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ELECTRON SPIN RESONANCE STUDIES OF THE RADIOLYSIS OF BI-π-CYCLOPENTADIENYLALKYLS OF MOLYBDENUM AND TUNGSTEN

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Summary

Exposure of $(C_5H_5)_2Mo(CH_3)_2$ and $(C_5H_5)_2W(CH_3)_2$, prepared from the corresponding dichlorides, to ^{60}Co γ-rays at 77 K gave $H_2\dot{C}ML_3$ carbene species characterised by their ESR spectra, together with a central feature possibly due to the parent cations. Dilute solutions in CD_3OD gave features assigned to the parent anions which were converted on bleaching with visible light into methyl radicals, and $H_2\dot{C}ML_3$ radicals. From the magnitude of the ^1H and ^{183}W hyperfine coupling constants, it is deduced that the SOMO for $H_2\dot{C}WL_3$ radicals is strongly localised on carbon.

Dilute solutions in aqueous sulphuric acid also gave species with $A(2H) = 20$ G, identified as the carbene derivatives, $H_2\dot{C}ML_3$. These were formed on annealing, as signals assigned to $HSO_4\cdot$ radicals were lost.

There have been a variety of recent ESR studies of paramagnetic organometallic complexes formed by chemical or electrochemical redox processes from more stable diamagnetic precursors. In particular, a range of d^1 complexes have been prepared from $(C_5H_5)_2ML_2$ complexes, with M = Ti [1,2], M = Nb or Ta [3] and M = Cr, Mo or W [4]. Also, the cation $[(Cp)_2MoCl_2]^+$ and related species have been prepared in solution [5].

We have recently helped to establish methods whereby ionizing radiation can be harnessed to give good yields of electron-gain or electron-loss species in rigid media [6–8] but there have, as yet, been few attempts to prepare paramagnetic organometallic derivatives in this way. We were able to prepare the titanium(III) complex, $[Ti(Cp)_2Cl_2]^-$ in this way [9] and also a range of electron adducts from metal carbonyl halides such as $[Mo(Cp)(CO)_3I]$, $[W(Cp)(CO)_3I]$ and $[Fe(Cp)(Co)_2Cl]$ have been prepared by this procedure [10].

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The aim of the present study was to attempt to prepare the anions and cations of $(Cp)_2Mo(CH_3)_2$ and $(Cp)W(CH_3)_2$ using ionizing radiation and to study them using ESR spectroscopy. In the event, we have not obtained much information about the parent ions, but some interesting products have been detected.

Experimental

Preparation

The bicyclopentadienylmolybdenum(IV) dichloride and tungsten(IV) precursors to the corresponding dimethyl analogues were prepared and characterised according to published procedures [11]. The hydride precursors to the dichlorides were prepared and characterised in a similar manner [12]. Methylation of the dichlorides was conducted both with zinc dimethyl at 0 °C [13] and stoichiometric methyllithium at room temperature [14] in an atmosphere of prepurified nitrogen. The reaction mixture with methyllithium was refluxed for 1 h and allowed to stand for several hours at room temperature, after which time a precipitate was observed. Recrystallization of the solid from ether-light petroleum at −78 °C gave yellow $(C_5H_5)_2W(CH_3)_2$ (m.p. ca. 200 °C-decomp) and orange-brown $(C_5H_5)_2Mo(CH_3)_2$ (m.p. ca. 200 °C-decomp). All preparations and purifications were performed under nitrogen or in vacuo. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee, and Huffman Laboratories, Wheat Ridge, Colorado.

The deuterated dimethyl analogue of bicyclopentadienyltungsten(IV) dichloride was prepared from the bicyclopentadienyltungsten(IV) dichloride and deuterated methyllithium. Deuterated methyllithium was prepared from deuterated methyl iodide and lithium sand [14]. Methyllithium was obtained commercially (Pfaltz & Bauer) as a 1 *M* solution in diethyl ether. Zinc dimethyl was also commercially obtained (Alfa Ventron) as was deuterated methyl iodide (Aldrich). Molybdenum pentachloride (re-sublimed), tungsten hexachloride (re-sublimed), sodium borohydride, and sodium cyclopentadienide (2–3 *M* in tetrahydrofuran) were obtained from Alfa Ventron.

The purity of these products was checked by NMR spectroscopy (360 MHz). Incidentally, it was established that treatment of the bicyclopentadienylmolybdenum(IV) dichloride and tungsten(IV) dichloride with an excess of methyllithium at −78 °C gave products which show further alkylation of the cyclopentadienyl rings [13].

Methyl-d_3-alcohol-d_1 100 atom% (Aldrich Chemical Ltd.) was employed as a solvent for the preparation of electron-gain centres. Solution of these compounds in CD_3OD was conducted in a nitrogen atmosphere and the solutions were immediately frozen to 77 K as small glass beads.

