Unexpected Paramagnetism of Mono- and Polynuclear 18 Valence Electron Metal Carbonyl Complexes [(CnRn)(CO)2M]k(L) (M = Cr, Mn; k = 1, 2, 4). Implications for Photoreactivity

Wolfgang Kaim,*[†] Thomas Roth,[†] Barbara Olbrich-Deussner,[†] Renate Gross-Lannert,[†] Jeanne Jordanov,*[‡] and Eberhard K. H. Roth[‡]

Contribution from the Institut für Anorganische Chemie der Universität, Pfaffenwaldring 55, D-7000 Stuttgart 80, Germany, and Département de Recherche Fondamentale/SESM/SCPM, Centre d'Etudes Nucléaires de Grenoble, 85 X, F-38041 Grenoble Cedex, France. Received November 18, 1991

Abstract: Several mono- and polynuclear complexes of the organometallic 16 valence electron fragments $(C_nR_n)(CO)_2M$, M = Cr ($n = 6$, R = H) and Mn ($n = 5$, R = H, Me), with conventional two-electron nitrogen-donor ligands L (acceptor-substituted pyridines, $\eta^{1,2}$-pyrazine) or with $\eta^{1,4}$-tetracyanoethylene (TCNE) show sizable metal-based paramagnetism in the solid state at room temperature. In contrast to paramagnetic $(C_6H_6)(CO)_2Cr(py)$, the corresponding complex $(C_5H_5)(CO)_2Mn(py)$ of unsubstituted pyridine and the dinuclear complex $[(C_5H_4Me)(CO)_2Mn]_2(\mu\text{-}1,4\text{-}Me_2PC_6H_4PMe_2)$ of a basic, π-accepting diphosphine exhibit essentially diamagnetic behavior. Magnetic susceptibilities at 300 K can be correlated with ligand "strengths" as represented by basicities of L. The susceptibilities of the paramagnetic species were found to decrease considerably at lower temperatures, indicating a diamagnetic ground state for all compounds. The easy accessibility of low-lying magnetic states of integer spin is attributable to the low symmetry of the complexes, to the intrinsically small ligand field splitting of low-valent chromium and manganese, and to the presence of one weak ligand, L. Analysis of the tetranuclear complex $[(C_5Me_5)(CO)_2Mn]_4(\eta^4\text{-}TCNE)$ reveals magnetic coupling between the four metal centers but no direct involvement of TCNE as a radical. The measured susceptibilities correlate with the photolability of the compounds and with the small g factors of singly reduced complexes, all effects being caused by the low-lying d_{z^2} orbital.

Conventional wisdom holds that the ligand field splitting in organometallic compounds, especially in metal carbonyl complexes obeying the 18 valence electron (VE) rule, is so large that these species exist exclusively in the low-spin configuration.[1] Only in a few instances have higher spin states ever been established in isolable organometallics with unsaturated hydrocarbon ligands; the best known examples are sandwich compounds[2,3] where the 17 VE manganocenes and their derivatives may exhibit spin crossover between low-spin ($^2E_{2g}$) and high-spin ($^6A_{1g}$) configurations[3] due to the intrinsically small ligand field splitting of low-valent manganese. In this paper we describe the presence of low-energy magnetically excited states in mono-, di-, and tetranuclear 18 VE carbonylmetal complexes of manganese(I) and chromium(0), both with conventional ligands such as pyridines or bridging pyrazine and with the highly "noninnocent" tetracyanoethylene (TCNE) ligand.

