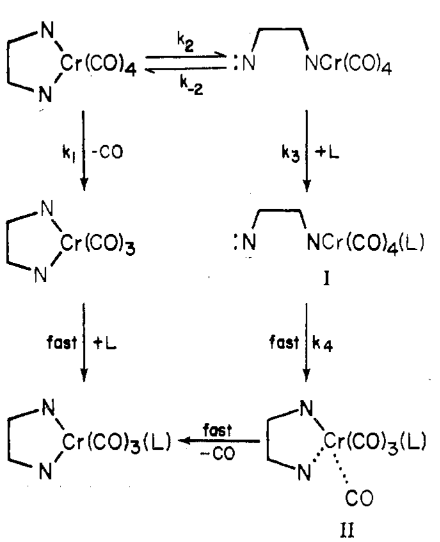

(4)

dipy ligand in carbonyl dissociation in that there is no reason to expect carbonyls in I to be appreciably more labile than in the (dipy)Cr(CO)$_4$ substrate, which undergoes CO loss via a dissociative path governed by k_1. Rate data for ligand replacement reactions of (2,2,8,8-tetramethyl-3,7-dithianonane)tetracarbonyltungsten(0) with phosphites are interpretable in terms of an analogous intermediate,[7] and, while examples of seven-coordination about the small Cr atom are not plentiful, a seven-coordinate activated complex or intermediate has been proposed for reactions of Cr(CO)$_6$ with strong nucleophiles such as tri(*n*-butyl)phosphine.[8] Further, the high "local concentration" of the free end of dipy should favor the formation of such a species.[9]

The steady-state rate law corresponding to mechanism 4 is

$$-\mathrm{d}[(\mathrm{dipy})\mathrm{Cr(CO)}_4]/\mathrm{d}t = k_1[(\mathrm{dipy})\mathrm{Cr(CO)}_4] + k_2k_3[(\mathrm{dipy})\mathrm{Cr(CO)}_4][\mathrm{L}]/(k_{-2} + k_3[\mathrm{L}]) \qquad (5)$$

which may be arranged, in terms of the pseudo-first-order rate constant, k_{obsd}, to,

$$1/(k_{\mathrm{obsd}} - k_1) = 1/k_2 + k_{-2}/k_2k_3[\mathrm{L}] \qquad (6)$$

Thus a plot of $1/(k_{\mathrm{obsd}} - k_1)$ vs. $1/[\mathrm{L}]$ is expected to be linear, with slope k_{-2}/k_2k_3 and intercept $1/k_2$. From k_{obsd} data for L = P(OCH$_2$)$_3$CCH$_3$ (the system for which k_{obsd} plots were linear over 2 or more half-lives), the value of k_1 was estimated as follows. From values of k_{obsd} were subtracted the arbitrary constant (k_1) which provided the best linear plot of $1/(k_{\mathrm{obsd}} - k_1)$ vs. $1/[\mathrm{L}]$. The value of k_1 thus determined, 9.0×10^{-5} sec^{-1}, is in excellent agreement with values of the first-order rate constants obtained at very low ligand concentrations (see Figure 1), for which the contribution to the rate of the reversible dissociation path is expected to be minimal.

The existence of the reversible dissociation path for reactions of (dipy)Cr(CO)$_4$ raises the possibility that such a path also exists for the analogous reactions with phosphites of (*o*-phen)Cr(CO)$_4$ (*o*-phen = *o*-phenanthroline) and related substrates containing substituted *o*-phen ligands of varying basicities.[10] The greater rigidity of the *o*-phen's presumably would lead to greater $k_{-2}/k_3[\mathrm{L}]$ ratios (eq 5), rendering ligand-dependent rate behavior less likely to be observed. However, greater values for k_{-2}, and thus slower rates of reaction, would be expected for the more basic *o*-phen's should their reactions proceed predominantly through the reversible dissociation mechanism. The opposite behavior is, in fact, observed.[10] The existence of this mechanism in competition with that involving rate-determining dissociation of CO for the (dipy)Cr(CO)$_4$ system does offer an attractive explanation for the deviation of the dipy complexes from an otherwise excellent linear free energy plot of log k (eq 2) vs. the pK_a of the bidentate ligand for dipy and *o*-phen complexes.[10]

