# Electron Paramagnetic Resonance Studies of Radical Pairs $[M(CO)_5^-]_2$ (M = Cr, Mo, W) trapped in Single Crystals of PPh<sub>4</sub><sup>+</sup>HM(CO)<sub>5</sub><sup>-†</sup>

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 $\gamma$ -Irradiated single crystals of PPh<sub>4</sub><sup>+</sup>HM(CO)<sub>5</sub><sup>-</sup> (M = Cr, Mo, W) exhibit powerful EPR spectra due to two distinct interacting pairs of M(CO)<sub>5</sub><sup>-</sup> radicals. *g*- and fine-structure (*D*) matrices were determined from measurements at 77 K of EPR spectra obtained as a function of angle in the *ac* and *aa'* planes of crystallographically aligned single crystals of the Mo and W compounds. The data are compared with those obtained previously for the Cr compound. In all three cases, *g* and one of the *D*-tensors are aligned with the tetragonal *c*-axis of the crystal, and the principal *g*-values are appropriate for d<sup>7</sup> square-pyramidal M(CO)<sub>5</sub><sup>-</sup> radicals. Classical dipolar calculations show that the two radical pairs correspond to the closest and next-closest pair of undamaged anions in the crystals, the former lying along *c* and the latter along a skew direction. The *D*-values for the Mo and W closest pairs indicate a substantial contribution from anisotropic exchange to the coupling of the two unpaired electrons.

An outcome of our recent EPR spectroscopic research<sup>1-3</sup> on radiation-damaged single crystals of hydridocarbonyls has been the observation of surprisingly strong signals from radical pairs in the electronic triplet (S = 1) state. In some instances, such signals dominate the EPR spectrum, and monoradical signals are comparatively weak. In all such systems examined to date, these signals are clearly due to antiferromagnetically coupled pairs of radicals generated by the loss of hydrogen atoms from a limited number of nearestneighbour hydridocarbonyl anions within the host crystal. The reason for the high yield of radical pairs relative to monoradicals remains obscure; their presence, however, offers a unique opportunity to explore the magnetic properties of isolated pairs of transition-metal-centred radicals. The simplest example of this phenomenon hitherto<sup>3</sup> is radiationdamaged  $PPh_4^+HCr(CO)_5^-$ , which displays an intense EPR spectrum of two distinct pairs of  $Cr(CO)_5^-$  radicals together with a very weak spectrum of the monoradical. The simplicity of this particular system lies in the correspondence of the local four-fold symmetry axis of the  $HCr(CO)_5^-$  radical anions with the c-axis of the tetragonal host:<sup>4</sup> the anions lie either parallel or antiparallel to the crystal c-axis (Fig. 1), and the g-matrices of the radical and the radical pairs are diagonal in the crystal-axis system. A natural extension of the study of  $[Cr(CO)_5]_2$  pairs was to the Mo and W congeners in order to ascertain the contribution of anisotropic (pseudodipolar) exchange<sup>5</sup> to the spin-spin (zero-field) interaction tensors. Disappointingly at the time, our attempts to synthesize the requisite Mo- and W-containing crystals were fruitless. More recent attempts, employing recrystallization from mixed solvents at low temperatures, have yielded single crystals of a size suitable for EPR spectroscopy. This article is a comparative study of radical-pair EPR spectra observed for the three hosts,  $PPh_4^+HM(CO)_5^-$  (M = Cr, Mo, W).

#### Experimental

The compounds  $PPh_4^+HM(CO)_5^-$  (M = Mo, W) were prepared according to established procedures.<sup>6</sup> In a typical synthesis,  $M(CO)_5NMe_3^-$  (2.5 mmol) and THF (40 cm<sup>3</sup>) were loaded into a 100 cm<sup>3</sup> Schlenk flask. After cooling the solution to  $-78 \,^{\circ}$ C, it was titrated with a 0.2 mol dm<sup>-3</sup> THF solution of sodium-naphthalene until a dark green colour persisted. With the temperature held at  $-78 \,^{\circ}$ C, a solution of [PPh<sub>4</sub>][Br] (2.5 mmol) in 20 cm<sup>3</sup> of methanol was added. Solvent was removed from the resulting yellow solution *in vacuo* and the residue was dissolved in 40 cm<sup>3</sup> of a THF-diethyl ether mixture. This yellow solution was filtered through Celite and concentrated at 0 °C to *ca.* 10 cm<sup>3</sup>. Hexane (20 cm<sup>3</sup>) was added to precipitate out a yellow-orange solid which was subsequently washed with three 20 cm<sup>3</sup> portions of hexane and dried *in vacuo.* Single crystals were grown at  $-30 \,^{\circ}$ C from THF-hexane. All manipulations were carried out in a drybox to the rigorous exclusion of air and moisture. Solvents were dried and degassed immediately prior to use.