The organometallic 16 VE fragments $(C_5H_nMe_{5-n})(CO)_2Mn$ and $(C_6H_6)(CO)_2Cr$ have been employed in numerous instances for the coordination and stabilization of unusual two-electron donor ligands.[4] Complexes with more conventional ligands were often found to be quite labile;[5–7] however, the origin of this (photo)-lability has remained obscure. The occurrence of sizable paramagnetism as demonstrated in this paper suggests that unusually low-lying ligand-field excited states are responsible for the photodissociative behavior[5] of the compounds and for the small g factors of reduced species.[8]

Experimental Section

Materials. Syntheses and analytical characterizations of the complexes $(C_5H_4Me)(CO)_2Mn(N^1\text{-}3\text{-}cnpy)$ (**1**) (3-cnpy: 3-cyanopyridine),[8b] $(C_5H_4Me)(CO)_2Mn(pz)$ (**4**) (pz: pyrazine),[8a] $[(C_5H_4Me)(CO)_2Mn]_2\text{-}(\mu\text{-}pz)$ (**5**),[8a] $(C_5Me_5)(CO)_2Mn(\eta^1\text{-}TCNE)$ (**6**) (TCNE: tetracyanoethylene),[9] $[(C_5Me_5)(CO)_2Mn]_4(\eta^4\text{-}TCNE)$ (**7**),[10] $(C_5H_5)(CO)_2Mn(py)$ (**8**) (py: pyridine),[11] and $[(C_5H_4Me)(CO)_2Mn]_2(\mu\text{-}1,4\text{-}Me_2PC_6H_4PMe_2)$ (**9**)[12] have been reported. Complexes $(C_5H_4Me)(CO)_2Mn(N^1\text{-}4\text{-}acpy)$ (**2**) (4-acpy: 4-acetylpyridine)[5a,c] and $(C_6H_6)(CO)_2Cr(py)$ (**10**),[7] previously characterized as labile species, were prepared as pure solids by

the following procedures, working under argon and in the absence of intense light.

$(C_5H_4Me)(CO)_2Mn(N^1\text{-}4\text{-}acpy)$ (**2**). A 2.18-g (10 mmol) amount of $(C_5H_4CH_3)(CO)_3Mn$ was irradiated in 250 mL of THF for 4 h with a mercury high-pressure lamp. The red THF solvate formed was reacted with 1.21 g (10 mmol) of 4-acetylpyridine; the resulting mixture was stirred for 14 h in the dark. After evaporation of the solvent, the residue was chromatographed on a column (40 × 1.5 cm) by using Florisil, 100–200 mesh (Merck). Elution with toluene/pentane (1/1) yielded

(1) Cf.: Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*; VCH Publishers: Weinheim, 1989. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.

(2) (a) Chesky, P. T.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 5186. (b) Mougenot, P.; Demuynck, J.; Benard, M.; Bauschlicher, C. W., Jr. *Ibid.* **1988**, *110*, 4503. (c) Bachmann, B.; Hahn, F.; Heck, J.; Wünsch, M. *Organometallics* **1989**, *8*, 2523.

(3) (a) Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, P.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 2033. (b) Hebendanz, N.; Köhler, F. H.; Müller, G.; Riede, J. *Ibid.* **1986**, *108*, 3281 and literature cited.

(4) (a) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1. (b) Cf.: Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 1051.

(5) (a) Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160. Most of the photolabile manganese complexes described in this paper were not isolated as solid materials. (b) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (c) Roth, T. Ph.D. Thesis, University of Stuttgart, 1992.

(6) Cf.: (a) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (b) Srivastava, S. C.; Shrimal, A. K.; Srivastava, A. *J. Organomet. Chem.* **1991**, *414*, 65.

(7) Strohmeier, W.; Hellmann, H. *Chem. Ber.* **1964**, *97*, 1877.

(8) Gross, R.; Kaim, W. (a) *Inorg. Chem.* **1986**, *25*, 498; (b) *J. Organomet. Chem.* **1987**, *333*, 347.

(9) (a) Olbrich-Deussner, B.; Gross, R.; Kaim, W. *Inorg. Chem.* **1989**, *28*, 3113. (b) Kaim, W.; Gross, R. *Comments Inorg. Chem.* **1988**, *7*, 269. (c) Crystal structure and paramagnetism were reported for $(C_5H_5)(CO)_2Mn$-(TCNE): Braunwarth, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1989**, *372*, C23.

