

by electron transfer) to form a radical pair ( $\text{Pt}^1\text{-X} + \text{R}\cdot$ ). This pair can either collapse to the regular adduct<sup>6</sup> or diffusively separate to form  $\text{Pt}^1\text{-X}$  and  $\text{R}\cdot$ . Depending on the reactivity of the reactant alkyl halide, two pathways may then develop. For very reactive halides (as are described in this communication),  $\text{Pt}^1\text{-X}$  can rapidly abstract further halide to yield dihalide and organic radical. CIDNP effects result from the diffusive encounter of these product radicals. Alternatively, for less reactive halides, the organic radical will initiate a chain process to produce regular adduct (and/or hydrido complex).

In the reaction of isopropyl iodide with **1a**, the chain process ( $k_b$ ) to form hydrido complex and the abstraction process ( $k_a$ ) to form diiodo complex are competitive. For isopropyl bromide, however, the chain mechanism dominates,<sup>1</sup> as might be expected since in terms of bond strength,  $\text{C-Br} \gg \text{C-I}$ .

Regular adduct formation in the reaction of benzyl bromide with **1a** could arise in two possible ways: (a) *via* the  $\text{S}_{\text{N}}2$  process and (b) by radical pair collapse ( $k_c$ ). However, **4a** is also formed and if its formation were competitive with the collapse mechanism, the product ratio should be dependent on solvent viscosity<sup>15</sup> ( $k_d$  will decrease with respect to  $k_c$  as viscosity increases). However, we find that changing the solvent from benzene to *tert*-butylbenzene (a viscosity increase of *ca.* 45-fold) leads to no significant change in product ratio. This observation suggests that *trans*- $\text{Pt}(\text{CH}_2\text{C}_6\text{H}_5)\text{Br}(\text{PEt}_3)_2$  is *not* formed by path b. In this case, a competition between an  $\text{S}_{\text{N}}2$  process (to form regular adduct) and a radical abstraction process (to produce dibromide) is indicated. For the reaction of benzyl chloride with **1a**, only the  $\text{S}_{\text{N}}2$  path is operative because in comparing  $\text{RCl}$  vs.  $\text{RBr}$  reactivities,  $\text{Cl/Br} \sim 10^{-2}$  for a nucleophilic displacement, whereas for a radical abstraction process  $\text{Cl/Br} \sim 10^{-4}$ . The radical process would then become noncompetitive for benzyl chloride.

A further example concerns  $\alpha$ -haloester additions to **1a**. Using ethyl  $\alpha$ -chloropropionate, the regular adduct is cleanly produced and occurs *via* a radical chain process.<sup>1</sup> In the corresponding  $\alpha$ -bromoester reaction with **1a**, both regular adduct and dibromide are produced.<sup>16</sup> However, *only* the regular adduct formation is inhibited by the presence of 5 mol % duroquinone. It appears here that the radical chain and abstraction processes are competitive, but the  $\text{S}_{\text{N}}2$  process is not.

Summarizing, several possible routes exist for these reactions, and the choice of a particular path will depend on many factors, *e.g.*, the nature of the carbon-halogen linkage, the nucleophilicity of the metal complex, the ability of the metal complex to undergo one-electron processes (*i.e.*, relative positioning of oxidation levels and availability of suitable mechanisms for one-electron transfer), steric effects, and ligand exchange processes. A subtle balance of these factors will direct which path (if any) dominates the oxidative addition process.