In the limit of high [L], $k_3[\mathrm{L}] >> k_{-2}$, and rate law 5 reduces to that reported by Angelici and Graham,[1] i.e.

$$-\mathrm{d}[(\mathrm{dipy})\mathrm{Cr(CO)}_4]/\mathrm{d}t = (k_1 + k_2)[(\mathrm{dipy})\mathrm{Cr(CO)}_4] \qquad (7)$$

Thus the existence of the reversible dissociation path in this system cannot explain the observed[1] variation in the first-order rate constants with the identity of L. Figure 1 indicates, however, that, while the present data are in good agreement with those of Angelici and Graham for P(OCH$_2$)$_3$CCH$_3$, there is a significant variation in the data for P(OC$_2$H$_5$)$_3$, which was rigorously purified in this study but which was used as obtained from a commercial source by Angelici and Graham.[1] It would thus appear reasonable to presume that differences in the purity of the ligands are the cause of observed variations in k, particularly since it has been observed that impurities in the phosphites which have been employed in other kinetic investigations of metal carbonyl derivatives have had pronounced effects on the rates of those reactions.[7,11]

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Registry No. (dipy)Cr(CO)$_4$, 15668-63-0; P(OCH$_2$)$_3$CCH$_3$, 1449-91-8; P(OC$_2$H$_5$)$_3$, 122-52-1.

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Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Acetate Complexes of Dirhodium and Diruthenium. Aquation and Reduction–Oxidation

C. R. Wilson and H. Taube*

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Previous to 1968, the only well-established example of Rh(II) in combination with saturated ligands was Rh$_2$(OAc)$_4$ and its adducts.[1] At that time, Maspero and Taube succeeded in synthesizing the fully hydrated species Rh$_2$$^{4+}$(aq) in the anaerobic reaction[2]

$$\mathrm{Cr^{2+}(aq) + (H_2O)_5RhCl^{2+} \rightarrow (H_2O)_5CrCl^{2+} + {}^1/_2Rh_2{}^{4+}(aq)}$$

In attempts to find a convenient route to preparing Rh$_2$$^{4+}$(aq) at relatively high concentration both Ziolkowski[3] and the present authors studied the hydrolysis of Rh$_2$(OAc)$_4$ in strong noncomplexing acids but without producing Rh$_2$$^{4+}$(aq). In 1969 Legzdins et al.[4] published a communication indicating that new homogenous hydrogenation catalysts could be obtained through the protonation of Rh$_2$(OAc)$_4$ and its subsequent interaction with triphenylphosphine. They proposed the aquo ion Rh$_2$$^{4+}$(aq) as an intermediate even though their

Table I. Ultraviolet and Visible Absorptions for Acetato- and Aquorhodium(II) Species

Species	λ, nm (ε, cm^{-1} *M*$^{-1}$ (mol of dimer)$^{-1}$)	Conditions
$Rh_2(OAc)_4$	585 (241),[a] 440 (106),[a] 250 sh[g] (4 × 10^3),[b] 218 (1.7 × 10^4),[b] 587 (230),[c] 443 (94)[c]	In water
$Rh_2(OAc)_3{}^{+}$ [a]	610, 425, 350 sh, 250 (7.02 × 10^3), 218 9.62 × 10^3)	0.05 *M* HTFMS, 0.1 *M* $HClO_4$
$Rh_2(OAc)_2{}^{2+}$ [a]	638 (71), 423 (99), 368 (102), 258 (8.90 × 10^3), 220 (7.20 × 10^3)	1 *M* $HClO_4$
Legzdins' species[d]	612 (55.0), 423 (61.8), 256 (3.1 × 10^3)	HBF_4 in methanol-water
$Rh_2{}^{4+}$	648 (93),[a] 402 (126),[a] 250 (1.97 × 10^4)[a,f] 630 (79.8),[e] 412 (118),[e] 250 (2.12 × 10^4)[e]	3 or 1 *M* $HClO_4$

[a] This work. [b] Reference 6. [c] Reference 1. [d] Reference 5. [e] Reference 2. [f] 1 *M* $HClO_4$. [g] Shoulder.

electronic spectrum disagreed with the published one. In marked contrast to the observations made in these laboratories they found their species to be air stable. In a later paper, Legzdins and coworkers[5] repeated their claim to having prepared the ion $Rh_2{}^{4+}$(aq) by acid hydrolysis of $Rh_2(OAc)_4$, reporting that the total acetate released corresponded "essentially quantitatively" to that expected for complete protonation of $Rh_2(OAc)_4$. In an attempt to remove the contradictions between our earlier experiments and those quoted, the present work was undertaken. In the process, new aquoacetato complexes of dirhodium(II) were identified and some interesting redox behavior of both rhodium and ruthenium acetate was uncovered.

