

drying at 120 °C for 14 h yielded 2.119 g of dark gray solid. The dark deposits were shown by ESCA to be Pt<sup>0</sup>, with only the two signals of zero-valent Pt at 75.4 (4f<sup>5/2</sup>) and 71.85 (4f<sup>7/2</sup>) eV present.<sup>6</sup> The distribution of platinum was fairly uniform; no agglomerates could be detected with SEM. Similar photoplatinization of white, undoped anatase<sup>7</sup> and faint yellow tungsten oxide (WO<sub>3</sub>) could also be accomplished. The mechanism of the photodeposition probably follows that found in other heterogeneous photoprocesses at semiconductors.<sup>1</sup> The photogenerated hole causes oxidation of acetate while the photogenerated electron leads to reduction of the platinum complex. The irreversibility of the oxidative decarboxylation of the acetate<sup>8</sup> hinders any back-reaction between the reduced metal species and oxidation product and suggests that carboxylic acids are excellent choices as electron donors for heterogeneous photoreductions.

To study the role of the electron donor in the process a similar suspension of lightly doped anatase in a solution of sodium hexachloroplatinum(IV), pH ~6, at 60 °C was irradiated in the absence of acetate. The deposition of metal was obviously slower, but after irradiation for 21 h the powder had darkened significantly and after separation had gained 62 mg of weight (total weight, 962 mg), presumably owing to deposition of metallic platinum. In this case water plays the role of donor and is oxidized, less efficiently, at the illuminated particle.

A homogeneous photodecomposition of the platinum(IV) complex in the presence of acetic acid was also found. Irradiation of a homogeneous deaerated, buffered mixture of 7.5 mL of H<sub>2</sub>PtCl<sub>6</sub> (~0.11 M) and 7.5 mL of glacial acetic acid at pH 4 led to deposition of a metallic mirror of platinum on the cell wall together with evolution of CO<sub>2</sub>. After 13.4 h, 0.89 mmol of CO<sub>2</sub> had been trapped as BaCO<sub>3</sub> and 131 mg (0.67 mmol) of metallic Pt had been photodeposited. The solution color first changed from bright orange to bright red (after ~7 or 8 h, no black solids were present) and was a faint orange at the end of the photolysis. The photodeposited Pt was found to give again only the two ESCA signals of zero-valent Pt (74.8 and 71.4 eV). The homogeneous photodeposition permitted the photoplatinization of aluminum oxide (Woelm, neutral), a material whose wide band gap (>7 eV) prevents light absorption by the solid.<sup>9</sup> The mechanism of this homogeneous process was not investigated; similar photoreductions of platinum(IV) complexes to platinum(II) involving coordinated oxalate or malonate have been reported,<sup>10</sup> but reduction to the metal was not found.

Our reasons for proposing different heterogeneous and homogeneous routes to metal deposition are based on the following: (a) the rate of CO<sub>2</sub> evolution in the presence of TiO<sub>2</sub> (~400 μmol/h) is much larger than in equivalent Al<sub>2</sub>O<sub>3</sub> suspensions (~47 μmol/h) or in the absence of powder (~66 μmol/h); (b) the Pt deposition rate under homogeneous conditions is slower by a factor of ~2; (c) the ratio of Pt deposited to CO<sub>2</sub> evolved, 2.6:1 in the presence of TiO<sub>2</sub> (compared with a predicted complete heterogeneous deposition ratio of 4:1), is greater than the ratio in the absence of powder (1.3:1) or with Al<sub>2</sub>O<sub>3</sub> present (0.8:1); (d) the homogeneous process is characterized by a long induction period where no Pt deposition occurred while deposition of metallic Pt was noticed in the TiO<sub>2</sub> experiments within 25 min. Finally we have observed conditions, such as for the deposition of Cu on TiO<sub>2</sub><sup>7</sup> (see below), where no homogeneous deposition process occurs.