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- (4) Separate experiments, in which the reactions of **2** or **3** with alkyl halide under a variety of conditions were studied, showed **4** to be formed too slowly for such routes to be significantly involved here.
- (5) Although the radical trap *t*-BuNO has been used to study the reactions of  $\text{Pt}(\text{PPh}_3)_3$  with  $\text{CH}_3\text{I}$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ , and  $\text{C}_2\text{H}_5\text{I}$ ,<sup>6</sup> the results appear ambiguous in view of a recent report<sup>7</sup> that *t*-BuNO actually induces radical decomposition of  $\text{Pd}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ . It should be noted, however, that **2a** is stable toward radical decomposition under the usual reaction conditions in the absence of *t*-BuNO.
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- (8) Reactions were carried out using 0.04–0.10 M solutions of **1**. <sup>31</sup>P nmr spectroscopy (<sup>1</sup>H noise decoupled, FT mode) enabled monitoring and product analysis of the reaction. Spectra were recorded at  $-55^\circ$  in toluene (or benzene-toluene mixtures) to slow intermolecular phosphine exchange processes. Unambiguous identification of all complexes was possible by comparison of <sup>31</sup>P nmr chemical shift and  $J(^{195}\text{Pt}-^{31}\text{P})$  values with authentic samples. At  $-55^\circ$ , in the presence of liberated  $\text{PEt}_3$ , the hydrido and dihalide species are converted and detected as the corresponding cations,  $[\text{PtH}(\text{PEt}_3)_3]^+\text{I}^-$  and  $[\text{PtI}(\text{PEt}_3)_3]^+\text{I}^-$ . When the reactions are carried out in toluene, small quantities of *trans*- $\text{Pt}(\text{CH}_2\text{C}_6\text{H}_5)(\text{PEt}_3)_2$  are also detected. Organic products were determined by glc and <sup>1</sup>H nmr spectroscopy.
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- (13) If the organic halide has a functional group which can bind to the metal, other paths are also possible. See J. A. Osborn in "Prospects in Organotransition-Metal Chemistry" (U.S.-Japan Monograph), Plenum Press, New York, N.Y., 1974; A. V. Kramer, unpublished results.
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- (16) Due to its extreme reactivity, even at  $-65^\circ$ , we have not been able to detect CIDNP effects in this system. Interestingly, <sup>31</sup>P nmr data at  $-55^\circ$  indicate that in the radical chain path, the  $[\text{CH}_3\text{CHCOOEt}]$  radical is competitively captured by **1a** at both carbon (to form the regular addition adduct) and oxygen. The O-bonded complex rearranges at ambient temperatures to the more stable regular (C-bonded) adduct.

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## On the High-Spin-Low-Spin Equilibrium of Manganocene and Dimethylmanganocene

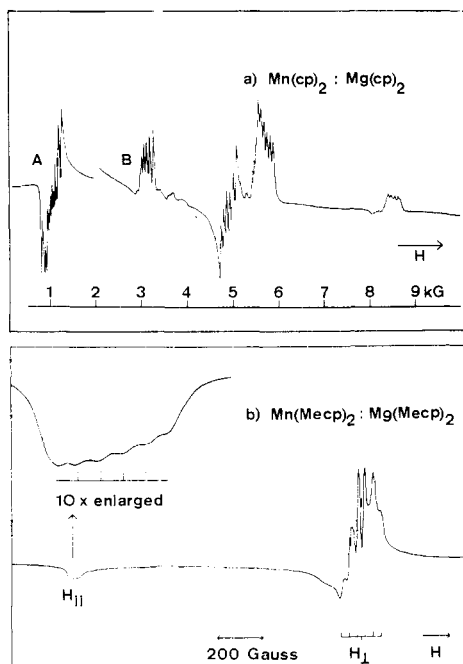
Sir:

Investigations concerning the nature of the electronic ground state of manganocene,  $\text{Mn}(\text{cp})_2$ , have been performed for more than 20 years.<sup>1-12</sup> Among the metallocene series,  $\text{Mn}(\text{cp})_2$  is of particular interest, because both high-spin,  $a_{1g}^1e_{2g}^2e_{1g}^2(^6A_{1g})$ , and low-spin,  $a_{1g}^2e_{2g}^3(^2E_{2g})$  or  $a_{1g}^1e_{2g}^4(^2A_{1g})$ , configurations could be realized in the ground state, depending on the magnitude of the axial ligand field splittings  $D_s$  and  $D_t$ .<sup>8-12</sup> In the fifties magnetic susceptibility ( $\chi_m$ ) measurements,<sup>1-4</sup> chemical evidence,<sup>1-5</sup> and esr results<sup>7</sup> led to the conclusion that both  $\text{Mn}(\text{cp})_2$  and related 1,1'-dimethylmanganocene,  $\text{Mn}(\text{mecp})_2$ , were "essentially ionic ( $S = 5/2$ ) cyclopentadienides" in liquid and solid solutions as well as in pure solid state, in spite of some difficulties encountered in the interpretation of the anomalously small  $\chi_m$  found in the pure solids at low temperatures. It was therefore somewhat surprising when in 1972 Rabalais, *et al.*,<sup>11</sup> reported a HeI photoelectron spectrum ascribed to gaseous  $\text{Mn}(\text{cp})_2$  possessing a  $e_{2g}^4a_{1g}^1(^2A_{1g})$  ground state configuration. This interpretation was, however, criticized by Evans, *et al.*<sup>12</sup> The Oxford group<sup>12</sup> recently measured the HeI photoelectron spectra of both  $\text{Mn}(\text{cp})_2$  and  $\text{Mn}(\text{mecp})_2$ , and using ligand field theoretical arguments came to the conclusion that gaseous  $\text{Mn}(\text{cp})_2$  is essentially a high-spin ( $^6A_{1g}$ ) complex, while  $\text{Mn}(\text{mecp})_2$

**Table I.** Magnetic Parameters and Derived Quantities for Low-Spin Mn(cp)<sub>2</sub> and Mn(mecp)<sub>2</sub> at 4.2°K

Molecule	Host lattice	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^a$	$A_{\perp}^a$	$k_{\parallel}V_{23}^b$	$\delta$ (cm <sup>-1</sup> ) <sup>c</sup>
Mn(cp) <sub>2</sub>	Fe(cp) <sub>2</sub>	3.519 (4)	1.222 (10)	52.3 (0.6)	≤ 26 <sup>d</sup>	0.48	200
Mn(cp) <sub>2</sub>	Ru(cp) <sub>2</sub>	3.562 (4)	1.031 (20)	58.7 (0.7)	≤ 70 <sup>d</sup>	0.46	170
Mn(mecp) <sub>2</sub>	Mg(mecp) <sub>2</sub>	3.00 (2)	1.889 (2)	13.7 (1.5)	24.6 (2.0) <sup>e</sup>	0.75	740
Mn(mecp) <sub>2</sub>	Fe(mecp) <sub>2</sub>	3.06 (2)	1.850 (2)	11.4 (3.0)	24.5 (2.0)	0.69	630

<sup>a</sup> <sup>55</sup>Mn hyperfine parameters in units of 10<sup>-4</sup> cm<sup>-1</sup>. <sup>b</sup> Calculated from  $g$  values *via* eq 2. <sup>c</sup> Low symmetry distortion parameter, calculated from  $g$  values and eq 1, assuming  $\zeta = 260$  cm<sup>-1</sup>. <sup>d</sup> Not resolved at 4.2°K; estimated from line widths. <sup>e</sup> Indications for  $A_x \neq A_y$  present.



**Figure 1.** (a) X-Band esr spectrum of Mn(cp)<sub>2</sub> diluted in polycrystalline Mg(cp)<sub>2</sub> at 4.2°K. The signal amplitude of part B has been multiplied by a factor of 6 relative to part A. (b) X-Band esr spectrum of Mn(mecp)<sub>2</sub> diluted in polycrystalline Mg(mecp)<sub>2</sub> at 4.2°K. <sup>55</sup>Mn hfs splittings ( $A_{\parallel}$  and  $A_{\perp}$ ) are indicated with stick diagrams.

vapour exists as a mixture of comparable amounts of low-spin and high-spin configurations.