Results and Discussion

Aquation of $Rh_2(OAc)_4$. When 0.005 *M* $Rh_2(OAc)_4$ in a 1 *M* solution of a strong noncomplexing acid such as trifluoromethylsulfonic, perchloric, or *p*-toluenesulfonic is heated at 100° under argon for 20–30 min, cooled, diluted, and eluted onto Dowex 50W–X2 cation-exchange resin, the principal species observed are $Rh_2(OAc)_4$ and a species which moves slowly with 0.05 *M* acid and more quickly with 0.1 *M* acid. Its spectrum is recorded in Table I and resembles that of a solution of $Rh_2(OAc)_4$. The ion-exchange behavior is indicative of a species of 1+ charge, hydrated tri-*μ*-acetato-dirhodium(II) ion, $Rh_2(OAc)_3{}^{+}$(aq). If the heating is continued for 1 hr, the principal species is of higher charge and greatly resembles the wintergreen color of the aquo ion $Rh_2{}^{4+}$(aq). The spectrum in general features remains quite similar to that of $Rh_2(OAc)_4$, which is also recorded in Table I. The ion is eluted slowly with 0.5 *M* acid and more quickly with 1 *M* acid, indicating a 2+ charge. The species in question is presumably hydrated di-*μ*-acetato-dirhodium(II) ion, $Rh_2(OAc)_2{}^{2+}$(aq). Both of these ions can be reconverted to the parent $Rh_2(OAc)_4$ by adding excess acetate. The 2+ ion is very air stable; even at 60° oxidation in 1 *M* acid by air is rather slow. Thus, it appears to resemble the hydrated di-*μ*-bicarbonato-dirhodium(II) obtained from protonation of $Rh_2(CO_3)_4{}^{4-}$.[7] If the ion is eluted with 1 *M* sulfuric acid and heated for 20 min at 60°, cooled, diluted, and passed onto an anion-exchange column, a diffuse green band is retained which does not elute with water but does elute with perchlorate solutions. This indicates that there are indeed new substitutable coordination positions on the Rh–Rh moiety since the parent $Rh_2(OAc)_4$ does not behave this way and since an anionic species is formed. Attempts to observe the next aquation products were frustrated by very low yields and ease of oxidation of the compound. Only trace amounts were ever observed. When the preparative

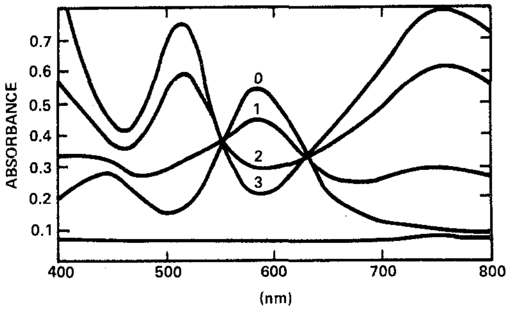


Figure 1. Oxidation of 2.28 × 10^{-3} *M* $Rh_2(OAc)_4$ in 1 *M* H_2SO_4 by Ce(IV): (0) initial, (1) 0.73 × 10^{-3} *M* Ce(IV), (2) 1.69 × 10^{-3} *M* Ce(IV) (3) final, 2.28 × 10^{-3} *M* Ce(IV).