The beads were irradiated in a Vickrad ^{60}Co γ-ray cell at a dose rate of ca. 1 Mrad h^{-1} at 77 K. The beads became deep purple upon irradiation. ESR spectra were recorded with a Varian E-109 spectrometer equipped with 100 kHz field modulation, Hewlett Packard 5255A Frequency Converter and Varian E-935 ESR Data Acquisition System. All ESR measurements were recorded at 77 K.

After the ESR spectra of the frozen beads were recorded at 77 K, the beads were photobleached with a white light source (ca. 0.5 h), using a plexiglass heat shield. The ESR spectra of the photobleached samples were recorded at 77 K and the beads annealed to determine further spectral changes.

Some experiments were performed using methyltetrahydrofuran solvent. The initial spectra were dominated by features from solvent radicals, but by careful annealing it was possible to establish that features very similar to those for the CD_3OD solutions were obtained from the Mo and W derivatives.

For the preparation of electron-loss centres, we initially attempted to use various freon solvents, especially $CFCl_3$, which has proven to be most effective for the preparation of a range of organic radical cations [8,15–18]. However, poor ESR spectra were obtained, so we turned our attention to solutions in aqueous sulphuric acid. Whilst this medium does not normally give radical-cations directly, it does sometimes yield cations by reaction with $HSO_4\cdot$ radicals on annealing [19,20].

^1H NMR studies

$(C_5H_5)_2W(CH_3)_2$ and $(C_5H_5)Mo(CH_3)_2$ exhibit two sharp singlets in deuterobenzene at 3.5 and 0.4 ppm, assigned to the C_5H_5 and CH_3 protons respectively [13]. (Elemental analyses for $(C_5H_5)_2Mo(CH_3)_2$ were also in good accord with expectation.) When other methyl derivatives of the bicyclopentadienyltungsten dichlorides were prepared by the reaction of the dichlorides with excess methyllithium, compounds of apparent composition $[C_5(CH_3)_2H_3]_2W(CH_3)_2$ were obtained (H, Found: 5.54; calcd.: 5.50%). Proton spectra in deuterium oxide show splittings comparable to those observed elsewhere for similar methylated cyclopentadienyl derivatives [13]. The molybdenum analogue showed similar splittings. Proton NMR measurements were recorded on a Nicolet 360 MHz NMR spectrometer at the University of Illinois.

Results and discussion

Solutions of the molybdenum and tungsten complexes in CD_3OD were violet after irradiation, showing that trapped electrons were formed as well as electron-gain centres from the metal complexes. However, solutions in methyltetrahydrofuran were orange, showing that electron addition was more efficient in this solvent (e_t^- centres are blue in this solvent). Strong central features (Fig. 1a) are assigned to the parent anions together with solvent radicals (mainly $\cdot CD_2OD$). On annealing, weak residual signals assigned to $[(C_5H_5)W(CH_3)_2]^-$ were obtained free of signals from solvent radicals, so that all three g-components could be measured (Table 1). This was not possible for the molybdenum derivative, so that only g_{max} and g_{min} could be obtained. However, the intermediate g-value must be close to that of the free-spin (ca. 2.002), as for the tungsten derivative.

At high gain, features due to $D\dot{C}O$ radicals were observed together with other lines derived from the complexes. The $D\dot{C}O$ radicals, formed from the solvent, were rapidly destroyed on exposure to visible light, whilst the remaining features were greatly enhanced (Fig. 1b). The central features assigned to the parent radical anions were lost concomitantly.

These features are assigned to methyl radicals (1/3/3/1 quartet, $A(^1H)$ 22.5 G) and $H_2\dot{C}ML_3$ radicals (anisotropic $M_I = \pm 1$ features, $A(^1H)$ 20 G). The outermost features for the tungsten complex (Fig. 1b) are tentatively assigned to ^{183}W hyperfine satellites for $H_2\dot{C}^{183}WL_3$ radicals (^{183}W has $I = 1/2$ and is 14.28% abundant). Outer lines for the molybdenum complex were less well defined and have not been interpreted. In accord with these assignments, all the outer lines were lost when