Single crystals of each compound were selected with the aid of a polarizing microscope and were irradiated at ambient temperature for *ca.* 16 h in a 400 TBq <sup>60</sup>Co source. A Picker diffractometer was used to establish that the crystals were isomorphous (P4/n) with PPh<sub>4</sub><sup>+</sup>(HCr(CO)<sub>5</sub><sup>-4</sup> and to

**Fig. 1** ac plane of the PPh<sub>4</sub><sup>+</sup>HCr(CO)<sub>5</sub><sup>-</sup> crystal showing anions only. A and B refer to the two radical pairs described in the text; S1 and S2 are possible assignments for the pair B



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	cell dime			
М	a	с	ref.	
Cr	13.234 (2)	7.472 (2)	3	
Мо	13.231 (8)	7.614 (5)	this work	
W	13.256 (2)	7.609 (1)	this work	

" Tetragonal space group P4/n.

determine the unit-cell parameters (Table 1). After checking for the presence of EPR signals and site-splitting behaviour<sup>8</sup> appropriate for the tetragonal system, the crystals were aligned absolutely on the Picker diffractometer in accordance with the known structural parameters. These aligned specimens were glued inside the ends of 4 mm quartz tubes such that the *a* or *c* crystal axis was parallel to the tube axis. A pointer was attached at right angles to the tube to indicate the direction of a second crystal axis.

EPR spectra were recorded and measured with a Varian Associates E-12 spectrometer and standard accessories. Crystallographically aligned specimens were placed inside a liquid-nitrogen filled Dewar in the rectangular resonant cavity of the spectrometer such that the tube axis was vertical and the tube pointer lay immediately above a horizontal brass protractor graduated every 5°. EPR spectra were measured at 77 K as a function of angular departure of the tube pointer from the direction of the d.c. magnetic field,  $B_0$ , for the *ac* and *aa'* planes, *i.e.* the (010) and (001) planes. Measurements were also taken for a skew direction of  $B_0$ , with direction cosines  $(\sqrt{3}/2, 1/\sqrt{8}, 1/\sqrt{8})$  with respect to the axis system, in order to determine the relative signs of matrix off-diagonal elements.<sup>3,8</sup>

#### Results

The EPR spectra of y-irradiated single crystals of both  $PPh_4^+HMo(CO)_5^-$  and  $PPh_4^+HW(CO)_5^-$  bore many resemblances to those already observed in radiation-damaged  $PPh_4^+HCr(CO)_5^{-3}$  For most orientations, the spectra consisted of a number of pairs of lines of equal intensity all centred about the same field position. Although a resonance was detected at the spectrum centre, it was generally weak in comparison with the other lines. When  $B_0$  lay along a crystal axis, the spectra simplified considerably: two intense pairs of lines were then observed (Fig. 2) together with a number of weaker resonances. In both types of crystal the outer pair of lines (A) was much weaker relative to the inner pair (B) than was the case for  $PPh_4^+HCr(CO)_5^-$ . The outer pair exhibited no 'site-splitting',8 and showed a separation in magnetic field intensity for  $B_0 \parallel a$  which remained constant throughout the aa' plane, and which was approximately half the value measured along c. The inner pair showed site-slitting behaviour upon departure from the crystal axes which was consistent with the tetragonal symmetry of the hosts (four sites in general, two within a crystal plane and one along the crystal axes). The resonant magnetic fields of the components of the pairs were markedly anisotropic, and 'crossed' (i.e. zero separation) for certain orientations; doublet separations ranged from 0 to 150 G.