instructions described by Legzdins et al. are followed and the reaction solution is diluted with water under argon and eluted onto cation-exchange resin, the principal species observed is the hydrated di-*μ*-acetato-dirhodium(II) cation but no $Rh_2{}^{4+}$(aq). Legzdins et al. indicated that they obtained a very deliquescent green solid upon rotary evaporation of trifluoromethylsulfonic acid solutions of $Rh_2{}^{4+}$(aq). We too have observed such a solid, upon evaporation of solutions of $Rh_2(OAc)_2{}^{2+}$, but when a solution containing $Rh_2{}^{4+}$(aq) is evaporated under argon in trifluoromethylsulfonic acid, it decomposes into a thick yellow syrupy solution. Furthermore, Legzdins et al. found their species to be eluted from Dowex 50W-X8 with 2–3 *M* perchloric acid. Experience in this laboratory indicates that more cross linkage in the resin, X8, requires a greater concentration for elution of a particular cationic species. Thus a band that elutes with 3 *M* acid on X8 resin would elute more easily on our X2 resin, where the aquo ion *slowly* elutes with 3 *M* acid. This argues that the charge on the species Legzdins obtained is less than that on the aquo ion $Rh_2{}^{4+}$(aq), and hence acetate is still present. For their purposes, the principal point is that strong acid releases some acetate, opening up coordination positions on the dirhodium species and rendering it catalytically active. We agree that some acetate is released by strong acid, but do not agree that Legzdins et al. obtained $Rh_2{}^{4+}$(aq) in significant yield by this procedure. It should be noted that it is very difficult to remove even carbonate from [$Rh_2(CO_3)_4{}^{4-}$] by strong acid so as to produce $Rh_2{}^{4+}$.[7]

Oxidation of $Rh_2(OAc)_4$. When chlorine gas, lead dioxide, or Ce^{IV}(aq) is added to a blue-green solution of tetra-*μ*-acetato-dirhodium(II), orange and violet colors are seen which, with time, revert to a color similar to that of the original solution. If a piece of amalgamated mossy zinc is added, the original color is restored. Solutions of silver ion and acidic and neutral peroxide did not effect oxidation. Basic peroxide and persulfate were found to oxidize the rhodium acetate to bright yellow solutions characteristic of rhodium(III).

A potentiometric titration with ceric sulfate indicated that 1.03 equiv was consumed per dimer. In a similar spectrophotometric titration, shown in Figure 1, 1.05 equiv per dimer was consumed. Isosbestic points were observed. Cyclic voltammetric experiments further confirmed the existence of a redox process for rhodium acetate. The values of E_f are listed in Table II and are found to be slightly medium dependent. While the separation of the reduction and oxidation waves exceed 57 mV, under our conditions even the $Ru(NH_3)_6{}^{3+}$–$Ru(NH_3)_6{}^{2+}$ couple gives peak separations between 60 and 70 mV. The peak potentials in a given medium were the same whether the initial solution contained the oxidized or the reduced form. The aquated rhodium acetate dimer showed no waves.

The color of the oxidized species is sensitive to the medium as can be seen in Table III. The species is held by a cation-exchange resin where it is removed quite rapidly by 1

Table II. Reduction Potentials for Tetraacetatodirhodium: $Rh_2(OAc)_4^+ + e^- \rightarrow Rh_2(OAc)_4$

E_f, V[a]	Sepn, mV[b]	Medium	Comments
1.225	75	0.1 M H_2SO_4	Reduced form
1.217	60	0.1 M H_2SO_4	Oxidized with slight excess Ce(IV)
1.112	76	1 M HTFMS	Oxidized form, ion exchanged
1.310	88	0.1 M $NaClO_4$	Reduced form in acetonitrile
1.187		1 M H_2SO_4	From potentiometric titration with Ce(IV)

[a] ±5 mV. [b] ±10 mV. Entries represent $E_{r,a} - E_{r,e}$.

Table III. Molar Extinction Coefficients per Dimer for $Rh_2(OAc)_4^+$

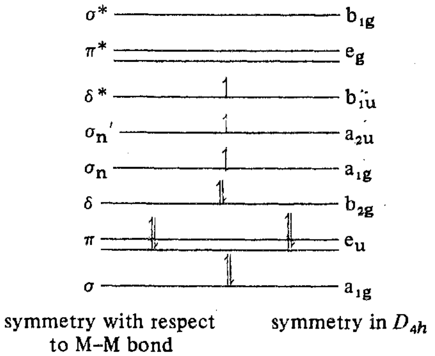
Wavelength, nm (extinction coeff)	Medium
758 (330), 513 (316)	1 M H_2SO_4, uv obscured by Ce(III)
758 (308), 515 (298), 217 (1.19×10^4)	1 M HTFMS
805 (359), 526 (317)	0.05 M NaCl
810 (476), 535 (410), 385 (2.23×10^3), 262 (4.65×10^3), 217 (1.19×10^4)	1 M HTFMS with excess NaCl (~0.1 M)

M strong, noncomplexing acid or lower concentrations of noncomplexing salts. The species is unstable and in tens of minutes disproportionates into the parent rhodium acetate and a yellow rhodium(III) product, separable by a cation-exchange resin.

