

ation Grant No. CHE78-18581) and James S. Frye for recording the  $^{31}\text{P}$  NMR spectra.

**Registry No.** Ia, 84500-95-8; Ib, 73682-36-7; Ic, 84520-53-6; Id, 73682-35-6; Ie, 84500-96-9; II (L = NCMc), 84500-97-0; II (L = CNBu-*t*), 84500-98-1; II (L = py), 84580-17-6; II (L = CNCy), 84537-04-2; III, 84580-18-7;  $[\text{Mo}(\text{CO})_2(\text{C}_6\text{H}_5\text{NH}_2)(\text{PPh}_3)(\mu\text{-SO}_2)]_2$ , 84500-99-2;  $[\text{Mo}(\text{CO})_2(\text{py})_2(\mu\text{-SO}_2)]_2$ , 84501-00-8;  $\text{Mo}(\text{CO})_2[\text{P}(\text{OMe})_3]_3(\text{SO}_2)$ , 84501-01-9;  $\text{Mo}(\text{CO})_2(\text{bpy})(\text{PPh}_3)_2$ , 15653-24-4; *cis,trans*- $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{CNCy})_2$ , 84501-02-0; *cis,trans*- $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{CNBu-}t)_2$ , 84501-03-1; *cis,trans*- $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{CNR})_2$  (R = *p*-tolyl), 84501-04-2; *fac*- $\text{Mo}(\text{CO})_3(\text{dppe})(\eta^2\text{-SO}_2)$ , 84580-19-8; *mer*- $\text{Mo}(\text{CO})_3(\text{dppe})(\eta^1\text{-SO}_2)$ , 82630-14-6; *fac*- $\text{W}(\text{CO})_3(\text{dppe})(\eta^2\text{-SO}_2)$ , 82630-10-2; *mer*- $\text{W}(\text{CO})_3(\text{dppe})(\eta^1\text{-SO}_2)$ , 82630-13-5; *fac*- $\text{Mo}(\text{CO})_3(\text{phen})(\eta^2\text{-SO}_2)$ , 84580-20-1; *fac*- $\text{Mo}(\text{CO})_3(\text{bpy})(\eta^2\text{-SO}_2)$ , 84501-05-3; *fac*- $\text{Mo}(\text{CO})_3(\text{py})_2(\eta^2\text{-SO}_2)$ , 84501-06-4; *fac*- $\text{W}(\text{CO})_3(\text{py})_2(\eta^2\text{-SO}_2)$ ,

84501-07-5;  $\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)$ , 12125-77-8;  $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ , 15038-48-9;  $\text{W}(\text{CO})_3(\text{C}_7\text{H}_8)$ , 12128-81-3;  $\text{W}(\text{CO})_3(\text{NCMe})_3$ , 84580-21-2; *cis,trans*- $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{SO}_2)(\text{NCMe})$ , 84501-08-6; *cis,trans*- $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{NCMe})_2$ , 23526-71-8;  $\text{Mo}(\text{CO})_4(\text{dppe})$ , 15444-66-3; *fac*- $\text{W}(\text{CO})_3(\text{dppe})(\text{NCMe})$ , 84501-09-7;  $\text{Mo}(\text{CO})_6$ , 13939-06-5;  $\text{W}(\text{CO})_3(\text{NCMe})_3$ , 16800-47-8.

**Supplementary Material Available:** Analytical data (Table I), CO and SO infrared frequencies (Nujol mull and solution data) for complexes not listed in Table VI (Table II), observed and calculated structure factors for  $\text{Mo}(\text{CO})_3(\text{P-}i\text{-Pr}_3)_2(\text{SO}_2)$  and  $[\text{Mo}(\text{CO})_2(\text{py})(\text{PPh}_3)(\text{SO}_2)]_2$  (Tables Xb and XIb), and a room-temperature  $^{31}\text{P}$  NMR spectrum of II (L = CNCy) in  $\text{CH}_2\text{Cl}_2$  (Figure 5) (30 pages). Ordering information is given on any current masthead page.