In view of this controversy, it seemed worthwhile to reinvestigate the neutral d<sup>5</sup> metallocenes by esr. In this communication we show that both Mn(cp)<sub>2</sub> and Mn(mecp)<sub>2</sub> can be found in high-spin (<sup>6</sup>A<sub>1g</sub>) as well as in low-spin (<sup>2</sup>E<sub>2g</sub>) ground states, depending on the molecular environment. We have investigated polycrystalline samples of both compounds undiluted and diluted in several diamagnetic host systems (organic solvents and isostructural sandwich complexes) by electron spin resonance (esr) at various temperatures between 4.2 and 300°K. The X-band esr spectrum of Mn(cp)<sub>2</sub> diluted in Mg(cp)<sub>2</sub> showing hyperfine structure attributable to the <sup>55</sup>Mn nucleus ( $A \approx 65$  G) at liquid helium temperature is shown in Figure 1a. This spectrum is somewhat dependent on temperature and can be considered typical for a high-spin d<sup>5</sup> system exhibiting zero field splittings of the same order of magnitude as the applied microwave frequency ( $\sim 0.3$  cm<sup>-1</sup>).<sup>13-15</sup> This interpretation was corroborated by additional esr measurements at Q-band frequency ( $\sim 1.2$  cm<sup>-1</sup>) and is consistent with earlier magnetic susceptibility studies.<sup>2,3</sup>

In contrast Mn(cp)<sub>2</sub> diluted in isostructural d<sup>6</sup> host lattices shows low-temperature esr signals very similar to the spectra observed for isoelectronic ferricenium cation<sup>16</sup> known to have a <sup>2</sup>E<sub>2g</sub> ground state.<sup>16-19</sup> Low-spin spectra are also obtained for Mn(mecp)<sub>2</sub> diluted in Mg(mecp)<sub>2</sub> and Fe(mecp)<sub>2</sub>. In some cases <sup>55</sup>Mn hyperfine structure is resolved at 4.2°K, as shown in a typical spectrum of

Mn(mecp)<sub>2</sub> in Mg(mecp)<sub>2</sub> in Figure 1b. All low-spin spectra broadened significantly upon warming and usually became unobservable well below 77°K. Magnetic parameters (with experimental uncertainties in parentheses) are listed in Table I. The observed  $A_{\parallel}$  and  $A_{\perp}$  values seem at first sight surprisingly small for a Mn(II) complex exhibiting a single unpaired electron in an orbital of predominantly 3d<sub>g</sub> character, but the theoretical treatment explains the experimental values rather well, as will be shown below.

Neglecting excited configurations and using the same notation as for the treatment of the related case of Co(cp)<sub>2</sub> (low-spin d<sup>7</sup>, <sup>2</sup>E<sub>1g</sub>),<sup>20,21</sup> we can write the lowest Kramers doublet as

$$\phi^{\pm} = c\phi_2^{\pm} \pm is\phi_3^{\pm}$$

where  $\phi_2$  and  $\phi_3$  are e<sub>2g</sub> molecular orbitals and where the

$$\phi_2 = c_0 d_{x^2-y^2} + c_0' \phi_2^{\text{cp}}$$

$$\phi_3 = c_0 d_{xy} + c_0' \phi_3^{\text{cp}}$$

coefficients  $c$  ( $\cos \rho$ ) and  $s$  ( $\sin \rho$ ) obey the relationship<sup>16,21</sup>

$$\frac{2cs}{c^2 - s^2} = \frac{\zeta}{\delta} \quad (1)$$

In this approximation the magnetic tensors exhibit axial symmetry and are given by the expressions

$$g_{\parallel} = g_e + 8csk_{\parallel}V_{23} \quad (2)$$

$$g_{\perp} = g_e(c^2 - s^2)$$

$$A_{\parallel} = Pc_0^2 \left( \frac{\Delta g_{\parallel}}{k_{\parallel}} - \frac{4}{7} - \kappa_0 \right) \quad (3)$$

$$A_{\perp} = Pc_0^2 \frac{g_{\perp}}{g_e} \left( \frac{2}{7} - \kappa_0 \right)$$