Chloride ion associates with the mixed oxidation state of the rhodium acetate dimer. Saturation with respect to absorption changes is reached in 0.1 M NaCl and the change in the spectrum is much more marked than in the case of the parent rhodium(II) acetate[1] where concentrations on the order of 2 M NaCl are needed to produce significant change. With the tetraacetate, association is observed only in concentrated solution or in KBr pellets, but no halide-containing solids were isolated. High chloride levels do accelerate the decomposition of the oxidized rhodium acetate, but, by working quickly, it is possible to isolate a chloride salt. A rust-colored solid is obtained when a saturated solution of $Rh_2(OAc)_4$ in methanol is bubbled with chlorine gas until an orange color is produced, purged with excess argon, and reduced to dryness by rotary evaporation. The solid dissolves slowly, with some decomposition, in 1 M trifluoromethylsulfonic acid. It dissolves readily in water, giving maxima at 758 and 512 nm. The presence of chloride was confirmed by precipitation with silver ion.

The magnetic susceptibility of the purple solutions of freshly prepared and ion-exchanged $Rh_2(OAc)_4^+$ in 1 M trifluoromethylsulfonic acid was measured by the NMR method of Evans[9] as modified by Bailey.[10] Because of the small shifts, a different technique was used. A 5.24×10^{-3} M concentration of $Rh_2(OAc)_4^+$ showed a paramagnetic shift of 1.84 Hz. This yielded a corrected[11] susceptibility per mole of dimer of 2740×10^{-6} cgsu or a μ at 35° of 2.6 ± 0.3 BM. In a second experiment a 7.22×10^{-3} M solution of $Rh_2(OAc)_4^+$ yielded a shift of 1.50 Hz for a corrected susceptibility of 1770×10^{-6} cgsu/mol of dimer or a μ at 35° of 2.1 ± 0.4 BM also per mole of dimer.

Reduction of $Ru_2(OAc)_4Cl$. Investigation of the ruthenium complex was undertaken to clarify some questions of spectral assignments. Tetra-μ-acetato-diruthenium chloride, a compound with a "mixed oxidation state" was prepared according to the procedure of Stephenson and Wilkinson.[12,13] The electronic spectrum, magnetic susceptibility, and X-ray structure have been examined by Cotton and coworkers.[14] They assigned the 425-nm band to the $a_{1g} \leftarrow b_{2g}$ and/or $a_{2u} \leftarrow b_{2g}$ transitions, both vibronically allowed. Taking the 310-nm shoulder as the $b_{1u} \leftarrow b_{2g}$ transition, the b_{1u} orbital is estimated to be about 9 kK above the a_{1g} and a_{2u} orbitals. The qualitative MO diagram is shown.



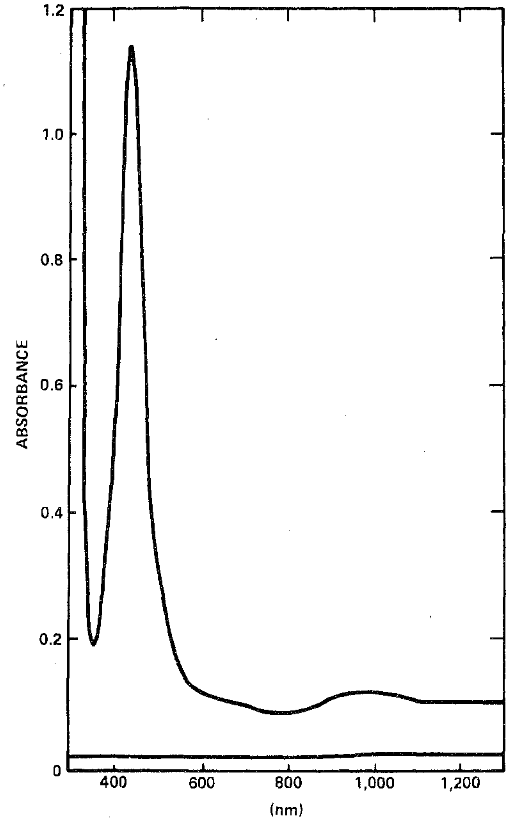


Figure 2. Visible and near-infrared spectrum for Ru_2Ac_4Cl in D_2O (blank shown at bottom).