## Active Site of Allantoic Purple Acid Phosphatase and a Model Complex for Strongly Coupled Diiron Sites

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**Abstract:** Magnetic susceptibility determination is able to make powerful structural predictions for the porcine allantoic purple acid phosphatase which is shown to be a diiron enzyme and for the model complexes of type  $[\text{Fe}(\text{cbpN})]_2\text{O}$ , which have the same magnetic properties. The presence of the diiron active site in the purple (oxidized) form of the phosphatase is shown by the very low magnetic susceptibility, which can only be attributed to very strong magnetic coupling between two Fe(III) species, and given the absence of any other plausible bridging group, the site can be assigned as Fe—O—Fe. The model complex  $[\text{Fe}(\text{cbpN})]_2\text{O}$  is shown to have this specific site by X-ray crystallography. This complex is also the first example of a central Fe—O—Fe linkage which can be reversed by heating in vacuo or by dissolving in dimethylacetamide. The reduced stability of the Fe—O—Fe linkage is presumably due to the steric strain enforced by the bulky cbpN ligands.

The efficacy of magnetic susceptibility measurements for structure elucidation is sometimes underestimated. With an ultrahigh sensitivity superconducting magnetometer, it is possible to make accurate measurements on quite small samples, or substances, like enzymes, which contain a small unpaired spin density.<sup>1,2</sup>

We are attracted by the controversial nature of the description of the central prosthetic group of purple acid phosphatase, "progesterone induced glycoprotein" (PIG)<sup>3,4</sup> obtained from porcine allantoic fluid (and the very similar protein from beef spleen<sup>5</sup>), which had been suggested to contain either one or two iron sites,<sup>3,4</sup> the known diiron protein hemerythrin,<sup>6</sup> the diiron (sulfur-bridged) protein ferreacid,<sup>7</sup> and model compounds designed to simulate the magnetic properties of these materials.

The enzyme PIG, reputed to have either one or two central iron atoms per molecular weight unit, is an ideal subject for high-precision magnetic susceptibility, since one can expect to distinguish reliably between the magnetic contributions of one and two iron atoms better than with most other physical techniques to which the substance is accessible. The results however produced a surprise. The observed magnetic moment was small ( $\leq 1.0 \mu_B$  for one sample and  $1.1 \mu_B$  for another) and constant (4–50 K) within experimental error, less than for even one iron site<sup>8</sup> in the oxidized (purple) form of the protein.<sup>9</sup> This can only reasonably be explained in terms of antiferromagnetic interactions between pairs of iron atoms. In fact, the magnetic moment is so low, that even coupling between two Fe sites of unequal oxidation states

is ruled out, for in that case residual electron spin is required. For example, Fe(II) coupled with Fe(III) would leave one unpaired electron, whereas our measurement indicates less than a third of an electron per pair of iron atoms, particularly when spin-orbit coupling is taken into account. Of the possible kinds of equivalent interacting species, Fe(II) is chemically unlikely in the oxidized form, Fe(IV) is quite rare and therefore just as unlikely, so that a pair of Fe(III) sites remains as the plausible species. The possible

(1) O'Connor, C. J.; Sinn, E.; Cukauskas, E. J.; Deaver, B. S., Jr. *Inorg. Chim. Acta* **1979**, *32*, 29.

(2) O'Connor, C. J.; Deaver, B. S., Jr.; Sinn, E. *J. Chem. Phys.* **1979**, *70*, 5161.

(3) Campbell, H. D.; Dionysius, D. A.; Keough, T.; Wilson, B. E.; de Jersey, J.; Zerner, B. *Biochem. Biophys. Res. Commun.* **1978**, *82*, 615.

(4) Antanais, B. C.; Aisen, P.; Lilienthal, H. R.; Roberts, R. M.; Bazer, F. W. *J. Biol. Chem.* **1980**, *255*, 11 204.