(10) Gross-Lannert, R.; Kaim, W.; Olbrich-Deussner, B. *Inorg. Chem.* **1990**, *29*, 5046.
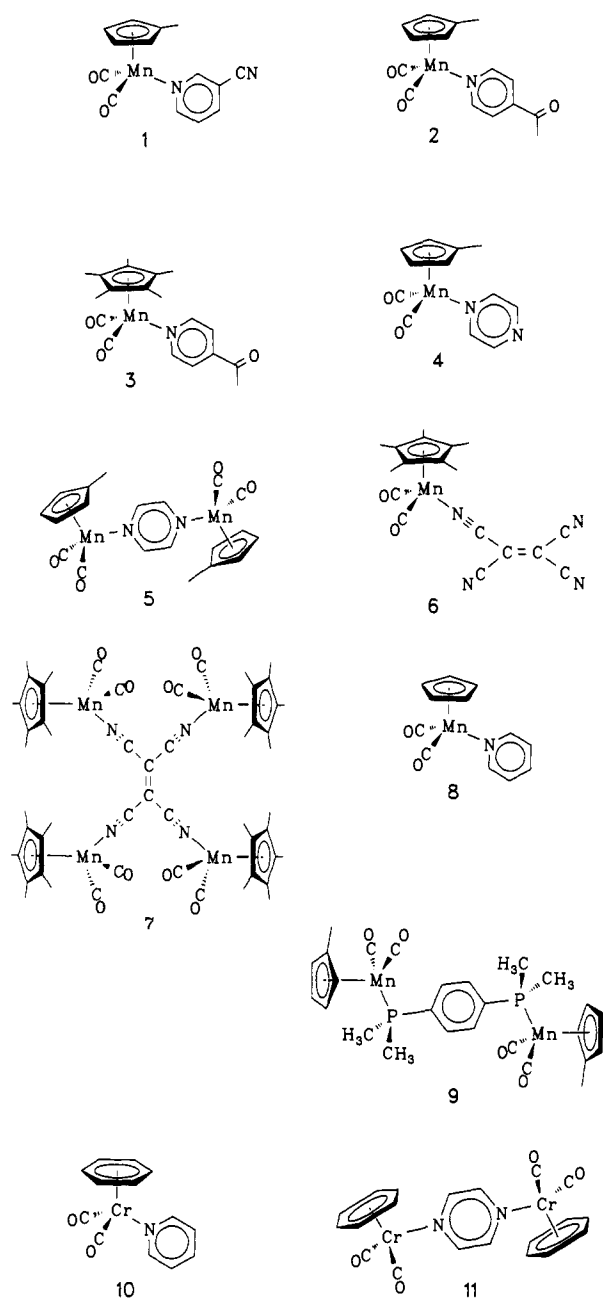
(11) Strohmeier, W.; Gerlach, K. *Z. Naturforsch.* **1960**, *15b*, 675.

(12) Gross-Lannert, R.; Kaim, W.; Lechner, U.; Roth, E.; Vogler, C. *Z. Anorg. Allg. Chem.* **1989**, *579*, 47.

[†] Institut für Anorganische Chemie.
[‡] Centre d'Etudes Nucléaires de Grenoble.