The observed anisotropy is typical<sup>9</sup> of spectra having their origin with electronic triplets (S = 1) for which the appropriate spin-Hamiltonian is

$$\mathscr{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + Js_1 \cdot s_2$$

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Fig. 2 First-derivative EPR spectrum of a  $\gamma$ -irradiated single crystal of PPh<sub>4</sub><sup>+</sup>HW(CO)<sub>5</sub><sup>-</sup> at 77 K and 9052. 4 MHz for  $B_0 \parallel a$ 

where  $S = (s_1 + s_2)$  is the operator for total spin. The last two terms represent the electronic interaction energy, and are purely anisotropic  $(S \cdot D \cdot S)$  and purely isotropic  $(Js_1 \cdot s_2)$ , respectively. J, the isotropic electron-exchange parameter, may be equated to the energy difference between the singlet and triplet levels of the coupled pair of electrons. Providing this energy difference is larger than the EPR microwave quantum, the triplet levels may<sup>10</sup> be considered in isolation and the isotropic term in J ignored, even though it may be the dominant term of the interaction. Two intense  $\Delta m_s = \pm 1$ transitions together with a weak  $\Delta m_s = \pm 2$  transition (the 'half-field' line) are then observed. (For smaller values of J, singlet-triplet mixing occurs<sup>10</sup> and weak additional transitions may be detected.) In the present examples, where zerofield splittings never exceeded 150 G, the anisotropic fine-structure term may be considered a perturbation to the electronic Zeeman term. The triplet EPR spectrum then consists of a pair of lines centred to first order about the value of g for the particular direction of the magnetic field, B; good approximations to the scalar elements of the tensor  $g \cdot D \cdot g$ may be obtained from measures of  $\beta g^3 \Delta B/3$ , where  $\Delta B$  is the fine-structure splitting in G and g corresponds to the centre of the spectrum.<sup>11</sup>

Values of  $g^2$  and of  $\beta g^3 \Delta B/3$  for each of the triplet species A and B were plotted against angle for the *aa'* and *ac* crystal planes of both PPh<sub>4</sub><sup>+</sup>HMo(CO)<sub>5</sub><sup>-</sup> and PPh<sub>4</sub><sup>+</sup>HW(CO)<sub>5</sub><sup>-</sup> (see Fig. 3 and 4, for example). Best-fit values of the matrix elements of  $g^2$  and  $g \cdot D \cdot g$  (Table 2 and 3) were obtained in the usual manner<sup>8</sup> from the parameters of least-squares sinusoidal curves fitted to the data. Standard algebraic manipulations<sup>8</sup> led to the principal values and directions of g and D (Table 2 and 3).

In the case of the tungsten crystal, weak satellites, of intensities appropriate for <sup>183</sup>W (I = 1/2) in natural abundance, were associated with each strong line of the triplet spectrum. They were attributed to hyperfine interaction of the unpaired electrons with <sup>183</sup>W nuclei. It proved possible to follow the variation of this hyperfine coupling over a small range of angles in the *ac* plane, and to extract the hyperfine matrix (Table 3). This result has been discussed elsewhere<sup>12</sup> in connection with the electronic structure of the M(CO)<sub>5</sub><sup>-</sup> radicals.



Fig. 3  $g^2$  for species A and B as a function of angle in the *ac* plane of PPh<sub>4</sub><sup>+</sup>HMo(CO)<sub>5</sub><sup>-</sup>

Isotropic exchange parameters J were estimated (Table 4) from measurements of the spectral intensities (I) of A and B as a function of temperature (T) and least-squares best fits to the data of an assumed temperature dependence of the form:

$$I^{-1} = \alpha T [3 + \exp(J/kT)]$$

#### Discussion

The EPR spectra observed in both PPh<sub>4</sub><sup>+</sup>HMo(CO)<sub>5</sub><sup>-</sup> and PPh<sub>4</sub><sup>+</sup>HW(CO)<sub>5</sub><sup>-</sup> were readily interpreted in terms of two electronic triplet (S = 1) species, A and B, which have small values of the fine-structure parameter,  $D (= 1.5D_{zz})$ , and positive values of the isotropic exchange parameter, J. Spectra were always centrosymmetric, independent of orientation, showing that all carriers had a common *g*-matrix (Table 2 and 3). For most orientations a weak resonance was detected at the centre of the spectrum. This was assigned to mono-