(5) Davis, J. C.; Lin, S.; Averill, B. A. *Biochemistry* **1981**, *20*, 4062.

(6) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H., paper to be presented at San Diego A.C.A. meeting, August 1982.

(7) Hawkins, C. J.; Clark, R. E.; Brewer, G. A.; Sinn, E., unpublished work.

(8) Sinn, E.; O'Connor, C. J.; de Jersey, J.; Zerner, B. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, April 1982; American Chemical Society: Washington, DC, 1982; INOR 79. "Abstracts of Papers", 179th National Meeting of the American Chemical Society, Houston, TX, April 1980; American Chemical Society: Washington, DC, 1980; INOR 25.

(9) (a) Details of preparation and purification will be given elsewhere: Sinn, E.; O'Connor, C. J.; de Jersey, J.; Zerner, B. *Inorg. Chim. Acta, Biochem. Sect.*, in press. (b) On treatment with dithionite at pH 4.9, 50% of the iron content is removed rapidly, while the remainder is lost slowly, which also bespeaks a pair of Fe atoms.

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Table I

complex	% C	% H	% N	room temp magnetic moment, $\mu_B$
Fe(cbpN)·2H <sub>2</sub> O	calcd 59.10 found 58.99	5.11 4.88	6.46 6.84	4.94
[Fe(cbpN)O <sub>2</sub> ]	calcd 59.46 found 59.54	4.52 4.34	6.50 6.58	4.70
[(Fe(cbpN)) <sub>2</sub> O]·3 <i>o</i> -xyl <sup>a</sup>	calcd 67.61 found 67.11	5.67 5.61	5.38 5.48	2.20
[(Fe(cbpN)) <sub>2</sub> O]·2dcb <sup>b</sup>	calcd 59.32 found 59.38	4.32 4.48	5.46 5.46	2.18

<sup>a</sup> *o*-xyl = *o*-xylene. <sup>b</sup> dcb = *m*-dichlorobenzene.

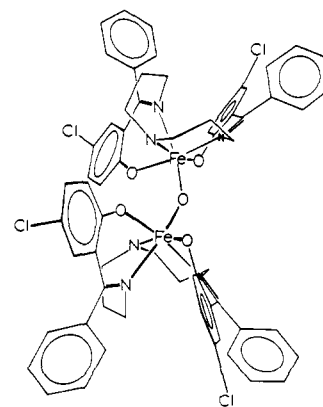
Table II. Visible-Near-Infrared Spectra (cm<sup>-1</sup> × 10<sup>-3</sup>)

complex	solid state	toluene <sup>a,b</sup>	dimethylformamide <sup>a,b</sup>	dimethylacetamide <sup>a,b</sup>
(Fe(cbpN))·2H <sub>2</sub> O	7.6 <sup>c</sup>	23.5 (4750) sh	23.5 (4600) sh	22.7 (3550) 20.5 (3000) sh
[Fe(cbpN)]O <sub>2</sub> [(Fe(cbpN)) <sub>2</sub> O] or solvent	<i>c,d</i> 11.0	24.5 (7700) sh	24.5 (7600) sh	22.5 (3500) 20 000 (3000) sh

<sup>a</sup> 0.001 M. <sup>b</sup> Extinction coefficients in parentheses. <sup>c</sup> Broad charge-transfer absorption band above 16 000 cm<sup>-1</sup>. <sup>d</sup> No absorption band below 16 000 cm<sup>-1</sup>.

spin states are high spin, low spin, or intermediate, but with the weak ligands expected to be present,<sup>10</sup> spin pairing is quite unlikely, and intermediate spins are extremely rare and unlikely in a nonheme protein.<sup>11</sup> This leaves a pair of high-spin Fe(III) species as the plausible active site and establishes that there is not one iron atom present but two (or no irons at all, which is ruled out by analysis). It further establishes that not only are two iron atoms present, but they exist in so closely linked a form that complete demagnetization ( $-J \geq 80$  cm<sup>-1</sup>) takes place in the low-temperature region.

