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On Charge Transfer-assisted Polynucleation Reactions. A Trinuclear Carbonyltungsten Complex of Ambident 4,4′-Bipyrimidine

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Abstract

Coordinative saturation of the ligand 4,4′-bipyrimidine has been achieved in the $N^1,N^{1'}$-bis-(pentacarbonyltungsten)-$N^3,N^{3'}$-tetracarbonyltungsten complex. Electrochemical and spectroscopic studies of the compound and its anion radical exhibit an MLCT absorption maximum at unexpected high energy, despite a small HOMO/LUMO gap. Inspection of band widths shows that large Franck–Condon contributions from the structurally flexible $W(CO)_5$ fragments are responsible for the hypsochromic shift relative to the mononuclear chelate system. The propensity of polyfunctional π acceptor ligands towards complete coordinative saturation with electron rich metal fragments is discussed.

Introduction

4,4′-Bipyrimidine, bpm, is a rather weakly basic ($pK_{BH^+} = 1.5$) ambidentate ligand [1] which can bind, for example, two $W(CO)_5$ fragments at the peripheral $N^1,N^{1'}$ centers (compound 2) before converting to the more stable $N^3,N^{3'}$-coordinated tetracarbonyl chelate complex (1) [2], see eqn. (1).

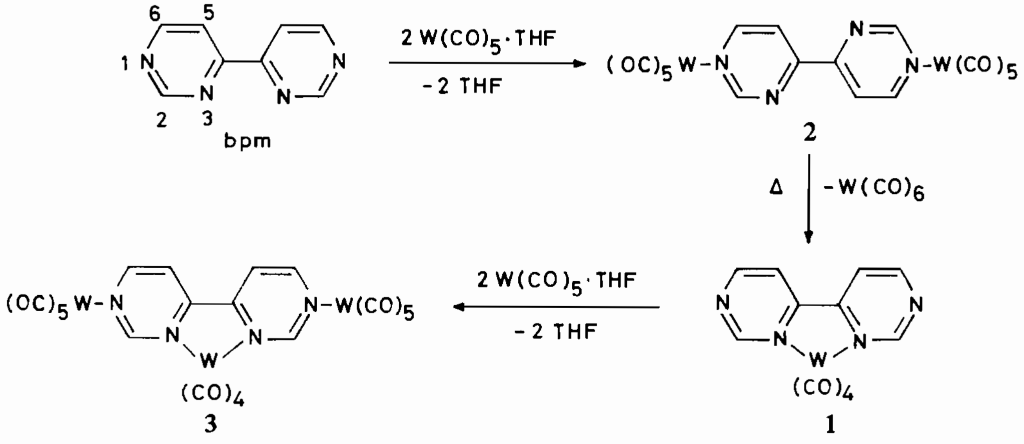
Spectroscopic studies of deeply coloured tetracarbonyl species such as **1** have established efficient back bonding in these complexes, *i.e.* a considerable amount of electron density is transferred to the low-lying π^* level of the ligand from the filled metal d orbital of appropriate symmetry [1, 2]. We can show here that a chemically relevant consequence of such back donation in **2** is the increase in basicity at the other coordination centers of bpm, *i.e.* the ligand thus becomes sufficiently nucleophilic to bind yet another two neutral metal carbonyl fragments $W(CO)_5$ at $N^1,N^{1'}$ to form the first trinuclear carbonylmetal complex (**3**) of a bidiazine ligand.

Experimental

Instrumentation, spectroscopic and electrochemical methodology have been described [2, 3]. Bpm and its $W(CO)_4$ complex were synthesized according to published procedures [2, 4].

$W(CO)_4(\mu,\eta^4\text{-}bpm)[W(CO)_5]_2$ (3)

80 mg (0.176 mmol) (bpm)$W(CO)_4$ (**1**) were reacted with *ca.* two equivalents of (THF)$W(CO)_5$,



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generated photolytically from 150 mg (0.42 mmol) $W(CO)_6$ in 200 ml THF. The dark solution was left for one day at room temperature, after which some precipitate had been formed. Further precipitation by the addition of hexane under conditions where **1** and **2** remain soluble yielded 115 mg (59%) of **3** as a virtually black powder. Poor solubility, dissociative lability in coordinating solvents, and light sensitivity of the material prevented purification by recrystallization or column chromatography at low temperatures [2, 3].

