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The Reaction of Heterocyclic Anion Radicals with Group VI Carbonyls. ESR Characterization of Paramagnetic Binuclear Complexes

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Tetracarbonyl complexes of group VI metals with chelating 2,2'-bipyridine or 1,4-diazadiene ligands undergo reversible one-electron reduction [1, 2] and yield persistent radical anions on treatment with alkali metals [2, 3]. Recently the preparation and electrochemical behaviour of binuclear pentacartonyl complexes with bridging diazines was reported, these compounds exhibit considerably lowered, reversible reduction potentials [4]. Attempts to chemically reduce the complexes failed, however; only the anion radical of the free ligand was obtained [4]. This communication shows that the reaction of pyrazine (pz) or 4,4'-bipyridine (4,4'-bipy) radical anions $L^{\cdot-}$ with $M(CO)_6$, M = Mo, W *does* yield the radical anions of pentacarbonyl complexes (1) which could be identified and analyzed by high resolution ESR (Fig. 1).

$$K^+L^{\cdot-} \xrightarrow[DME]{\text{excess } M(CO)_6} K^+[(OC)_5M{-}L{-}M(CO)_5]^{\cdot-} + 2\,CO \quad (1)$$

The ion radical complexes obtained are persistent in solution for several months. This remarkable stability contrasts to the failure to generate corresponding chromium complexes in the same way or to form paramagnetic complexes from isomeric radical anions like pyridazine$^{\cdot-}$ or 2,2'-bipyridine$^{\cdot-}$ [3]; the peculiar reactivity in these systems is under further investigation.

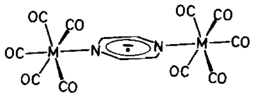
ESR analysis of the symmetric (D_{2h}) radical anion complexes provides valuable information (Table I): Besides ^1H and ^{14}N coupling the hyperfine interaction of metal isotopes ($^{95,97}Mo$, ^{183}W) and of carbonyl ^{13}C nuclei in natural abundance is observed (*cf.* Fig. 1).

When compared to the free ligand anion radicals (Table I), the paramagnetic complexes show distinct differences:

i) The proton coupling a_H is slightly reduced upon complexation, indicating a flow of spin density to the nitrogen centres and, possibly, to the metal carbonyl fragments. Complexation of $pz^{\cdot-}$ by AlR_3 does not lead to a comparable effect [5].

ii) Consequently, the nitrogen constants a_N of the complexes have increased significantly relative to the free anion radicals, and metal isotope coupling reveals non-zero spin population at the metal centre [2].

The ^{13}C satellite lines (Fig. 1) are of particular interest: Careful computer simulation shows that this hyperfine splitting is caused by eight equivalent carbon atoms in natural abundance, suggesting a configurationally stable structure with six-coordinate metal atoms and two sets of 8 equatorial and 2 axial carbonyl groups (2).



(2)

Unambiguous identification of $a_{^{13}C}$ and its magnitude – a_C = 0.33 mT was reported for ^{13}C enriched $Fe_3(CO)_{12}^{\cdot-}$ [6] – allow to analyze the disputed [1–3] spin distribution in metal carbonyl complexes of reduced ligands. It seems likely now to describe the stabilized [2, 4] radical anion ground state of these systems by hyperconjugative interaction of the ligand LUMO (π^*) with antibonding metal–carbonyl σ^* orbitals. This interpretation would not only explain the considerable ^{13}C splitting because of the overlap between π-system and equatorial σ_{M-CO}

TABLE I. ESR Parameters for Radical Anions of Binuclear Bispentacarbonyl Complexes, a_X in mT.

	$pz^{\cdot-}$	$pz(Mo)_2^{\cdot-}$	$pz(W)_2^{\cdot-}$	4,4'-bipy$(Mo)_2^{\cdot-}$	4,4'-bipy$(W)_2^{\cdot-}$	4,4'-bipy$^{\cdot-}$
a_N	0.718	0.818	0.823	0.432	0.433	0.362
a_H	0.264	0.253	0.254	0.201	0.192	0.237
				0.071	0.080	0.044
a_M		0.150	0.286	0.088	0.163	
a_C^{CO}		0.11	0.12	0.07	0.08	
g	2.0035	2.0042	2.0061	2.0039	2.0050	2.0032