The power of the magnetic susceptibility results does not end there for we can postulate the nature of the coupling between the iron atoms. It is well-known to inorganic chemists that a one-atom bridge, and in particular Fe-O-Fe, is the most likely linkage (together with possible other, but magnetically much less important, bridging groups) to produce these magnetic properties,<sup>12-15</sup> just as is proposed for hemerythrin.<sup>16</sup> In fact there are no other linkages, compatible with the protein, for which strong coupling is precedented. Other bridging groups which might be present are incidental to our argument as they would contribute minimally to the coupling and would not greatly alter the constraint of a closely linked Fe<sub>2</sub> pair imposed by the Fe-O-Fe type of bridge. The very strong coupling produced by M-O-M or M-OH-M bridges has been documented for several types of compounds, and the simultaneous presence of other bridging had no great effect on the magnetism. For example, the interchange of SO<sub>4</sub><sup>2-</sup> and acetate groups had little effect on the coupling produced by a simultaneously present OH bridge,<sup>17</sup> nor did interchange of ClO<sub>4</sub><sup>-</sup> and CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> groups or removal of these groups in O- and OH-bridged compounds.<sup>18</sup> The possible simultaneous presence of other bridging groups, such as phosphate in some samples of the pro-

Figure 1. Scale drawing of the [Fe(cbpN)]<sub>2</sub>O molecule.

tein,<sup>19</sup> would be unimportant in the magnetism, much like the similar tetrahedral bridges in small molecule models. Although ESR spectra are routinely observed, these must be due to the same paramagnetic impurity that is also responsible for the small residual low-temperature magnetic moment in the enzyme.

PIG is not accessible to X-ray crystallography at this stage, but some new smaller molecule complexes which we have studied as models for such Fe<sub>2</sub>-active sites have also been structurally characterized. The entire series of compounds derived from FeL, where L = cbpN<sup>20</sup> and closely related ligands, was initially observed to have extremely subnormal magnetic moments, precisely mimicking PIG in the low-temperature region, and was deduced by the same reasoning to contain an Fe<sup>III</sup><sub>2</sub>O core, rather than the initial Fe(II) species. Similar spurious ESR signals are also observable, which, however, represent only a fraction of a percent of the Fe(III) of the complex. Two members of the series (FeL)<sub>2</sub>O were characterized by X-ray work.<sup>21</sup> The (FeL)<sub>2</sub>O structure with L = cbpN is shown in Figure 1.

(10) Buhl, W.; Bazer, F. W.; Ducsay, C.; Chun, P. W.; Roberts, R. M. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1979**, *38*, 733.

(11) Sinn, E. *Struct. Bonding (Berlin)*, to be published.

(12) Murray, K. S. *Coordn. Chem. Rev.* **1974**, *12*, 1.

(13) Lewis, J.; Mabbs, F. E.; Richards, A. J. *J. Chem. Soc. A* **1967**, 1014.

(14) Kessel, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 1883.

(15) Ou, C. C.; Wallman, R. G.; Hendrickson, D. N.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 4717.

(16) Kurtz, D. M., Jr.; Shriver, D. G.; Klotz, I. M. *Coord. Chem. Ev.* **1977**, *24*, 145.

(17) Thich, J. A.; Toby, B. H.; Powers, D. A.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1981**, *20*, 3314.

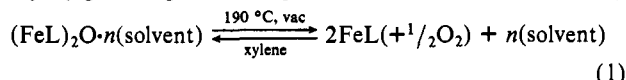
(18) Butcher, R. J.; O'Connor, C. J.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 537. Butcher, R. J.; Overman, J. W.; O'Connor, C. J.; Sinn, E. "Abstracts of Papers", 177th National Meeting of the American Chemical Society, Honolulu, HI, April 1979; American Chemical Society: Washington, DC, 1979; INOR466.

(19) Keough, D. T.; Beck, J. L.; de Jersey, J.; Zerner, B. *Biochem. Biophys. Res. Commun.* in press.