On the basis of Cotton's interpretation, one would expect to find additional electronic transitions in the near-infrared spectrum. The spectrum in D_2O confirmed this and is shown in Figure 2. A new broad band at about 1000 nm is observed. Comparison with the extinction of the 425-nm band [ϵ 699 cm^{-1} M^{-1} (mol of dimer)$^{-1}$] yielded a value of about 60 cm^{-1} M^{-1} (mol of dimer)$^{-1}$ for the long-wavelength band. If the spectrum is measured in a KBr pellet, the band is actually found to be composite, with peaks at 960 and 1110 nm. These two peaks reasonably can be taken to correspond to the $b_{1u} \leftarrow a_{2u}$ and $b_{1u} \leftarrow a_{1g}$ transitions. The a_{1g} and a_{2u} levels are then separated by 1.4 kK.

Cotton et al.[15] have recently reported the electrochemical reduction of tetrabutyratodiruthenium(1+) complex. Cyclic voltammetric investigation of the tetraacetate in aqueous 0.1 M sulfuric acid confirms the presence of a single redox wave at 0.292 V vs. NHE (83-mV separation); this compares with a value of 0.242 (0.00 vs. SCE) reported for the butyrato complex in ethanol with tetrabutylammonium perchlorate as electrolyte. The solution is reduced within minutes by zinc amalgam and may be reoxidized by air. The visible spectra of the reduced and oxidized forms are quite similar with the 425-nm band of the oxidized form being replaced by a band at 438 nm, ϵ 501 cm^{-1} M^{-1} (mol of dimer)$^{-1}$ (the near-infrared spectra were not examined).

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Registry No. $Rh_2(OAc)_4$, 15956-28-2; $Rh_2(OAc)_3{}^+$, 55590-55-1; $Rh_2{}^{4+}$, 55569-94-3; $Rh_2(OAc)_2{}^{2+}$, 55590-54-0; $Rh_2(OAc)_4Cl$, 55569-93-2; $Ru_2(OAc)_4Cl$, 24729-38-2.

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Contribution from the Department of Chemistry,
University College, Cardiff, Wales, United Kingdom

Ligand Field Theory of Metal Sandwich Complexes. Ground States and Spectroscopic Properties of d^5 Configurations

Keith D. Warren

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Recently the ligand field model has proved to be of considerable utility for the interpretation of the low energy d–d transitions of metal sandwich complexes[1,2] and for understanding the magnetic susceptibility and magnetic resonance phenomena shown by such species.[3,4] Thus far the familiar strong-field approach has proved to be the most satisfactory, and for d^2, d^3, and d^4 systems and their complementary counterparts full interaction matrices have been given,[2,5] assuming the effectively axial ($C_{\infty v}$) symmetry which obtains[6] for these complexes. For d^4, d^5, d^6, and d^7 systems, as for the analogous O_h compounds, either high-spin or low-spin ground states are in principle possible within the usual range of ligand field parameters, but for both metallocenes and bis(arene) compounds the d^6 and d^7 configurations show exclusively low-spin $^1\Sigma^+$ ($\sigma^2\delta^4$) and $^2\Pi$ ($\sigma^2\delta^4\pi$) ground states, while for the d^4 complex chromocene the low-spin $^3\Delta$ ($\sigma\delta^3$) ground state is well established.[3,5,7]

For d^5 systems however the evidence is confused and at times conflicting. Although it is now clear that the ferricenium cation, $FeCp_2{}^+$, shows a low-spin $^2\Delta$ ($\sigma^2\delta^3$) ground level and the bis(arenes) a similarly low-spin $^2\Sigma^+$ ($\sigma\delta^4$) ground state, it is still not altogether clear whether the ground state of manganocene, $MnCp_2$, corresponds to the high-spin $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) or to the low-spin $^2\Delta$ ($\sigma^2\delta^3$) situation. The purpose of the present note is therefore to set out the results of a complete ligand field calculation for d^5, $C_{\infty v}$, systems and to correlate these with the known ground state and spectroscopic properties of d^5 metal sandwich complexes.