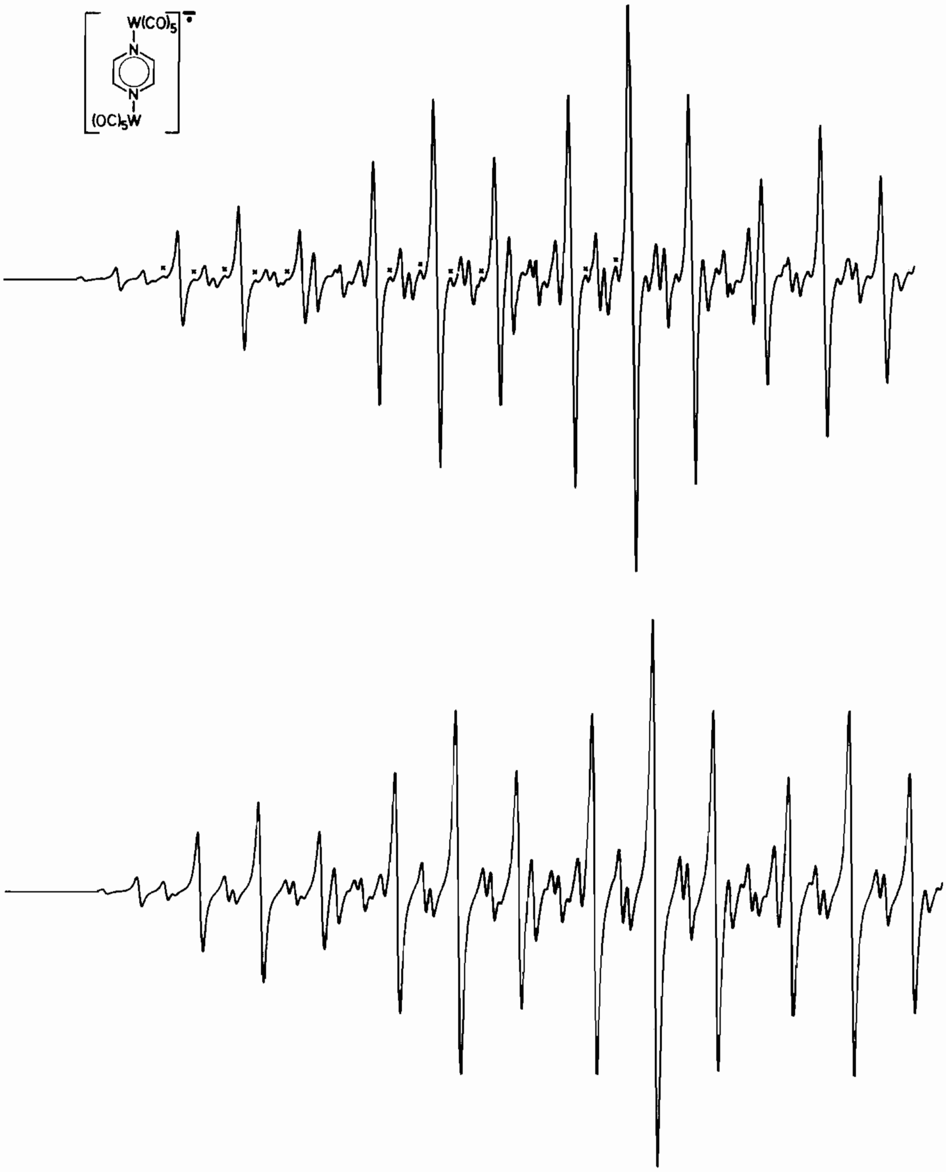


Fig. 1. ESR spectrum (low-field section) of bis(pentacarbonyltungsten)pyrazine radical anion in 1,2-dimethoxyethane at 300 K with computer simulation (below). Dotted lines are ^{13}C satellites which can be simulated separately with 8 carbon atoms in their natural abundance of 1.1%.

bonds, it would also help to understand the trend to larger metal [7] and carbon splitting in the tungsten derivatives because of the lower lying σ^*_{W-CO} orbitals.

Moreover, this model can be further applied to explain the ^{31}P coupling constants in paramagnetic dicarbonyl complexes containing P-ligands [2, 8]: *cis*-configuration leads to relatively small $a_{^{31}P}$ splitting [8], while *trans*-configurated complexes with their σ_{M-P} bonds in optimum position for hyperconjugative interaction exhibit very large ^{31}P coupling constants [2, 8].

Acknowledgement

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