The situation is entirely analogous to that in irradiated crystals of the isomorphous PPh<sub>4</sub><sup>+</sup>HCr(CO)<sub>5</sub><sup>-,3</sup> where the dominant paramagnetic species are two pairs of antiferromagnetically coupled Cr(CO)<sub>5</sub><sup>-</sup> radicals, and monoradical spectra are comparatively weak. By analogy with the isoelectronic d<sup>7</sup> species Fe(CO)<sub>5</sub><sup>+</sup>, the pentacarbonyl anion radicals, M(CO)<sub>5</sub><sup>-</sup> (M = Cr, Mo, W) are expected<sup>12-14</sup> to have square-pyramidal geometry. Their observation as products of radiation damage of PPh<sub>4</sub><sup>+</sup>HM(CO)<sub>5</sub><sup>-</sup>, with uniaxial *g*-matrices aligned (Table 2 and 3) along the four-fold symmetry axes of the crystals, is no surprise, therefore (Fig. 1 and 5). We note that the principal values of *g* for the Mo and W species reported here are close to those attributed to the pentacarbonyl anion radicals<sup>12</sup> in PPN<sup>+</sup>HM(CO)<sub>5</sub><sup>-</sup> crystals and in frozen 2-MeTHF.<sup>15</sup> We conclude that, just as in the case of PPh<sub>4</sub><sup>+</sup>HCr(CO)<sub>5</sub><sup>-</sup>, the triplets A and B are composed of



Fig. 5 The lower four d-orbitals and anticipated g-shifts for a d<sup>7</sup> metal carbonyl



Fig. 4 Values of  $g \cdot D \cdot g$  and best-fit sir soidal curves for species B in PPh<sub>4</sub><sup>+</sup>HMo(CO)<sub>5</sub><sup>-</sup>

	tensor			principal values and direction cosines of $g$ and $D$		
	a	a'	с	x	у	Z
				2.0230	2.0230	2.0006
g <sup>2 a</sup>	4.0923 0.0 0.0	0.0 4.0923 0.0	0.0 0.0 4.0024	1.0000 0.0000 0.0000	0.0000 1.0000 0.0000	0.0000 0.0000 1.0000
				39.8	39.8	- 79.5
$egin{array}{c} m{g} \cdot m{D} \cdot m{g}^b \ (A) \end{array}$	163.0 0.0 0.0	0.0 163.0 0.0	0.0 0.0 - 318.3	$ \begin{array}{c} 1.0000 \\ 0.0000 \\ 0.0000 \\  D  = 1 \end{array} $	0.0000 1.0000 0.0000 19.2 MHz;   <i>E</i>   = 0.0	0.0000 0.0000 1.0000 MHz
				27.7	29.1	- 57.9
$\begin{array}{c} \boldsymbol{g} \cdot \boldsymbol{D} \cdot \boldsymbol{g}^{b,c} \\ (B) \end{array}$	- 35.1 - 154.1 - 84.0		84.0 84.0 64.3	$0.2608 \\ 0.2608 \\ -0.9295 \\  D  = 8$	-0.7071 0.7071 0.0000 86.9 MHz; $ E  = 0.7$ 1	0.6573 0.6573 0.3688 MHz

**Table 2** The  $g^2$  and  $g \cdot D \cdot g/MHz$  matrices for the  $[Mo(CO)_5^-]_2$  radical-ion pairs in a PPh<sub>4</sub><sup>+</sup>HMo(CO)<sub>5</sub><sup>-</sup> crystal at 77 K; principal values of g and D in MHz and their direction cosines in the aa'c axis system

<sup>a</sup> g<sup>2</sup> matrix common to all species. <sup>b</sup> Signs of diagonal elements chosen to give traceless matrix. <sup>c</sup> Off-diagonal signs appropriate for one of four sites.

pairs of  $M(CO)_5^-$  radicals aligned along the crystal *c* axes. By analogy with the results for the chromium crystal,<sup>3</sup> we associate A with a pair of nearest-neighbour damaged anions, lying along *c*, and B with the next nearest pair of anions, lying in a skew direction (Fig. 1). The principal directions of the finestructure tensors and the results of point-dipolar calculations support this association (Table 5). spin value, we expect D for the  $[Cr(CO)_5^-]_2$  pair to be dominated by the contribution from the classical dipolar interaction tensor:<sup>16</sup>

$$\frac{1}{2}\beta\sum_{i,j}\rho_i\rho_j r_{ij}^{-3} \{ \boldsymbol{g} \cdot \boldsymbol{g} - 3(\boldsymbol{g} \cdot \boldsymbol{r}) \wedge (\boldsymbol{g} \cdot \boldsymbol{r}) \}$$