TABLE 1

ESR PARAMETERS ASSIGNED TO $Cp_2M(CH_3)_2^+$, $Cp_2M(CH_3)_2^-$ AND $H_2\dot{C}M(Cp)_2(CH_3)$ (M = Mo, W) AT 77 K

Complex	Solvent	Nucleus	Hyperfine coupling (G) [a]			g-values		
			A_x	A_y	A_z	g_x	g_y	g_z
$Cp_2Mo(CH_3)_2^+$	$CFCl_3$	^1H		ca. 5 (av)			g_{av} ca. 2.005	
$Cp_2Mo(CH_3)_2^+$	$Cp_2Mo(CH_3)_2$	^1H		ca. 5 (av)			g_{av} ca. 2.005	
$Cp_2W(CH_3)_2^+$	$CFCl_3$	^1H		ca. 5 (av)			g_{av} ca. 2.006	
	$CpW(CH_3)_2$	^1H		ca. 5 (av)			g_{av}	ca. 2.006
$Cp_2Mo(CH_3)_2^-$	CD_3OD					2.0060	ca. 2.002	1.997
$Cp_2W(CH_3)_2^-$	CD_3OD					2.0075	2.002	1.9995
$H_2\dot{C}Mo(CH_3)Cp_2$ [b]	CD_3OD	^1H	25	20	15		2.002 (av)	
	D_2SO_4	^1H		ca. 20 (av)			2.002 (av)	
$H_2\dot{C}W(CH_3)Cp_2$ [b]	CD_3OD	^1H	26.5	19.5	14.5		2.002 (av)	
	D_2SO_4	^1H		ca. 20 (av)			2.002 (av)	

[a] $G = 10^4$ T; [b] Or possibly $H_2\dot{C}MCp_2$.

$(C_5H_5)_2W(CD_3)_2$ in CD_3OD was studied, and features due to $\cdot CD_3$ radicals were greatly enhanced.

Solutions in $CFCl_3$, CCl_4 and other similar solvents gave a single symmetrical line centred on $g = 2.005$, with several shoulders separated by ca. 5 G, and a maximum spread of g-values in the range 2.009–1.996. It is well established that only radical-cations are formed from dilute solutions under these conditions [15–18], so we conclude that these species are the parent d^1 cations. Unfortunately, satellite lines associated with ^{183}W or ^{95}Mo and ^{97}Mo were so poorly defined that all we can deduce is that the maximum hyperfine coupling for ^{183}W was ca. 60 G. These results are reasonable for d^1 dicyclopentadienylmetal complexes [1,2,21,22], the splitting of ca. 5 G being assigned to the methyl protons. Unfortunately, the results are so poorly defined that little structural information can be derived except that we can conclude that the SOMO is well removed from neighbouring orbitals. Also, we were unable to detect methyl radicals on annealing in the range 77–160 K. We know that when $Me_4Sn\cdot^+$ cations decompose to give methyl radicals, these can be trapped and detected by ESR spectroscopy [23], so we conclude that these cations do not lose methyl radicals in this temperature range.

Exposure of solutions in aqueous sulphuric acid, or D_2O/D_2SO_4 gave, initially, $HSO_4\cdot$ and $\cdot SO_3$ radicals, but on annealing, features assigned to $H_2\dot{C}ML_3$ radicals grew in as those due to $HSO_4\cdot$ radicals were lost. These were not sufficiently intense for us to detect satellite lines from metal nuclei.

Exposure of the pure compounds to γ-rays at 77 K gave central lines assignable to the parent cations, together with anisotropic $M_I = \pm 1$ features for $H_2\dot{C}ML_3$ radicals. Methyl radicals were not detected, but the parent anion may have been present in relatively low yields.

We conclude that the parent anions and cations have all three components of their g-tensors close to the free-spin value, and hence that the SOMO's for both the d^1 and d^3 complexes are remarkably isolated from neighbouring orbitals. This accords with the strong bonding exhibited by the methyl and cyclopentadienyl ligands, and the low symmetry of these complexes. However, on exposure to visible