(20) cbp is 2-hydroxy-5-chlorobenzophenone; cbpN is the pentadentate ligand produced by condensing 1,5,9-triazanonane with two units of cbp.

(21) Mockler, G. M.; Sinn, E., unpublished work. One of the compounds, L = cbpN, crystallized with xylene solvate, space group *P1*, *Z* = 2, *a* = 13.229 (2) Å, *b* = 15.419 (3) Å, *c* = 22.371 (3) Å,  $\alpha$  = 104.03 (3)°,  $\beta$  = 114.70 (4)°,  $\gamma$  = 91.23 (4)°, *R*, *R*<sub>w</sub> = 6.4, 8.9%. Fe-O = 1.807 (3), 1.804 (3) Å, Fe-O-Fe = 144.5 (2)°. The same compound, crystallized from *m*-dichlorobenzene contains C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> solvate and crystallizes in *P2*<sub>1</sub>/*c* but has very similar geometry of the Fe<sub>2</sub>O group.  $-J$  = 80 cm<sup>-1</sup> from susceptibility determination down to 4 K.

All the complexes have an additional unusual property. They can be heated in vacuo to produce a purple high-spin Fe(II) product, which when dissolved in aromatic hydrocarbons in air reforms the (FeL)<sub>2</sub>O dimer. The weight loss is consistent in each case with (1). This is the first case of a reversal of such an Fe-O-Fe linkage, e.g., the very similar oxo-bridged dimers formed with such ligands as the tetradentate salen and its cbp analogue, are simply destroyed by heating. The purple products of reaction 1 rapidly gain weight when exposed to air and then are invariably



analyzed as FeL·O<sub>2</sub>, and in no case does either the infrared or the hydrogen analysis support the presence of water. The nature of these complexes, presumable Fe(II) from the magnetism and spectra, has not yet been established. They are inaccessible to X-ray crystallography at this stage: on dissolving in hydrocarbon solvents, they revert to the red(FeL)<sub>2</sub>O complexes. The data are given for the L = cbpN case in Tables I and II.

The magnetically coupled (FeL)<sub>2</sub>O, formed when the high-spin iron(II) [FeL]·nH<sub>2</sub>O (e.g., [Fe(cbP)]·2H<sub>2</sub>O, Tables I and II) is recrystallized from benzene or a substituted benzene solvent, is stable in air at room temperature in the solid state, but the binucleation is reversed in freshly distilled dimethylacetamide: a purple solution is obtained and the spectrum reverts to that of Fe<sup>II</sup>L parent. This is presumable because the highly substituted ligand exerts sufficient steric crowding to make the Fe-O-Fe linkage somewhat unstable, but not sufficient to prevent it forming at all, as with the highly substituted porphyrins and other ligands used in synthetic oxygen carriers.<sup>22-24</sup>

(22) Leal, O.; Anderson, D. L.; Bowman, R. G.; Basolo, F.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 5125.

(23) Little, R. G.; Ibers, J. A.; Baldwin, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 7049.

While (FeL)<sub>2</sub>O is an acceptable model for the hemerythrin magnetic properties, it is not a good hemerythrin model otherwise. In fact none such yet exist. It does carry a half-molecule of oxygen with partial reversibility, but it does not carry dioxygen. However, it is a good model for the PIG iron site (in its oxidized form) to the extent that the latter is understood: it is a nonheme, non-porphyrin system, containing O-donor atoms in addition to the μ-oxo bridge and the magnetic coupling. An important step in a further understanding of the enzyme is in mimicking some of its salient properties in model complexes such as the ones described. The model is supported by observation of similar magnetic properties<sup>25</sup> in the purple phosphatase from beef spleen.<sup>3</sup> It must therefore be considered that not only this enzyme but also the purple acid phosphatases from plant sources<sup>26</sup> may have similar Fe<sub>2</sub> centers.