This general method of catalyst preparation is of interest because high dispersion and small clusters of the metal on the support surface should exist. Metal deposition probably only occurs near sites where photons strike the surface and the light flux can be made very small. The low temperature conditions of the photodeposition also would minimize surface diffusion of metal atoms which would produce larger aggregates. There

is a potentially wide range of metals that might be photodeposited on semiconductor powders by this method. For aqueous suspensions of TiO<sub>2</sub>, M<sup>n+</sup>/M couples with redox potentials positive of the H<sup>+</sup>/H<sub>2</sub> potential (which corresponds closely to the flat-band potential of n-TiO<sub>2</sub>) should be available, with a wider range possible in nonaqueous solvents. In recent experiments<sup>7</sup> PdCl<sub>4</sub><sup>2-</sup>, Ag<sup>+</sup>, and Cu<sup>2+</sup> have been photocatalytically reduced and deposited as metals on undoped anatase powder in the presence of acetate, with evolution of CO<sub>2</sub>. Several experiments have demonstrated the use of these powders as catalysts. For example, platinized TiO<sub>2</sub> and WO<sub>3</sub> powders showed high catalytic activity for the thermal hydrogenation of neat benzene (and cyclohexene) to cyclohexane at temperatures of 80 °C and below. Similarly the platinized anatase powders did result in efficient photocatalytic decarboxylation of saturated carboxylic acids.<sup>1</sup> Besides the possibility of forming highly active, solid supported metal catalysts, the photodeposition of metals on solid substrates is attractive for light controlled metal deposition (e.g., in printed circuits) and for treatment of some waste streams (e.g., those containing low levels of Cu<sup>2+</sup>).<sup>11</sup> Research extending the scope of the photodeposition of metals on solids and concerning their catalytic activity now is in progress in this laboratory.<sup>12</sup>

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## Intramolecular Antiferromagnetic Exchange in Tris(o-semiquinone) Complexes of Vanadium(III), Chromium(III), and Iron(III)

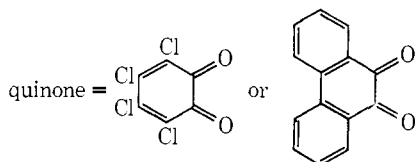
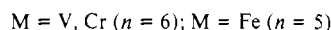
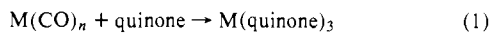
Sir:

Examples of transition metal complexes containing paramagnetic ligands are relatively few in number. Complexes consisting of both paramagnetic metal ions and paramagnetic ligands are of particular importance for the fundamental information they offer about metal-ligand bonding and specifically about interactions between metal centers and paramagnetic organic substrate molecules. Spin-spin exchange

between metal and ligand can be sufficiently strong in this class of compounds so as to result in overall diamagnetism. Radical-anion coordination has been invoked for several types of ligands, notably the O<sub>2</sub> in oxygenated heme systems<sup>1</sup> and neutral complexes containing diimine<sup>2</sup> and 1,2-dithiolene ligands,<sup>3</sup> although these compounds exhibit normal magnetic behavior. Systems where exchange is weak are exceedingly rare and are confined almost exclusively to complexes containing nitroxyl ligands.<sup>4</sup> Aspects of the antiferromagnetic interaction between ligand and metal in compounds of this form can be examined using EPR and variable-temperature magnetic susceptibility measurements.

An inherent problem associated with the characterization of complexes containing paramagnetic ligands is establishing that the ligand is, in fact, the paramagnetic center of the molecule. Frequently the unpaired spin resides in a molecular orbital delocalized over both ligand and metal. Semiquinones, however, have been reported to form complexes with diamagnetic metal ions which seem to be clear examples of radical-anion coordination.<sup>5-7</sup> Their EPR spectra and weak metal hyperfine coupling in cases where a nuclear spin is available indicate a localized electronic structure with the unpaired electron contained within the electronic framework of the ligand. The semiquinones offer a unique opportunity to examine metal-ligand spin-spin exchange within a chelated complex. We would like to present the preliminary results of an investigation on the magnetic properties of a series of complexes best formulated as containing high-spin, trivalent metal ions with three chelated semiquinone ligands.