5694 *J. Am. Chem. Soc., Vol. 114, No. 14, 1992*

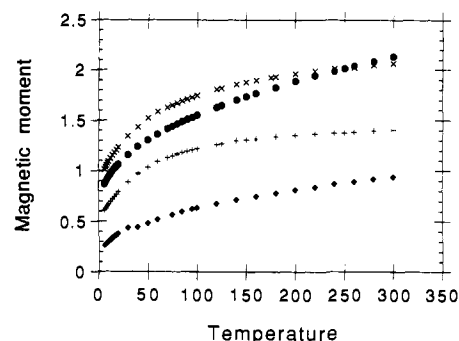*Kaim et al.*

Chart I

Figure 1. Effective magnetic moments μ_{eff} (μ_B) per molecule as a function of temperature: 4-acetylpyridine complexes 2 ($\times$) and 3 (+); pyridine complexes 8 ($\blacklozenge$) and 10 ($\bullet$).

cm^{-1}. λ_{max} (toluene): 477 nm. Cyclic voltammetry (acetone, 0.1 M Bu$_4$NPF$_6$): E_{ox} = -0.44 V versus Fc/Fc$^+$ (ΔE_{pp} 80 mV).

[(C$_6$H$_6$)(CO)$_2$Cr]$_2$(μ-pz) (11). A 2.14-g (10 mmol) amount of (C$_6$H$_6$)Cr(CO)$_3$ and 0.40 g (5 mmol) of pyrazine were dissolved in 150 mL of THF and irradiated for 5 h under argon at 0 °C with a Hg high-pressure lamp. After continued stirring for 12 h in the dark the mixture was filtered and the solvent removed from the filtrate in vacuo. The residue contains extremely labile mononuclear (C$_6$H$_6$)(CO)$_2$Cr(pz) and the less soluble dinuclear complex 11 which was isolated as a blue-black product by fractional crystallization from toluene/pentane (1/2) at -30 °C in 0.45 g (20%) yield. High sensitivity toward air and light precluded a satisfactory elemental analysis. ^{1}H NMR (acetone-d_6): δ 5.63 (s, 12 H), 8.58 (s, 4 H). $\tilde{\nu}$(C≡O) (acetone): 1820, 1880 cm^{-1}. λ_{max}: 685 (acetone, $\Delta\tilde{\nu}_{1/2}$ = 3100 cm^{-1}), 703 (THF), 725 (toluene), 740 nm (pentane).[5c] Cyclic voltammetry (acetone/0.1 M Bu$_4$NPF$_6$): E_{red} = -1.93 V versus Fc/Fc$^+$, ΔE_{pp} 60 mV; E^{pa} = -0.28 V versus Fc/Fc$^+$ for irreversible oxidation.

Instrumentation. Magnetic data were obtained by use of SHE Corp. and Quantum Design SQUID susceptometers. Magnetization measurements were carried out at 5 K and at applied fields varying between 0.2 and 20 kOe in order to determine the nonsaturating conditions for each sample. The measurements were done with several samples from different preparations of the same compound after purity checks (IR, NMR, UV/vis); in particular, there were no high-spin Mn(II) ESR signals detectable of the samples used for the magnetic measurements (such signals developed after exposure to air). Magnetic susceptibility data were measured in the 2-300 K (Quantum Design) and 5-300 K (SHE) temperature range at 7 kOe (1), 3 kOe (2), 3 kOe (3), 3.5 kOe (4), 3.5 kOe (5), 10 kOe (6), 5 kOe (7), 1 kOe (8), 7 kOe (9), 5 kOe (10), and 5 kOe (11). Sample holder and ligand diamagnetism corrections were made, and fitting procedures were followed as published.[13]

EPR/ENDOR spectra were taken on a Bruker ESP 300 system with EN 003 ENDOR interface, ER 035M Gaussmeter, and a HP 5350B microwave counter. NMR measurements were performed on a Bruker 250-MHz spectrometer. IR data were obtained on a Perkin-Elmer 684 infrared spectrometer. UV/vis spectra were recorded on Bruins Instruments Omega 10 equipment. Elemental analyses were obtained by using a Perkin-Elmer analyzer 240 in a conventional setup, which required the brief exposure of the complexes to air. Cyclic voltammetry was performed at a glassy carbon working electrode at 100 mV/s standard scan rate using a PAR 273 potentiostat and a three-electrode cell with a Ag/AgCl or SCE reference.