The magnetic, ESR, and crystallographic measurements were made as described elsewhere.<sup>1,2,27</sup>

**Registry No.** Fe(cbP), 84752-95-4; [Fe(cbP)O<sub>2</sub>], 84775-37-1; [(Fe(cbP))<sub>2</sub>O], 84752-94-3; acid phosphatase, 9001-77-8.

**Supplementary Material Available:** Tables of interatomic distances and angles, fractional coordinates, and thermal parameters for [(Fe(cbP))<sub>2</sub>O]·3xyl (11 pages). Ordering information is given on any current masthead page.

(24) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Robinson, W. T.; Rodley, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 1326.

(25) Averill, B. A., personal communication.

(26) Nochumson, S.; O'Rangers, J. J.; Dimitrov, N. V. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1974**, *33*, 1378. Sugiura, Y.; Kawabe, H.; Tanaka, H. *J. Am. Chem. Soc.* **1980**, *102*, 6581. Fujimoto, S.; Nakagawa, T.; Ishimitsu, S.; Ohara, A. *Chem. Pharm. Bull.* **1977**, *25*, 1459. Fujimoto, S.; Nakagawa, T.; Ohara, A. *Ibid.* **1977**, *25*, 3283. Igaue, I.; Watanabe, H.; Takahashi, K.; Takekoshi, M.; Morata, A. *Agric. Biol. Chem.* **1976**, *40*, 823.

(27) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

## Paramagnetic Organometallic Molecules. 13.<sup>1</sup> Electron-Transfer-Catalyzed Reactions of Polynuclear Metal Carbonyls: Reactions of R<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>6</sub>

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**Abstract:** Polynuclear metal carbonyls are shown to be suitable substrates for rapid electron-transfer-catalyzed (ETC) reactions that offer a new convenient method for the synthesis of many carbonyl derivatives. The factors that influence the applicability and yields of these reactions are discussed and examples with a variety of nucleophiles and substrates given. The distinction between electron-induced nucleophilic substitution (EINS) and ETC reactions is emphasized. ETC reactions of R'RC<sub>2</sub>Co<sub>2</sub>(CO)<sub>6</sub> with MeCN and other Lewis bases using both electrolytic and chemical reductants are described in detail, in particular those where R' = R = CF<sub>3</sub>. The yields of the new products (CF<sub>3</sub>)<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>5</sub>L [L = MeCN, (MeO)<sub>3</sub>P, (PhO)<sub>3</sub>P, Ph<sub>3</sub>P, (C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>P], (CF<sub>3</sub>)<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>4</sub>L<sub>2</sub> [L = (RO)<sub>3</sub>P, Ph<sub>3</sub>P], and (CF<sub>3</sub>)<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>3</sub>L<sub>3</sub> [L = (RO)<sub>3</sub>P] are virtually quantitative, with reaction times no longer than 5 min. In most cases reaction is over in 1 min at 293 K. Yields from ETC reactions with other R'RC<sub>2</sub>Co<sub>2</sub>(CO)<sub>6</sub> compounds are variable but can be correlated with the lifetime of the radical anions. Spectroscopic data characterized the phosphite or phosphine ligand as having an axial conformation in R<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>5</sub>L complexes, but the X-ray structure of (CF<sub>3</sub>)<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>5</sub>(MeCN) shows that the MeCN is equatorial. Steric factors are believed to account for this. However, the MeCN ligand is very labile in solution, and the electrochemistry of the MeCN adduct is characterized by abnormal limiting currents at 293 K that are absent at lower temperatures. The compound (CF<sub>3</sub>)<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>5</sub>(MeCN) crystallizes in the space group *Pna*2<sub>1</sub>; *a* = 15.794 (5) Å, *b* = 9.803 (3) Å, *c* = 10.936 (4) Å, *Z* = 4, *V* = 1693.4 Å<sup>3</sup>.

Electron-transfer catalysis is a general class of reaction in which electron-transfer steps are utilized to accelerate transformations

which are slow under normal thermal conditions and/or to alter product distribution.<sup>2</sup> A unimolecular mechanism S<sub>RN</sub>1 for