We and others have found that neutral quinone complexes can be synthesized by the direct addition of orthoquinone ligands to a neutral metal carbonyl (eq 1).<sup>8</sup> For the present



investigation the metals used were V, Cr, and Fe,<sup>9</sup> and the quinones, 9,10-phenanthrenequinone and tetrachloro-1,2-benzoquinone. Crystallographic data available for all members of the series except V(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub> indicate monomeric, octahedral geometries.<sup>10</sup> The tris(quinone)chromium complexes, although even electron molecules, exhibit weak paramagnetism in solid. At 285 K Cr(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub> has a magnetic moment of 1.15 μ<sub>B</sub> which drops to a value of 0.30 μ<sub>B</sub> at 4.2 K. Similar behavior is observed for Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> which begins at 286 K with a moment of 1.08 μ<sub>B</sub> which drops to a value of 0.38 μ<sub>B</sub> at 4.2 K. The tris(quinone)iron complexes with two additional electrons exhibit similar behavior with moments of 3.43 and 3.96 μ<sub>B</sub> for Fe(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub> and Fe(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> at 286 K. Their low temperature moments are 1.52 and 2.14 μ<sub>B</sub> at 4.2 K, respectively. Mössbauer spectra for the two iron complexes recorded at 77 K are similar with isomer shifts of +0.536 (7) and +0.530 (4) mm/s for Fe(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> and Fe(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub>, and quadrupolar splittings of 0.940 (7) and 0.924 (4) mm/s for the two complexes, respectively. These values are typical for high-spin ferric ion in a chelated octahedral ligand field. The structural features of both Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub><sup>11</sup> and Fe(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub><sup>10</sup> are consistent with the semiquinone formulation for the complex. Both show M-O lengths which are typical of trivalent complexes of the metal ions with oxygen donor ligands and C-O lengths within the quinones of 1.28 Å, a semiquinone value. The temperature-dependent paramagnetism of the Cr and Fe complexes, therefore, results from a

surprisingly weak intramolecular antiferromagnetic interaction between the paramagnetic semiquinone ligands and the high-spin metal center. The observation that μ<sub>eff</sub> values at 4.2 K for both iron complexes are below the spin-only value for two unpaired electrons is possibly an indication of zero-field splitting or an intermolecular component in the exchange interaction. Further investigations on systems which preclude intermolecular exchange are in progress.

The vanadium complex V(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub>, obtained as a tetrabenzene solvate by procedures similar to those used to isolate Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub>·4C<sub>6</sub>H<sub>6</sub>,<sup>11</sup> is a S = 1/2 molecule. The EPR spectrum of V(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> recorded in ether solution at room temperature consists of eight lines centered at a ⟨g⟩ value of 2.0079 with <sup>51</sup>V (I = 7/2, 99.8%) hyperfine coupling of 4.1 (3) G. Vanadium hyperfine coupling in tris chelated complexes is normally within the 60-80-G range. Spectral values of ⟨g⟩ = 1.9831 and A(<sup>51</sup>V) = 84 (1) G and ⟨g⟩ = 1.9960 (5) and A(<sup>51</sup>V) = 61.5 (2) G have been reported for V(bipy)<sub>3</sub><sup>12</sup> and the V(1,2-dithiolene)<sub>3</sub><sup>3</sup> complexes. The ⟨g⟩ value and magnitude of the hyperfine observed for V(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> are similar to the values found in simple S = 1/2 semiquinone complexes. With a d<sup>2</sup>, trivalent vanadium ion spin coupling can occur with only two of the semiquinone ligands. The third remains coordinated as a paramagnetic radical anion.

The magnetic properties of the neutral M(quinone)<sub>3</sub> complexes with first row metals are unprecedented and clearly different from related complexes with nitrogen<sup>13</sup> and sulfur donor ligands. They are also quite different from the neutral tris(quinone) complexes of Mo reported earlier,<sup>14,15</sup> suggesting significant dissimilarities between complexes of metals of the first and second transition series.

