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Low-Energy Electronic Absorptions in 17-Electron Organometallic Piano Stool Radicals

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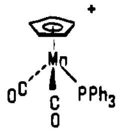
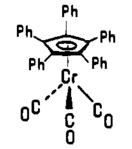
We report that certain 17-electron (17e) organometallic complexes with the "piano stool" structure (**1**) display very low energy (near- to mid-IR) electronic absorptions which are apparently ligand-field in origin. The states involved in the transitions have predominantly metal character and derive from a parent pair, for which degeneracy has been lifted by Jahn−Teller distortions or mixing of the ligands in the L_3 set. This observation gives a new method of characterizing radicals with quasidegenerate ground states which is especially useful for radicals in fluid solutions. The energies of the optical transitions may provide a sensitive probe for subtle geometric changes difficult to diagnose by other in situ methods.

1



2⁺



3

Pseudooctahedral 17e complexes such as **2⁺**, **3**, and $[(\eta^6\text{-arene})Cr(CO)_2L]^+$ are usually ESR-inactive in liquid solution, owing to rapid electronic relaxations and significant *g*-value anisotropies which make the time-averaged resonance undetectably broad.[1−5] In the course of studies of intervalence charge-transfer (IT) bands of dinuclear manganese componds,[6] we recorded the near-IR spectra of a mononuclear cation radical, $[CpMn(CO)_2PPh_3]^+$ (**2⁺**),[7] in CH_2Cl_2, observing a broad adsorption at $\bar{\nu}_0 = 5710$ cm^{-1}, $\epsilon \approx 100$ (cm M)$^{-1}$. Although this and related Mn(II) complexes are photolabile,[8] as are their 18-electron counterparts,[9] the absorption does not appear to arise from a photodecomposition product. As long as the radical was protected from specrophotometric source light of wavelengths below 750 nm by optical source filters, the absorption band persisted. When, however, the solutions under N_2 were deliberately exposed to strong visible light, the near-IR band bleached.

The neutral 17e radical $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3$ (**3**) offered an ideal isoelectronic analogue for quantification of these observations. This radical is extremely robust, shows no tendency to dimerize, and is available in high purity.[4] Its solutions in $CDCl_3$ display an electronic transition centered at the edge of the mid-range IR region, $\bar{\nu}_0 = 4000$ cm^{-1}. Since the absorption is near the low-energy limit of the Cary 14 spectrometer, **3** was also studied with a Mattson Polaris IR spectrometer. Figure 1 shows spectra from both sets of experiments with different concentrations of the radical. The band follows Beer's law with an absorptivity[10] ($\epsilon = 62$ (cm M)$^{-1}$], sufficiently low to eliminate a ligand-to-metal charge-transfer process as being responsible for the transition.[11]

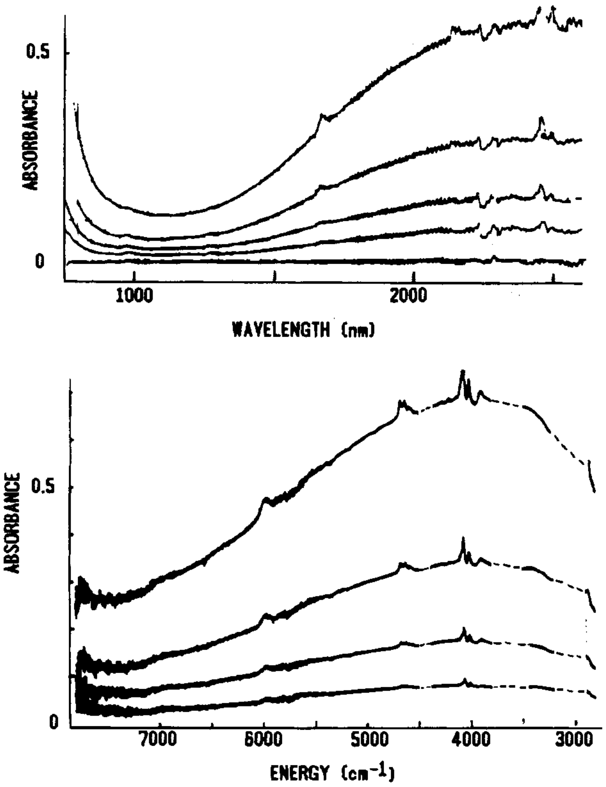


Figure 1. Spectra of $CDCl_3$ solutions of **3** (consecutively, 2.29, 4.56, 9.15, and 18.3 mM) referenced to pure $CDCl_3$ in 1 cm quartz cell. Top, recorded with Cary 14 spectrometer with cutoff filters eliminating light below 750 nm. Bottom, recorded with Mattson Polaris FTIR spectrometer.