unreacted yellow tricarbonyl; the red product was obtained with THF as eluent. Removal of solvent produced 2.3 g (74%) of the red complex. Calcd for C$_{15}$H$_{14}$MnNO$_3$ (311.2): C, 57.89; H, 4.53; N, 4.82. Found: C, 54.20; H, 4.49; N, 4.45. ^{1}H NMR (C$_6$D$_6$): δ 1.22 (s, 3 H), 1.71 (s, 3 H), 3.95 (s, 2 H), 4.10 (s, 2 H), 6.40 (d, 2 H), 8.42 (d, 2 H); J(2,3) = 5.35 Hz. $\tilde{\nu}$(C≡O) (THF): 1920, 1850 cm^{-1}. $\tilde{\nu}$(C=O) (THF): 1700 cm^{-1}. λ_{max} (toluene): 507 nm.

(C$_5$Me$_5$)(CO)$_2$Mn(N^1-4-acpy) (3) was synthesized accordingly, using (C$_5$Me$_5$)(CO)$_3$Mn. Precipitation from toluene/pentane (1/2) at -40 °C yielded 81% of the product as dark-purple crystals. Calcd for C$_{19}$H$_{22}$MnNO$_3$ (367.3): C, 62.13; H, 6.04; N, 3.81. Found: C, 61.78; H, 6.02; N, 3.89. ^{1}H NMR (C$_6$D$_6$): δ 1.53 (s, 15 H), 1.73 (s, 3 H), 6.48 (d, 2 H), 8.40 (d, 2 H); J(2,3) = 6.0 Hz. $\tilde{\nu}$(C≡O) (toluene): 1908, 1840 cm^{-1}. $\tilde{\nu}$(C=O): 1698 cm^{-1}. λ_{max} (toluene): 536 nm (ϵ 3300 M^{-1} cm^{-1}).

(C$_6$H$_6$)(CO)$_2$Cr(py) (10). A 1.1-g (4.5 mmol) amount of (C$_6$H$_6$)Cr(CO)$_3$ and 25 mL (0.31 mmol) of pyridine were dissolved in 100 mL of toluene and irradiated for 3 h at 0 °C under argon with a Hg high-pressure lamp (TQ 150, Hereaus, Germany). After 3 h of continued stirring in the dark the solvent and unreacted pyridine were removed under vacuum. Recrystallization of the solid residue in toluene/n-hexane (1/2) at -30 °C gave 0.9 g (75%) of the crystalline red complex. Calcd for C$_{13}$H$_{11}$CrNO$_2$ (265.1): C, 58.87; H, 4.18; N, 5.28. Found: C, 55.74; H, 4.27; N, 4.92. ^{1}H NMR (CDCl$_3$): δ 4.62 (br s, 6 H), 6.78 (br s, 2 H), 7.30 (br s, 2 H), 8.95 (br s, 1 H). $\tilde{\nu}$(C≡O) (toluene): 1820, 1875

Results

The photolabile yet isolable mononuclear complexes 1-4 and 6 show qualitatively similar yet quite unexpected[14] magnetic behavior (see Figures 1 and 2) despite very different electronic structures. For example, TCNE (E_{red} = +0.22 V versus SCE) with its very easily accessible π^* acceptor level gives rise to much lower lying metal-to-ligand charge-transfer excited states[8] than 3-cnpy (E_{red} = -1.98 V),[8b] 4-acpy (E_{red} = -1.61 V),[15] or pyrazine (E_{red} = -2.1 V).[8a]

(13) Jordanov, J.; Roth, E. K. H.; Fries, P. H.; Noodleman, L. *Inorg. Chem.* **1990**, *29*, 4288.

(14) Paramagnetism of a dimer of (C$_5$H$_4$Me)(CO)$_2$Mn with a bis(phosphavinyl) ether bridging ligand: Ziegler, M. L.; Balles, R.; Nuber, B.; Becker, G.; Schmidt, H.; Kanellakopulos, B.; Powietzka, B. *Angew. Chem.* **1987**, *99*, 929; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 900. As in ref 9c, it remained unclear whether the paramagnetism was caused by the unconventional ligand.