The miniscule variation in the anisotropic parameter D for species B along the series of Group 6 metals contrasts sharply with the marked variation for species A (Table 4). Because of the small departure of the  $Cr(CO)_{5}^{-}$  g-values from the free-

where *r* is the vector between atoms *i* and *j* bearing spin densities  $\rho_i$  and  $\rho_j$ . In Table 5 we reproduce the results of calculations of the dipolar contribution to *D* for the three closest pairs of Cr(CO)<sub>5</sub><sup>-</sup> anions in the PPh<sub>4</sub><sup>+</sup>HCr(CO)<sub>5</sub><sup>-</sup> crystal and

**Table 3** The  $g^2$ ,  $g \cdot a^2 \cdot g$  and  $g \cdot D \cdot g/MHz$  matrices for the  $[W(CO)_5^-]_2$  radical-ion pairs in a PPh<sub>4</sub><sup>+</sup>HW(CO)<sub>5</sub><sup>-</sup> crystal at 77 K; principal values of g, a and D in MHz and their direction cosines in the aa'c axis system

	tensor			principal values and direction cosines of g, a and D		
	a	a'	с	x	у	2
<b>~</b>				2.0676	2.0676	1.9906
g <sup>2 a</sup>	4.2750 0.0 0.0	0.0 4.2750 0.0	0.0 0.0 3.9624	1.0000 0.0000 0.0000	0.0000 1.0000 0.0000	0.0000 0.0000 1.0000
				70.7	70.7	-140.6
$\begin{array}{c} \boldsymbol{g} \cdot \boldsymbol{D} \cdot \boldsymbol{g}^{b} \\ (A) \end{array}$	302.1 0.0 0.0	0.0 302.1 0.0	0.0 0.0 556.9	$   \begin{array}{c}     1.0000 \\     0.0000 \\     0.0000 \\      D  = 2   \end{array} $	0.0000 1.0000 0.0000 10.9 MHz;   <i>E</i>   = 0.0	0.0000 0.0000 1.0000 MHz
				0	0	103
$\begin{array}{c} \boldsymbol{g} \cdot \boldsymbol{a}^2 \cdot \boldsymbol{g}^c \\ (A) \end{array}$	0 0 0	0 0 0	0 0 42470	1.0000 0.0000 0.0000	0.0000 1.0000 0.0000	0.0000 0.0000 1.0000
				29.1	31.1	-60.3
$g \cdot D \cdot g^{b,d}$ (B)	-37.7 -170.6 -87.4	170.6 37.7 87.4	- 87.4 - 87.4 69.3	$0.2547 \\ 0.2547 \\ -0.9329 \\  D  = 9$	-0.7071 0.7071 0.0000 0.4 MHz;   <i>E</i>   = 1.0 1	0.6597 0.6597 0.3602 MHz

<sup>*a*</sup>  $g^2$  matrix common to all species. <sup>*b*</sup> Signs of diagonal elements chosen to give traceless matrix. <sup>*c*</sup> a is the hyperfine interaction matrix for <sup>183</sup>W. <sup>*d*</sup> Off-diagonal signs appropriate for one of four sites.

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Table 4 Summary of anisotropic interaction parameters  $D^a$  and isotropic electron-exchange parameters J for radical pairs A and B in  $PPh_4^+HM(CO)_5^-$  (M = Cr, Mo, W) crystals

М	$ D /MHz^a$		$J/\mathrm{cm}^{-1}$		
	A	В	A	B	ref.
Cr	163	84	35	11	3
Мо	119	87	15	12	this work
W	211	90	8	4	this work

 $|D| = 1.5D_{zz}$ , where  $D_{zz}$  is the principal component of **D** of largest absolute value.

Table 6 Coulomb and exchange energies for two Cr 3d<sub>22</sub> orbitals separated by distance r along z

r/a <sub>0</sub>	$E(\text{Coulomb})/E_{h}$	$E(\text{exchange})/E_{h}$
3	0.4092	$7.42 \times 10^{-2}$
5	0.2191	$1.70 \times 10^{-3}$
7 (3.70 Å)	0.1494	$3.85 \times 10^{-6} (0.85 \text{ cm}^{-1})$
9` ´	0.1141	$4.43 \times 10^{-10}$
13 (6.88 Å)	0.0779	$5.05 \times 10^{-22}$

anism of communication between the electrons in these pairs. An obvious pathway for superexchange exists for A pairs (Fig. 6) via overlap of the  $d_{z^2}$  orbitals with the axial C and O 2p<sub>z</sub> orbitals of one constituent of the pair. Preliminary local density functional (LDF) molecular orbital calculations<sup>17</sup> using double-zeta density functions augmented with 4s and 4p polarization on Cr (Fig. 7) support this mechanism of electron exchange for the A pair of  $M(CO)_5^-$  radicals. For the B pairs, however, there is no obvious pathway for efficient electron exchange. The closest approach of atoms amongst the skew pairs is 4.6 Å between equatorial O atoms in the closest