Results and Discussion

The little soluble tetradecacarbonyltritungsten complex (**3**) could be characterized by vibrational and electronic spectroscopy, by cyclic voltammetry and by ESR studies of the anion radical form (Table I). As would be expected, the CO stretching frequencies comprise typical values for penta- and *cis*-tetracarbonyls [2] (Fig. 1).

TABLE I. Spectroscopic Data of Complexes $(bpm)W_x(CO)_y$

		Complex		
		1	**2**	**3**
$\nu(CO)^a$	A_1(p)		2065	2075
	A_1(t)	2000		2005
	E_1(p)		1935	1935
	A_1(p)		1907	~1905
	B_1(t)	1900		~1905
	A_1(t)	1895		~1905
	B_2(t)	1850		1855
$E_{red}{}^b$		−0.68	−0.67	−0.43
$E_{ox}(pa)^b$		+0.86	+1.01	+0.93 +1.15
$\Delta E_{red/ox}(pa)$		1.50	1.64	1.32
$E_{op}{}^{max\,c}$		2.04	2.70	2.14
χ^d		0.54	1.06	0.82
$a(N^{1,1'})^e$		0.30^g	0.378	0.34^g
$a(N^{3,3'})$		0.27	0.132	0.17^g
$a(H^{2,2'})$		f	0.132	0.17^g
$a(H^{5,5'})$		0.15^g	0.199	f
$a(H^{6,6'})$		0.15^g	0.144	0.34^g
g^e		2.0024	2.0046	2.0031

[a] Carbonyl stretching frequencies (in cm^{-1}) of penta-(p) and tetracarbonyltungsten fragments (t); THF solutions. [b] Potentials (in V *vs.* SCE) from cyclovoltammetry at a glassy carbon electrode in DMF/0.1 M $Bu_4N^+ClO_4^-$, scan rate 100 mV/s. (pa) refers to anodic peak potential for irreversible oxidation. [c] Energy (in eV) at absorption maximum in THF solution. [d] In (e)V, see eqn. (2) and text. [e] Hyperfine coupling constants *a* (in mT) and *g* factors of anion radical complexes. [f] Not observed. [g] Uncertainty +0.02 mT due to poor resolution.

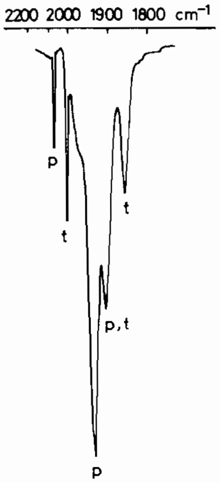


Fig. 1. IR spectrum of **3** in the carbonyl stretching region (THF solution). Pentacarbonyl- (p) and tetracarbonyltungsten bands (t) are indicated.

Electrochemistry reveals a very facile and reversible one electron reduction of the complex to yield a stable anion radical; multiple coordination of electrophilic carbonylmetal fragments is known to cause effective stabilization of the ligand LUMO [5]. The ESR parameters of $3^{-\cdot}$ are different from that of radical anions $bpm^{-\cdot}$, $1^{-\cdot}$ or $2^{-\cdot}$ [1, 6], coordination of metals to N^1 and N^3 centers is apparent from the characteristical [6–8] increase of both ^{14}N coupling constants relative to the values for the free ligand anion. The balanced spin distribution as illustrated also by the proton hyperfine splitting is related to the stability of radical $3^{-\cdot}$, the *g* factor lies between those of $1^{-\cdot}$ and $2^{-\cdot}$ (Table I).

Irreversible oxidation waves corresponding to electron removal from the tetracarbonyltungsten (~+0.8 V *versus* SCE) [9] and $W(CO)_5$ groups (~+1.1 V) [2] are also observed, yet despite the obvious narrowing of the redox potential difference, the energy of the metal-to-ligand charge transfer (MLCT) absorption maximum of **3** is higher than that of the mononuclear tetracarbonyltungsten complex (Table I, Fig. 2).