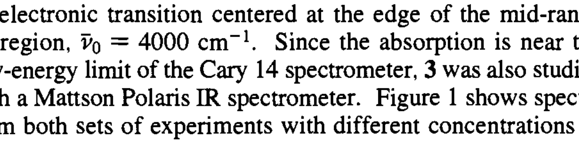


Figure 2. Proposed changes in electronic configurations of piano stool radicals **1** with changes in molecular symmetry, adapted from ref 2. Orbital occupancy shown for d^5, 17e system.

The origin of these transitions may be understood with reference to the accepted MO scheme for these radicals (Figure 2). In pseudo-C_{3v} symmetry, the putative t_{2g} orbital set splits into a degenerate e-type pair and an a_1-type orbital. Further symmetry lowering to C_s splits the degenerate pair into a′ and a″ orbitals, either of which may be the SOMO.[1,2] Although substitution of one ligand in the L_3 set (e.g., PR_3 for CO) is perhaps the most obvious way to achieve symmetry lowering, C_s symmetry is also exhibited in $L_3 = (CO)_3$ complexes by distortions of the CO−Cr−CO angles from 90°, probably from Jahn−Teller effects.[2,4,5]

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(1) Pike, R. D.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3913 ($CpMnL_3^+$ complexes).

(2) Fortier, S.; Baird, M. C.; Preston, K. F.; Morton, J. R.; Ziegler, T.; Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Watson, K. A.; Hensel, K.; Le Page, Y.; Charland, J.-P.; Williams, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 542 and references therein ($CpCrL_3$ complexes).

(3) Pierce, D. T.; Geiger, W. E. *Inorg. Chem.* **1994**, *33*, 373 and references therein [$(arene)CrL_3^+$ complexes).

(4) Hoobler, R. J.; Hutton, M. A.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. L.; Rieger, A. L.; Rieger, P. H.; Richards, T. C.; Geiger, W. E. *Organometallics* **1993**, *12*, 116.

(5) MacNeil, J. H.; Watkins, W. C.; Baird, M. C.; Preston, K. F. *Organometallics* **1992**, *11*, 2761.

(6) Atwood, C. G.; Geiger, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 5310.

(7) Complex **2⁺** was prepared as the BF_4^- salt in ca. 95% purity by oxidation with $Ag[BF_4]$: see ref 8. Its frozen glass ESR spectra matched literature.[1]

(8) Atwood, C. G. Ph.D. Thesis, University of Vermont, Burlington, VT, 1994.

(9) Kaim, W.; Roth, T.; Olbrich-Deussner, B.; Gross-Lannert, R.; Jordanov, J.; Roth, E. K. H. *J. Am. Chem. Soc.* **1992**, *114*, 5693.

(10) $\epsilon = 50$ (cm M)$^{-1}$ in the Cary 14 experiments.

(11) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*, Academic Press: New York, 1979; pp 15−19.

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The magnitude of the e-degeneracy splitting in (η^5-C_5R_5)-$Cr(CO)_3$ piano stool radicals has been estimated to be 200–3700 cm^{-1} on the basis of the indirect probes of line-broadening effects on *g*-value variations in solid-state ESR spectra.[2,4] LCAO-HFS calculations on $CpCr(CO)_3$ predicted a $^2A'$ ground state with a $^2A''$ excited state lying 3500–5000 cm^{-1} higher in energy,[2] in good agreement with the energy (4000 cm^{-1}) we measure for the optical transition in **3**. The present data do not give the basis for a choice between the two possible ground states, but optical experiments on oriented radicals should be capable of doing so.

The extinction coefficient and energy range of the radical ligand-field transition are similar to those of IT bands of weakly-coupled metal centers.[12] This fact may become important when interpreting the optical spectra of mixed-valent complexes containing 17e centers (e.g., $[(\mu\text{-fulvalenyl})Mn_2(CO)_4(PR_3)_2]^+$),[6] a matter that we will address in a future paper on ions of this type. Ligand-field transitions do not appear to affect the near-IR spectra of biferrocenium-type molecules, for $[Cp_2Fe]^+$ has no absorption band with an ϵ value above 5 $(M\ cm)^{-1}$ in this range.[8]

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