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- Professor F. Calderazzo has reported the preparation of Fe(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub> previously.<sup>8b</sup> We have found that irradiation of a benzene solution of Fe(CO)<sub>5</sub> and 9,10-phenanthrenequinone yields dark green crystals of a compound of stoichiometry Fe(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>4</sub>. A crystallographic structure determination carried out on this compound in our laboratory has indicated that the true formula of the complex is Fe(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub> with an additional quinone molecule included separately in the crystal structure. Professor Calderazzo also reported the synthesis of Cr(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub> and its room temperature magnetic susceptibility in a personal communication to us. Using slightly modified procedures we have obtained crystals of Cr(O<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)<sub>3</sub>·C<sub>8</sub>H<sub>6</sub>(OCH<sub>3</sub>) from anisole solution.
- The tetrachloro-1,2-benzoquinone complexes of V, Cr, and Fe may be isolated in crystalline form from benzene solution as tetrabenzene solvates, M(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub>·4C<sub>6</sub>H<sub>6</sub>. They are all isomorphous and crystallize in tetragonal space group P<sub>4</sub>2<sub>1</sub>2 or P<sub>4</sub>2<sub>1</sub>2 in a cell of dimensions a = 13.572 (3) and c = 25.022 (5) Å. There are four formula weights per unit cell with imposed twofold symmetry on the complex molecule. Since the spectral properties of the Cr complex isolated as the benzene solvate are identical with the mixed benzene-CS<sub>2</sub> solvate studied crystallographically,<sup>10</sup> we have assumed similar structural features. All physical measurements reported in this manuscript were carried out on the tetrabenzene solvated form the

complexes. A full molecular structure determination was carried out on  $\text{Fe}(\text{O}_2\text{C}_{14}\text{H}_8)_3 \cdot \text{O}_2\text{C}_{14}\text{H}_8$  and will be reported separately. A preliminary structure determination carried out on  $\text{Cr}(\text{O}_2\text{C}_{14}\text{H}_8)_3 \cdot \text{C}_6\text{H}_6(\text{OCH}_3)_3$  indicated a geometry similar to those of  $\text{Fe}(\text{O}_2\text{C}_{14}\text{H}_8)_3$  and  $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ ; so a complete refinement was not carried out. Physical measurements carried out on the 9,10-phenanthrenequinone complexes were on the solvated samples indicated above. Characterization of  $\text{V}(\text{O}_2\text{C}_{14}\text{H}_8)_3$ , which has proven to be quite unstable, remains incomplete.

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### 1,5-Methano[10]annulene. Synthesis and Characterization of the 3-Methoxy Derivative

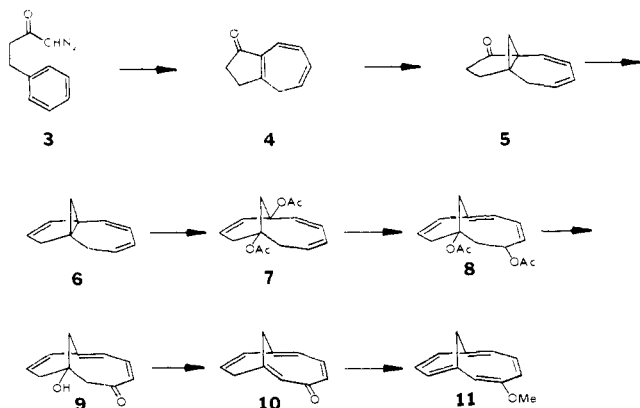
Sir:

Whereas the 10-electron  $\pi$  system of 1,6-methano[10]annulene (**1**) displays aromatic character<sup>1</sup> despite the lack of planarity,<sup>2</sup> a loss of aromaticity resulting from greater distortion of the  $\pi$  system has been predicted<sup>3</sup> for the isomeric 1,5-methano[10]annulene (**2**). Numerous research groups



have heretofore attempted to prepare **2** or derivatives thereof,<sup>4</sup> but only one has succeeded.<sup>5</sup> We describe herein our synthesis of 3-methoxy-1,5-methano[10]annulene and *NMR* evidence which argues against any significant difference in aromatic character between this compound and **1**.