In eq 2 and 3  $k_{\parallel}$  is an orbital reduction factor<sup>20</sup>

$$k_{\parallel} = 1 - c_0'^2(1 - \gamma)$$

where

$$\gamma = \frac{1}{2} \langle \phi_2^{\text{cp}} | L_z | i\phi_3^{\text{cp}} \rangle$$

and  $V_{23}$  is a vibronic quenching factor<sup>20</sup> resulting from reduced vibrational overlap between  $\phi_2$  and  $\phi_3$  due to dynamic Jahn-Teller coupling of the E<sub>2g</sub> electronic state with one or several of the e<sub>1g</sub> metallocene vibrational modes.<sup>22</sup>

From the  $g$  values ratios  $\zeta/\delta$  and total reduction factors,  $k_{\parallel}V_{23}$  have been obtained *via* eq 1 and 2 and are also listed in Table I. As expected the low symmetry distortion parameter  $\delta$  is substantially larger for Mn(mecp)<sub>2</sub> than for Mn(cp)<sub>2</sub>, while vibronic quenching is much more pronounced in Mn(cp)<sub>2</sub>. The limited hyperfine data can be reproduced from eq 3 with reasonable values for  $P$  ( $\approx 162 \times 10^{-4}$  cm<sup>-1</sup>, see ref 23),  $\kappa_0$  ( $\approx 0.5$ , see ref 23),  $c_0^2$  ( $\approx 0.9$ , see ref 16 and 24), and  $k_{\parallel}$  ( $\approx 0.9$ , see ref 16). The small values of  $|A_{\parallel}|$  and  $|A_{\perp}|$  result from the fact that the Fermi contact term  $\kappa_0$  subtracts from the anisotropic contributions to the hyperfine tensor in both of eq 3. Generalization of the ex-

pressions for the magnetic tensors by taking into account mixing with all states resulting from singly excited configurations<sup>25</sup> does not alter the above results significantly.

Our results indicate that free  $\text{Mn}(\text{cp})_2$  and  $\text{Mn}(\text{mecp})_2$  molecules are so close to the low-spin-high-spin crossover point that the small intermolecular forces as present in frozen solutions or molecular crystals are sufficient for inducing the observed changes in the electronic ground state configuration. Consistent with ligand field theoretical expectations the high-spin ground state is found preferentially in host systems favoring large metal to ring distances, while the low-spin ground state is induced by sandwich matrices exhibiting short metal to ring distances.

We conclude that the most reasonable explanation of the anomalous magnetic behavior<sup>2-7</sup> of undiluted  $\text{Mn}(\text{cp})_2$  and  $\text{Mn}(\text{mecp})_2$  is a temperature dependent high-spin-low-spin equilibrium. We found that a large part of the  $\chi_m(T)$  curve<sup>3,4</sup> of  $\text{Mn}(\text{cp})_2$  below the transition point can even be explained by an almost constant energy difference  $E(^6A_{1g}) - E(^2E_{2g}) \approx +0.5$  kcal/mol. This interpretation is consistent with our observation that the broad esr signal<sup>7</sup> of pure  $\text{Mn}(\text{cp})_2$  at  $g = 2$  disappears completely at 4.2°K; this band must be due to the thermally populated high-spin state.

