. Organics Division, and was used as received. 4,4'-Dimethyl-, 4,4'-diphenyl- and 4,4'-di(tertiary butyl)-2,2'-bipyridine were prepared from the corresponding 4-substituted pyridine by the action of Raney nickel [20]. The crystalline products were characterised by microanalysis and spectroscopic measurements and their purity was checked by GLC analysis (3% Dexsil 410). 4,4'-Diamino- and 4,4'-dimethoxy-2,2'-bipyridine were prepared from 4,4'-dinitro-2,2'-bipyridine-1,1'-dioxide by the action of iron powder/glacial acetic and by the action of sodium methoxide/phosphorus trichloride respectively [3]. 2,2'-Bipyridine-4,4'-dicarboxylic acid was prepared by permanganate oxidation of 4,4'-dimethyl-2,2'-bipyridine. The acid was converted to the bis(methyl ester) via the acyl chloride [20]. Reaction of 4,4'-dimethyl-2,2'-bipyridine with benzaldehyde under acid conditions produced 4,4'-distyryl-2,2'-bipyridine [21].

Preparation of 4,4'-dichloro-2,2'-bipyridine

4,4'-Dinitro-2,2'-bipyridine-1,1'-dioxide (1.25 g, 4.5 mmol) was added to degassed acetonitrile (50 ml) in a nitrogen atmosphere. Freshly distilled (under N₂) phosphorus trichloride (4 ml, 54 mmol) was added via syringe to the rapidly stirred solution. The mixture was heated at reflux under nitrogen atmosphere during 24 h. The reaction mixture was evaporated to dryness under reduced pressure and the residue was partitioned between chloroform and aqueous sodium hydroxide (5% solution). Solvent was removed from the chloroform fraction by distillation under reduced pressure, leaving crude (99% by GC/MS) 4,4'-dichloro-2,2'-bipyridine. Recrystallisation from ethanol gave the pure (by analysis and GC/MS) compound, m.p. 128.5–129.5°C, lit. [22] 143°C. (GC 1850 × 3 mm 3% Dexsil 410, 210°C, 20 psi N₂, RT 3 min). Yield 0.78 g, 3.4 mmol. $\lambda_{\max}$ (EtOH) 245, 282 nm.

Preparation of 4-chloro-4'-nitro-2,2'-bipyridine

4,4'-Dinitro-2,2'-bipyridine-1,1'-dioxide (0.82 g, 2.95 mmol) was added to dry acetonitrile (40 ml) under strict anaerobic conditions (drybox). Phosphorus trichloride (1.03 ml, 11.8 mmol) was added to the solution and the reaction mixture was stirred at ambient temperature for 24 h. The resulting clear, pale yellow solution was evaporated to dryness under reduced pressure and the residue was then partitioned between chloroform and aqueous sodium hydroxide (5% solution). A white solid was isolated from the chloroform solution and recrystallised from dichloromethane/petroleum ether (40–60°) to give a white powder, m.p. 164–167°C. Analysis: Found: C, 50.9; H, 2.4; Cl, 14.9; N, 18.3. C₁₀H₆ClN₃O₂ calcd.: C, 51.0; H, 2.6; Cl, 15.1; N, 17.8%. $\lambda_{\max}$ (EtOH) 282, 310 nm; $\delta(^1\text{H})$ (DMSO-*d*₆ solution) 7.72, 8.28 (H(5)), 8.42, 8.92 (H(3)), 8.76, 9.09 (H(6)) ppm. GC 1850 × 3 mm 3% Dexsil 410, 210°C, 20 psi N₂, RT 5 min. IR (Nujol mull) 3100w, 1603w, 1523s, 1355s, 1250w, 1090w, 1060w, 990w, 920w, 893m, 837m, 762w, 735m, 718s cm⁻¹.

Preparation of 4,4'-dinitro-2,2'-bipyridine

4,4'-Dinitro-2,2'-bipyridine-1,1'-dioxide (1.0 g, 3.6 mmol) was added to a dinitrogen-saturated, anhydrous chloroform solution (25 ml) of phosphorus trichloride (3.0 ml, 13.9 mmol) in an inert atmosphere. The reaction mixture was stirred and heated at reflux for 1.5 h, after which the reaction mixture was filtered (cannula) to remove unreacted dioxide (0.81 g). The filtrate was partitioned with aqueous sodium hydroxide (5% solution). The yellow solid isolated by evaporation of the chloroform layer was twice recrystallised from acetonitrile to give well-formed pale yellow crystals (0.09 g, 0.36 mmol), m.p. 192–193°C; lit [9] 191.5–194.5°C; GC 1700 × 4 mm 10% OV1, 300°C isothermal, 30 psi N₂, RT 5 min; 1850 × 3 mm 3% SE30, 230°C, 35 psi N₂, RT 9 min; 1850 × 3 mm 3% Dexsil 410, 230°C, 20 psi N₂, RT 8 min.