We have previously reported<sup>6</sup> the copper-catalyzed cyclization of diazo ketone **3** to give bicyclic trienone **4**. Subsequently, it was found that selective cyclopropanation of the carbonyl-conjugated olefin in **4** can be conveniently accomplished with dimethylloxosulfonium methylide<sup>7</sup> in  $\text{Me}_2\text{SO}$  (70 °C, 45 min; 67% yield). Thus, all the carbon atoms of **2** can be assembled in their proper arrangement in just two steps from simple starting materials; completion of the synthesis requires



only cleavage of the central C–C bond and functional group manipulations. Conversion of cyclopropyl ketone **5** to triene **6** via the corresponding tosylhydrazone<sup>8</sup> proved unexceptional (66% yield).

Lead tetraacetate in acetic acid (15 °C, 15 min) cleaves the propellane bond<sup>9</sup> in **6** to yield diacetate **7** which suffers subsequent isomerization to the fully conjugated triene diacetate **8** on further heating in acetic acid (75 °C, 6 h, 61% yield from **6**). Other electrophiles likewise open the central bond of propellane **6**.<sup>10</sup>

Saponification of **8** (KOH, MeOH, 25 °C, 45 min; 97% yield) followed by oxidation of the allylic alcohol ( $\text{MnO}_2$ ,  $\text{CH}_2\text{Cl}_2$ , 25 °C, 3 h; 52% yield) affords  $\beta$ -hydroxy ketone **9** which can be dehydrated via the corresponding mesylate ( $\text{MsCl}$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ ; then DBN,  $\text{CHCl}_3$ ) to give the sensitive tetraenone **10** (64% yield from **9**). The infrared spectrum of this homotropone exhibits an amazingly low frequency C=O stretching band ( $1590\text{ cm}^{-1}$ ; cf. tropone,<sup>11</sup>  $1582\text{ cm}^{-1}$ ). The title compound (**11**) is obtained by methylation of the cherry red enolate derived from **10** (LDA, THF, HMPA,  $-78\text{ }^\circ\text{C}$ , 2 min; then *n*-BuLi,<sup>12</sup>  $-78\text{ }^\circ\text{C}$ , 2 min; then excess  $\text{MeOSO}_2\text{F}$  and warm to 0 °C, 15 min; ~50% yield from **10**).

3-Methoxy-1,5-methano[10]annulene<sup>13</sup> (**11**) is bright orange in color:  $\lambda_{\text{max}}^{\text{hexane}}$  490 nm ( $\epsilon$  500), 300 (sh, 5400), 280 (20 300). Its <sup>1</sup>H NMR spectrum ( $\text{CCl}_4$ ) shows signals for seven methine hydrogens ( $\tau$  2.20–3.42 ppm), a methoxy group (6.07), and two nonequivalent bridge hydrogens (10.25 and 10.78,  $J = 10\text{ Hz}$ ). By comparison, the <sup>1</sup>H NMR spectrum of 1,6-methano[10]annulene (**1**) shows a multiplet for eight methine hydrogens ( $\tau$  2.50–3.20 ppm) and a singlet for two equivalent bridge hydrogens (10.50).<sup>1</sup> The remarkable similarity between these two NMR spectra argues against any significant difference in the ability of the two  $\pi$  systems to support an induced diamagnetic ring current. To the extent that this property can be regarded as a measure of aromaticity,<sup>14</sup> the 1,5- and 1,6-methano[10]annulene ring systems thus appear comparable in aromatic character. It remains to be established, however, whether the  $\pi$  system of **2** and its derivatives does in fact deviate more from planarity than that of **1**.

Other properties of the 1,5-methano[10]annulene ring system and synthetic approaches to the parent hydrocarbon (**2**) are currently being explored in our laboratory.

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