Fig. 6 Suggested superexchange pathways for the A pairs of M(CO)<sub>5</sub> radicals



Fig. 7 One of the semioccupied degenerate orbitals of the  $[Cr(CO)_5]_2$  A pair as prediced by a LDF MO calculation (see text)

for a number of unpaired-spin distributions. The first calculation is for unit spin density on the Cr nucleus; the remaining calculations are for 62% spin density on Cr, as suggested<sup>12</sup> by the hyperfine interaction with <sup>53</sup>Cr, and 38% spin spread over the CO ligands in various ways. The experimental value for A falls within the range of calculated values, and the principal directions of D naturally coincide. In view of a much better agreement with experiment (Table 5), we are inclined to assign B to the second-nearest pair of anions (S2 in Table 5 and Fig. 1) rather than to the third-nearest pair (S1 in Table 5 and Fig. 1). It would appear that dipolar contributions are indeed dominant for the Cr radical pairs, and accordingly, we take their D-values to be negative. For the heavier metals (Table 4), the experimental D-values for species A depart significantly from the calculated dipolar interactions. Evidently, non-classical contributions to the zero-field interaction are very important in the case of pairs A, but are almost negligible for the skew pairs B.

The positive J-values measured for the  $[M(CO)_5^-]_2$  pairs (Table 4) conform with the norm for radical pairs, i.e. antiferromagnetic coupling of the unpaired spins.<sup>5,10</sup> Calculation of the exchange integral for two  $3d_{z^2}$  atomic orbitals separated by a distance of one unit-cell length along c (Table 6) shows that direct exchange may be eliminated as the mech-

**Table 5** Dipolar interaction parameters D and  $E^a$  in  $[Cr(CO)_5]_2$ pairs

	Α	H	3
expt. <sup>b</sup>			
D  =	163.0	84	.0
E  =	0.0	0	.2
calcd.			
site <sup>c</sup>	с	<b>S</b> 1	S2
1d∫D	$-188.2 \ (0^{\circ})^{e}$	$-65.9 (5.9^{\circ})^{e}$	$-87.5 (7.7^{\circ})^{e}$
<sup>1</sup> }E	0.0	0.2	0.2
$\sum D$	-181.1 (0°)	-65.7 (8.2°)	-91.7 (7.4°)
<sup>2</sup> (E	0.0	-0.1	0.4
$\sum_{n=1}^{\infty} D$	-180.8 (0°)	-65.1 (7.3°)	-90.0 (8.1°)
3 (E	0.0	0.0	0.2
, ∫D	-154.0 (0°)	-69.9 (7.5°)	-93.0 (4.2°)
4 (E	0.0	-0.2	-0.3
₅ ∫D	-166.3 (0°)	-68.1 (6.5°)	-89.9 (5.9°)
י <i>\E</i>	0.0	-0.1	-0.2

<sup>a</sup> D = 3Z/2, E = (X - Y)/2, where X, Y, Z are the principal values of the fine-structure tensor in MHz, Z having the largest absolute value. <sup>b</sup> Experimental values from ref. 3. <sup>c</sup> Calculated values for classical dipolar interaction between  $Cr(CO)_5^-$  constituents of the pair. Sites c, S1, S2 correspond, respectively, to the nearest, third-nearest and second-nearest pairs of Cr nuclei in the crystal. <sup>d</sup> Assumed unpaired spin distributions: 1, 100% spin on Cr; 2, 62% on Cr, 38% equally distributed over all Cs and Os; 3, 62% on Cr, 38% equally distributed over all Cs; 4, 62% on Cr, 38% equally distributed over equatorial Cs and Os; 5, 62% on Cr, 38% equally distributed over equatorial Cs. " Values in brackets are angular departure from experimental direction of unique (Z) principal value.

such pair (S2). Tentatively therefore, we assume that superexchange via equatorial O 2p orbitals accounts for the triplet interaction in the B pairs. Such an exchange pathway is clearly less efficient than that proposed for A, and this is reflected in reduced J-values for B. Examination of the crystal structure (Fig. 8) shows that the cations are unlikely to play an intermediate role in superexchange between the anion pairs.