Preparation of tetracarbonyl(4,4'-dichloro-2,2'-bipyridine)molybdenum

[Mo(CO)₄(η^2, η^2 -bicyclo[2.2.1]hepta-2,4-diene)] [23] (1.05 g, 3.5 mmol) and 4,4'-dichloro-2,2'-bipyridine (0.78 g, 3.48 mmol) were dissolved in THF (30 ml). On stirring the solution rapidly became red-purple. After stirring overnight (total 16 h) the solution was filtered (cannula) and the solvent evaporated under reduced pressure. The red-purple residue was dissolved in methylene chloride and recrystallised by carefully laying light petroleum ether (40–60°) on top of the intensely

coloured solution with a syringe. Purple crystals were formed on storing the solution at 0°C for two days. These crystals were isolated by filtration, washed with light petroleum ether and dried in vacuo. Yield: 1.37 g (91%). Analysis: Found: C, 38.0; H, 1.4; Cl, 16.6; Mo, 22.5; N, 6.5. $C_{14}H_6Cl_2MoN_2O_4$ calcd.: C, 38.0; H, 1.4; Cl, 16.4; Mo, 22.2; N, 6.5%. The complexes *cis*-[Mo(CO)₄(4,4'-X₂-bpy)] X = NMe₂: Found: C, 47.3; H, 4.0; Mo, 20.9; N, 12.1; $C_{18}H_{18}MoN_4O_4$ calcd.: C, 48.0; H, 4.0; Mo, 21.3; N, 12.4%; X = NH₂: Found: C, 41.8; H, 2.6; Mo, 24.4; N, 13.8. $C_{14}H_{10}MoN_4O_4$ calcd.: C, 42.6; H, 2.5; Mo, 24.4; N, 14.2%. X = OMe: Found: C, 45.2; H, 2.8; Mo, 23.0; N, 6.5. $C_{16}H_{12}MoN_2O_6$ calcd.: C, 45.3; H, 2.8; Mo, 22.6; N, 6.6%. X = CMe₃: Found: C, 55.2; H, 5.0; Mo, 20.1; N, 5.4. $C_{22}H_{24}MoN_2O_4$ calcd.: C, 55.5; H, 5.0; Mo, 20.2; N, 5.9%. X = CH₃: Found: C, 49.6; H, 2.7; Mo, 24.4; N, 7.1. $C_{16}H_{12}MoN_2O_4$ calcd.: C, 49.0; H, 3.1; Mo, 24.5; N, 7.1%. X = $\text{CH}=\text{CHPh}$: Found: C, 62.9; H, 3.6; Mo, 16.5; N, 4.6. $C_{30}H_{20}MoN_2O_4$ calcd.: C, 63.4; H, 3.5; Mo, 16.9; N, 4.9%. X = COOH: Found: C, 43.9; H, 2.8; Mo, 21.3; N, 5.5. $C_{16}H_8MoN_2O_8$ calcd.: C, 42.5; H, 1.8; Mo, 21.2; N, 6.2%. X = COOMe: Found: C, 45.2; H, 2.3; Mo, 20.0; N, 5.8. $C_{18}H_{12}MoN_2O_8$ calcd.: C, 45.0; H, 2.5; Mo, 20.0; N, 5.8. X = Cl, NO₂: Found: C, 37.1; H, 1.3; Cl, 7.3; Mo, 21.4; N, 9.9. $C_{14}H_6ClMoN_3O_6$ calcd.: C, 37.9; H, 1.4; Cl, 8.0; Mo, 21.7; N, 9.5%. X = NO₂: Found: C, 37.4; H, 1.4; Mo, 19.3; N, 12.7. $C_{14}H_6MoN_4O_8$ calcd.: C, 37.0; H, 1.3; Mo, 19.8; N, 12.3% were prepared in a very similar manner: other spectroscopic properties of these complexes are listed in Tables 1–4. The complexes were all recrystallised from either CH₂Cl₂/petroleum ether or THF/petroleum ether mixtures. The use of [Cr(CO)₄(norbornadiene)] [23] in the same synthetic procedure with heating the mixture of reagents at reflux gave the complexes *cis*-[Cr(CO)₄(4,4'-X₂-bpy)]: X = CH₃: Found: C, 54.6; H, 3.3; Cr, 14.3; N, 7.9; $C_{16}H_{12}CrN_2O_4$ calcd.: C, 55.2; H, 3.5; Cr, 14.9; N, 8.1%. $\delta(^1H)$ (CD₂Cl₂ soln.) 2.49 (CH₃), 7.83 (H(3)), 7.17 (H(5)), 9.08 (H(6)) ppm; $\nu(CO)$ (CH₂Cl₂ soln.) 2012m, 1904s, 1881vs, 1829m cm⁻¹. λ_{max} (CH₂Cl₂ soln.) 492 nm. X = COOMe: Found: C, 49.0; H, 2.9; Cr, 11.7; N, 6.0. $C_{18}H_{12}CrN_2O_8$ calcd.: C, 49.5; H, 2.8; Cr, 11.9; N, 6.4%. $\delta(^1H)$ (CDCl₃ soln.) 8.72 (H(3)), 7.93 (H(5)), 9.43 (H(6)), 4.05 (CH₃) ppm; λ_{max} (CHCl₃ soln.) 585 nm. In like manner using [W(CO)₄(norbornadiene)] [23], the following complexes *cis*-[W(CO)₄(4,4'-X₂-bpy)] were prepared: X = CH₃: Found: C, 39.0; H, 2.5; N, 5.6; W, 37.9. $C_{16}H_{12}N_2O_4W$ calcd.: C, 40.0; H, 2.5; N, 5.8; W, 38.3%. $\delta(^1H)$ (CD₃CN soln.) 2.58 (CH₃), 6.59 (H(5)), 7.58 (H(3)), 8.56 (H(6)) ppm; $\nu(CO)$ (CH₂Cl₂ soln.) 2012m, 1896s, 1873vs, 1824m cm⁻¹; λ_{max} (CH₂Cl₂ soln.) 507 nm. X = COOMe: Found: C, 37.8; H, 2.1; N, 4.7; W, 31.9. $C_{18}H_{12}N_2O_8W$ calcd.: C, 38.0; H, 2.4; N, 4.9; W, 32.4%. $\delta(^1H)$ (CDCl₃ soln.) 4.08 (CH₃), 7.91 (H(5)), 8.79 (H(3)), 9.49 (H(6)) ppm; λ_{max} (CHCl₃ soln.) 574 nm.

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