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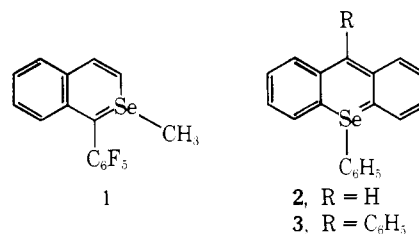
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## Synthesis and Characterization of a Selenabenzene<sup>1</sup>

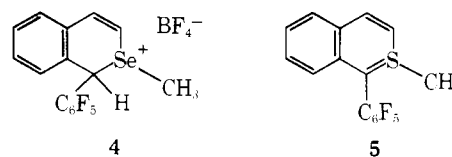
Sir:

Thiabenzene recently have been the subject of thorough investigations.<sup>2-4</sup> We now report the first example of an authentic selenabenzene, 1-pentafluorophenyl-2-methyl-2-

selenanaphthalene (**1**), and present evidence which refutes earlier claims<sup>5,6</sup> for stable 10-selenaanthracenes **2** and **3**.



Reaction of 2-selenanaphthalenium perchlorate<sup>7</sup> with pentafluorophenylmagnesium bromide in ether furnished 1-pentafluorophenyl-2-seleno-3-chromene (60%) which upon methylation with silver tetrafluoroborate-methyl iodide gave 1-pentafluorophenyl-2-methyl-2-seleno-3-chromenium tetrafluoroborate (**4**), (78%) as a mixture of diastereomers (1/2.8 cis/trans, by nmr).<sup>10</sup> Treatment of the diastereomeric mixture with dimsyl-*d*<sub>5</sub>-lithium (1 equiv) in toluene-*d*<sub>8</sub>-1,2-dimethoxyethane under nitrogen at low temperature<sup>11</sup> immediately produced a deep burgundy solution. The <sup>1</sup>H nmr spectrum<sup>12</sup> indicated that this solution contained **1**. Notable features were the characteristic up-field doublet of the 3-vinyl proton and the side bands accompanying the methyl singlet due to <sup>77</sup>Se-<sup>1</sup>H scalar coupling. The <sup>77</sup>Se-<sup>1</sup>H side bands clearly attest to the presence of a selenium-methyl bond,<sup>13</sup> and the high field doublet<sup>12</sup> at  $\delta$  4.89 reflects the ylide nature of the selenabenzene,<sup>14</sup> a phenomenon seen with the corresponding thiabenzene, 1-pentafluorophenyl-2-methyl-2-thianaphthalene (**5**), for



which  $\delta$  4.76 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz) was observed.<sup>3,17</sup> In the presence of DMSO-*d*<sub>6</sub>, further splitting of the methyl and 4-vinyl proton signals was observed. This is reasonably attributed to deuterium coupling, the deuterium being incorporated by an exchange reaction with the solvent at the methyl and 3-vinyl positions.<sup>18</sup>

The absorption band responsible for the intense color of **1** has  $\lambda_{\text{max}}$  500 nm (DMSO), closely comparable to the  $\lambda_{\text{max}}$  480 nm (DMSO) observed for **5** and to the  $\lambda_{\text{max}}$  in the visible region of other authentic thiabenzene.<sup>3</sup> The structure for **1** is also supported by mass spectral data.<sup>19</sup>

When the burgundy solution was allowed to stand at room temperature, thermal decomposition rapidly took place, as evinced by decolorization of the sample to a pale orange. Decay of the original sample was confirmed by <sup>1</sup>H nmr.<sup>20</sup> The visible spectrum of **1** was monitored with time to afford the interval for 50% decomposition (first half-life) of 47 min at 25°.<sup>21</sup>

It is apparent that **1** has a lifetime between two and three orders of magnitude shorter than the sulfur analog **5** under the same conditions, 249 hr.<sup>3</sup> This order of relative stabilities may be presumed to exist between other structurally analogous seleno- and thiabenzene. The instability of **1** points to the fact that selenabenzene, unless substituted by strongly electron withdrawing groups, are not likely to exhibit sufficient stability to be readily observed.

In light of these conclusions, the reported<sup>5,6</sup> synthesis and isolation of **2** and **3** and their description as stable compounds appeared suspect, particularly so since the physical properties of these solids were strikingly reminiscent of those<sup>22,23</sup> displayed by materials previously characterized