This initially unexpected result is attributed to the larger widths of charge transfer absorption bands for the complexes **2** and **3** with pentacarbonylmetal fragments (band half-widths $\Delta H_{1/2} = 6000–8000\ cm^{-1}$). High structural flexibility because of 'freely' rotating $W(CO)_5$ groups apparently facilitates considerable geometrical change between the ground and MLCT excited state so that higher vibrationally excited states become significantly populated on 'vertical' optical excitation [10, 11] and a broader absorption band results (Scheme 1: case A). In contrast, rotation and vibration are much more restricted in a rigid chelate complex such as **1** which

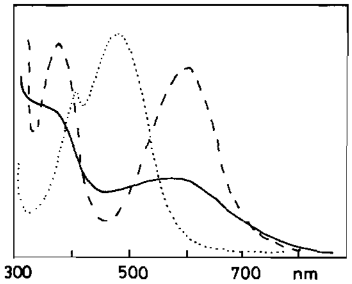
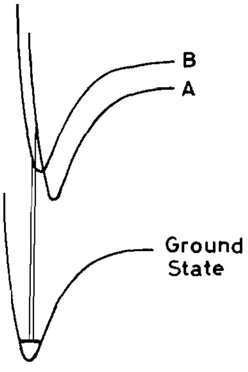


Fig. 2. Absorption spectra of **1** (– – –), **2** (······) and **3** (——) in THF. The absorbance scale is different for each spectrum.

displays a narrower MLCT absorption band ($\Delta H_{1/2}$ = 3800 cm^{-1}) and, consequently, a bathochromically shifted absorption maximum (Scheme 1 : case B).



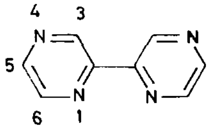
Scheme 1.

The large Franck–Condon contributions from the 'free' pentacarbonylmetal groups are thus responsible for the unexpected sequence, *viz.* mononuclear < trinuclear < binuclear complex, for the energies of absorption maxima (Table I). Conversely, this comparison illustrates the possible narrowing and bathochromical shift of MLCT absorption bands in tetracarbonyl chelate complexes [1–3, 5]; values of $\Delta H_{1/2}$ from 2000 to 5000 cm^{-1} have been reported for binuclear chelate complexes of $Mo(CO)_4$ in THF solution [5]. The discussion of the three compounds **1**–**3** also demonstrates the value of the relation (2) between redox potential difference $E_{red/ox}$ and optical transition energy E_{op}^{max} for the understanding of electronic structure [10–13].

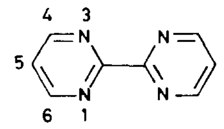
$$E_{op}^{max}\ (eV) = E_{red/ox}\ (V) + \chi \qquad (2)$$

While χ is still relatively small for the chelate complex **1** since E_{op} had to be determined in moderately polar THF [12], the pentacarbonyltungsten containing complexes **2** and **3** exhibit values about twice as large (Table I), in agreement with the rationalization given above.

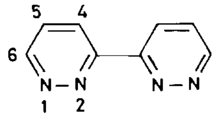
As concerns the chemical consequences of coordination between electron rich metal fragments and polydentate π acceptor ligands, it seems that efficient back donation alone can already activate all available sites for coordination. In fact, we have often found it difficult to obtain and isolate only partly coordinated species of such ligands because of their propensity towards saturation of all available coordination sites [5]—an effect which is not common in the chemistry of 'ordinary' ligands. In the same vein, Lever and coworkers have observed maximum additional coordination of Lewis acids and cations in complexes of the bidiazine ligand 2,2′-bipyrazine (bpz) [14, 15].



bpz



bpym



bpdz

An unexpected polynucleation reaction involving only uncharged species was reported recently for the potentially tetradentate acceptors TCNE and TCNQ, yielding first tetranuclear complexes with unique spectroscopic properties [16]. The latter case involves complete intramolecular electron transfer, yet even partial metal-to-ligand back donation can result in the formation of polynuclear complexes with ligands such as the ambident bidiazines. While bpz [14, 15] and 2,2′-bipyrimidine (bpym) examples [5, 17, 18] had already been reported, our results presented here for bpm suggest that the fourth member in the series of symmetrical bidiazine chelate ligands, *viz.* 3,3′-bipyridazine (bpdz) [2, 3], should also be able to form complexes with full coordinative saturation.

Acknowledgements

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