The marked differences in value of D for species A amongst the three cogeners far outweigh the small differences in unitcell parameters (Table 4). Differences in c between the Cr and Mo crystals, for example, can account for only a 6% difference in dipolar coupling between the constituents of pair A. An efficient anisotropic (pseudodipolar) exchange mechanism is presumably responsible for the large departure of  $D_A$  for Cr and Mo from the classical dipolar values. Such exchange connects the two metal  $d_{z^2}$  ground states via the same excited state ( $d_{xz}$  or  $d_{yz}$ ) that is responsible for the g shift.<sup>5</sup>

For the particular case of a  $d^7$  axially symmetric species in which a half-filled  $d_{z^2}$  mixes with filled  $d_{xz}$  or  $d_{yz}$  by spin-orbit coupling, we anticipate

$$\Delta g_{\parallel} = 0; \quad D_{zz} = 0$$
  
$$\Delta g_{\perp} = 6\lambda/\Delta E; \quad D_{xx} = D_{yy} = 3\lambda^2 J_{z^2, yz}/2\Delta E^2$$

The EPR experiment provides a measure of the traceless part of the fine-structure tensor only, so that the contribution to





Fig. 8 [100] and [001] projections of the crystal structure of  $PPh_4^+HCr(CO)_5^-$ 

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the parameter D from this mechanism will be

$$D_{\rm ps} = -\Delta g_\perp^2 J_{z^2, yz}/24$$

Since the superexchange route for this mechanism involves orthogonal p orbitals (Fig. 6), the coupling will be ferromagnetic and  $J_{z^2, yz/xz}$  negative. The resulting positive pseudodipolar contribution to D can then account for the observations if we assume that a change in sign of the parameter occurs between Mo and W (Fig. 9). Using these assumptions, we estimate from the differences between observed and calculated classical point-dipolar parameters (100% spin on the metal nuclei) values for  $J_{z^2, yz/xz}$  of -65, -110 and -73 cm<sup>-1</sup> for the Cr, Mo and W pairs, respectively. Alternatively, from the best-fit parabola to the data of Fig. 9,

$$D/MHz = -175(\pm 19) + 9.07(\pm 0.80) \times 10^4 \Delta g_{\perp}^2$$

we obtain a global value of  $J = -73 \pm 6 \text{ cm}^{-1}$  for all three metals. These values are unusually large in comparison with the isotropic couplings (Table 4) determined from the temperature dependences of triplet spectral intensity. The isotropic exchange couplings J for pairs A in these crystals are clearly the result of a fine balance between positive  $J_{z^2, z^2}$  and negative  $J_{z^2, yz/xz}$  terms. In all cases, the positive term dominates, although barely for W, and the ground state is a singlet (Table 4).

A small pseudodipolar contribution to the  $D_{\rm B}$  values can be discerned in the data (Table 4) which appears to reinforce the classical interaction. A reduced anisotropic exchange contribution in pairs B is certainly in line with the weaker isotropic exchange compared to the A pairs and the anticipated poorer orbital overlap. Furthermore, a reinforcement of the classical dipolar interaction by anisotropic exchange is expected in the case of the skew pairs B (for negative  $J_{z^2, yz(xz)}$ ) because of the relative disposition of the two contributing tensors: the pseudodipolar tensor lies along c, whereas the purely dipolar tensor lies approximately 75° from c. Although the non-classical contribution is evidently small in the case of the skew pairs, it may account for the discrepancies between measured and calculated principal directions (Table 5).

The presence of only two configurations of paired radicals and their preponderance over monoradicals are common puzzling features of the damaged  $PPh_4^+HM(CO)_5^-$  crystals. It



Fig. 9 D as a function of  $\Delta g_{\perp}$  for the three A pairs, and the least-squares fit of a parabolic function to the data

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would appear that photoejected H atoms do not escape beyond the cage of nearest neighbours, since the monoradical spectra are so weak. The absence of a third pair (S1, Table 5) is especially strange. We conclude that it must be formed along with the other two, but that it is unstable either with respect to the other sites or with respect to true dimer formation. Of the three nearest-neighbour anion pairs, it is the most propitiously aligned (Fig. 1) for the formation of  $Cr_2(CO)_{10}^{2-}$ , a well characterized diamagnetic metal-carbonyl anion.18

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