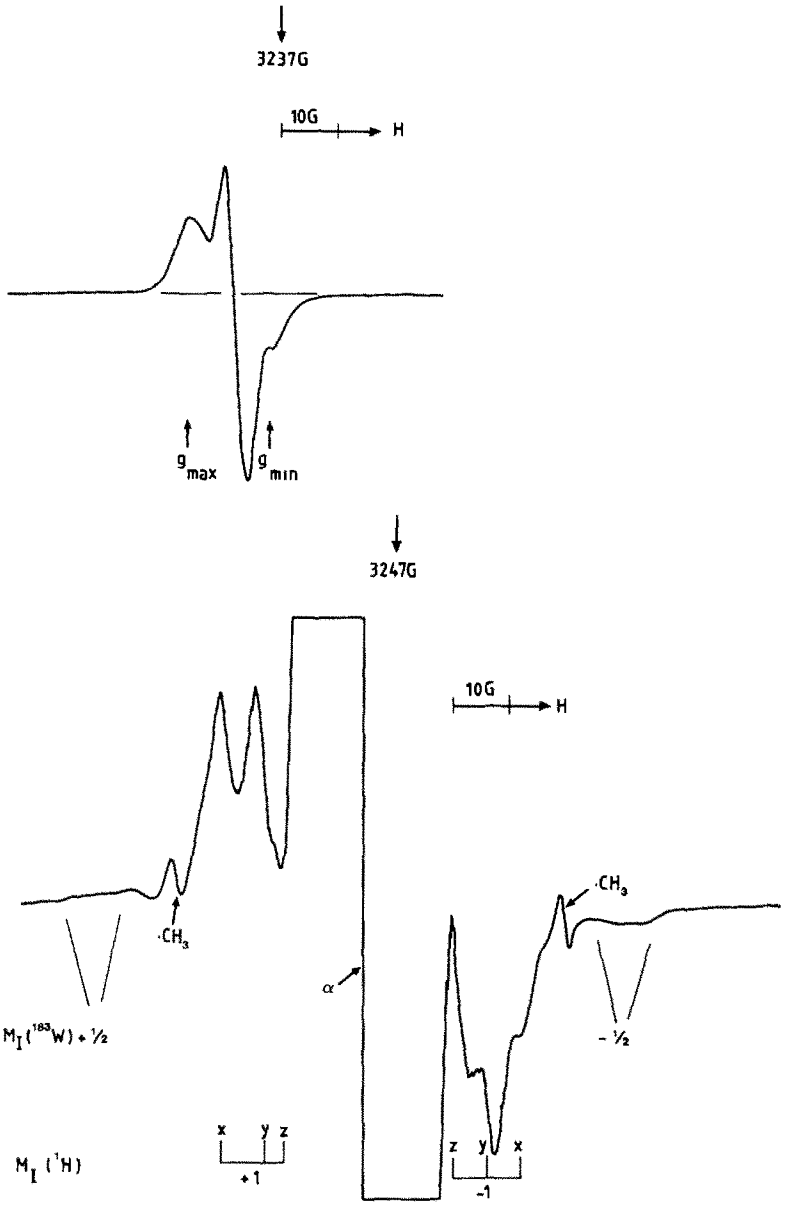

Fig. 1. First derivative X-band ESR spectra for $(C_5H_5)_2Mo(CH_3)_2$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, (a) showing features assigned to the anion $[(C_5H_5)_2W(CH_3)_2]^-$ together with an unresolved feature for solvent radicals and (b) after photobleaching, showing $M_I = \pm 3/2$ features assigned to methyl radicals (the $\pm 1/2$ lines are hidden beneath solvent radical signals: these were detected after partial annealing) and $H_2\dot{C}WL_3$ centres (± 1 features) and ^{183}W satellites. At lower gain the central features (α) comprise a multiplet of 7 lines assigned to $\cdot CD_3$ and $\cdot CD_2OD$ radicals: the features assigned to solute anions were absent.

light, the d^3 anions readily decompose, losing methyl radicals. These can extract hydrogen from other methyl groups or may be trapped as such. The optical transition in the 400 nm region responsible for this reaction probably has $\pi \rightarrow \sigma^*$

character, which would weaken the M–C bonds. The trapped methyl radicals are 'normal', that is, there is no indication of weak residual interaction with the $Cp_2MCH_3^-$ anions, such as is frequently observed [24–26].

The $H_2\dot{C}ML_3$ radicals [or possibly $H_2\dot{C}ML_2^+$ if hydrogen extraction occurs

$$Cp_2M(CH_3)_2^+ \rightarrow CH_4 + Cp_2M\dot{C}H_2^- \qquad (1)$$

during departure of $\cdot CH_3$ (eq. (1)) are of some interest since these are transition metal carbene derivatives which are of some current interest [27,28]. Our results, somewhat surprisingly, establish that there is very little π-delocalisation. Thus the isotropic proton coupling of ca. 20 G is close to the maximum value of ca. 22 G for an $H_2\dot{C}X$ radical suggesting that π-delocalisation is less than 10%. Also, the ^{13}W coupling is remarkably isotropic, suggesting that s-orbital population dominates. This is not expected if the source of coupling is π-delocalisation into metal d-orbitals, but is in accord with expectation and experience [29–31] if the metal acquires spin-density via spin polarisation of the C–M σ-electrons. Using recent values for the expected isotropic coupling for a fully occupied s-orbital on tungsten [32], we estimate ca. 2.4% s-character. In our other studies of transition metal complexes with near unit spin-density on adjacent ligand atoms, we find that spin-polarisation gives ca. (−) 2% spin-density on the metal outer s-orbitals [33]. This is for tetrahedral complexes which probably use d^3s hybrids for σ-bonding. The close similarity of these results suggests that the σ-bond for the $H_2\dot{C}$ group is also close to d^2s in nature. So far as we know, carbene complexes with the SOMO localised on the methylene group have not been previously described.

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