The complete strong-field electrostatic repulsion matrices have thus been evaluated using the methods described before,[2,5] and the results are given in the Appendix[8] and illustrated diagramatically in Figure 1. The diagonal one-electron core terms are as given earlier, and the ratios $Dt/Ds = 0.55$ (equivalent to $E(\delta) < E(\sigma) << E(\pi)$) and $C/B = 4.0$ are again assumed. With these parameters the high-spin to low-spin crossover is seen to occur at about $Dt/B = 2.8$ for the d^5 configuration as compared with the values of 2.9, 2.55, and 2.7 for the d^4, d^6, and d^7 systems, respectively. Consequently there is no a priori reason to expect $MnCp_2$ to be high spin while $CrCp_2$ remains low spin.

Nevertheless, until a short time ago it was widely accepted that the ground state of manganocene was in fact the high-spin $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) level. This was based largely on the spin-only magnetic behavior found[9] for $MnCp_2$ in solution in benzene and ether and in solid solution in $MgCp_2$. For the pure solid the spin-only moment of 5.92 BM was found above the phase transition temperature of 158°, but below that point the moment was substantially smaller, decreasing markedly with decrease in temperature, this being attributed to antiferromagnetic interactions. Moreover, ESR experiments[10] at 270 and 100°K on pure $MnCp_2$ gave an almost isotropic g value of 2.0, the signal losing intensity on cooling, again consistent with a high-spin ground state.

Subsequently, although the first photoelectron spectrum reported[11] for $MnCp_2$ was surprisingly interpreted in terms of a $^2\Sigma^+$ ground level, it was later shown[5] that the ligand field treatment of the data was more consistent with a high-spin $^6\Sigma^+$ ground level, and this was confirmed by experimental reinvestigation of the spectrum by Orchard et al.,[7] who concluded that $MnCp_2$ was essentially high spin in the vapor phase, although the methyl-substituted analog, $Mn(MeCp)_2$, existed as a mixture of high- and low-spin forms. Finally, INDO type MO calculations by Clack[12] also supported a high-spin ground state for $MnCp_2$ although $E(^2\Delta) - E(^6\Sigma^+)$ was estimated at only 800 cm^{-1}.

However, two very recent studies have shed much additional light on the situation. Thus ESR measurements by Ammeter, Bucher, and Oswald[13] have now shown that both $MnCp_2$ and $Mn(MeCp)_2$ can exist in either high-spin, $^6\Sigma^+$, or low-spin, $^2\Delta$, forms, depending upon the molecular environment: when diluted in $MgCp_2$ manganocene shows typical high-spin behavior at 4.2°K whereas in the isostructural $FeCp_2$ or in $RuCp_2$ the ESR spectrum is characteristic of a low-spin $^2\Delta$ ($\sigma^2\delta^3$) ground state and closely resembles that found for the isoelectronic ferricenium cation. Consequently the anomalous magnetic properties of undiluted $MnCp_2$ were explained in terms of a thermal equilibrium between the high- and low-spin forms, the observed magnetic moment being reproducible by assuming $E(^6\Sigma^+) - E(^2\Delta) \approx 175$ cm^{-1}. Furthermore, the broad ESR signal of pure $MnCp_2$ at $g = 2.0$ disappeared at 4.2°K and was therefore attributed to thermal population of the higher lying $^6\Sigma^+$ state. Here it is pertinent to note that $Mn(MeCp)_2$ would be expected to donate more strongly toward the metal than $MnCp_2$ and thus to lie further over on the low-spin side of the crossover point. This expectation is borne out both by the observation of Ammeter et al.[13] that $Mn(MeCp)_2$ is low spin in $Fe(MeCp)_2$ and in $Mg(MeCp)_2$ and by the fact that the magnetic moments observed[14] for pure $Mn(MeCp)_2$ below the transition temperature are appreciably