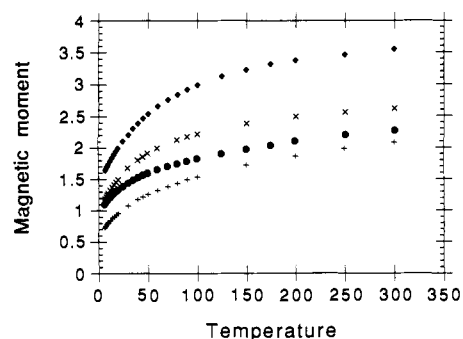(15) Kaim, W. *Z. Naturforsch.* **1984**, *39b*, 801.

Unexpected Paramagnetism of Metal Carbonyl Complexes

J. Am. Chem. Soc., Vol. 114, No. 14, 1992 5695

Figure 2. Effective magnetic moments μ_{eff} (μ_B) per molecule as a function of temperature: pyrazine complexes **4** (×) and **5** (+); TCNE complexes **6** (●) and **7** (◆).

Table I. Effective Magnetic Moments μ_{eff} (μ_B) of Solid Complexes $[(C_nR_n)(CO)_2M]_k(L)$ at 300 K;[a] Basicities pK_{BH^+}, and Reduction Potentials E_{red} (V versus SCE) of Ligands L

complex	μ_{eff} (300 K)	pK_{BH^+} (L)	E_{red} (L)
1	1.99	1.36	−1.98
2	2.06		−1.61
3	1.41		−1.61
4	2.61	0.65	−2.1
5	2.08	0.65	−2.1
6	2.26	<0	+0.22
7	3.54	<0	+0.22
8	0.64	5.3	<−2.5
9	0.56	≈6.4	−2.70
10	2.13	5.3	<−2.5
11	4.89	0.65	−2.1

[a] From SQUID susceptometry. For applied fields, see the Experimental Section.

The results from magnetic measurements on the solid complexes **1–7**, **10**, and **11** (see Figures 1 and 2 and Table I) clearly illustrate the occupation of energetically low-lying magnetic states of integer spin in these d^6 metal carbonyl complexes with 18 VE configuration. In each case, the effective magnetic moment decreases with temperature. In single-ion complexes, this type of dependence $\mu(T)$ is indicative of zero-field splitting of the metal ion ground state, with a nonmagnetic singlet sublevel ($M_s = 0$) being lowest. Accordingly, the magnetic data were analyzed in a first approximation using van Vleck's equation, (1), to calculate the average susceptibility, where $x = D/kT$, D is the axial term of the zero-field splitting, and TIP is temperature-independent paramagnetism.

$$X(T) = 2\frac{Ng^2\mu_B^2}{3kT}\frac{[2/x - 2\exp(-x)/x + \exp(-x)]}{[1 + 2\exp(-x)]} + TIP \quad (1)$$

A typical fit, e.g., for **6**, assumes the following values: $D = 14.6 \text{ cm}^{-1}$, $g = 1.23$, and $TIP = 0.9 \times 10^{-3}$. The calculated g factor is very low, whereas the D value is rather large. Zero-field splittings of similar magnitude have been reported for Fe^{2+} ($S = 2$) complexes.[16] Large zero-field distortions are assumed to indicate spin–orbit coupling that connects the ground singlet with the other components of the $^5T_{2g}$ state. It may be necessary, therefore, to include a spin–orbit contribution in a more advanced fitting model of this hitherto unprecedented low-symmetry situation.

Organomanganese complexes of coordinatively fully saturated ligands were studied in the case of the symmetrically bidentate pyrazine system[8a] (**5**) and of the potentially tetradentate TCNE molecule (**7**).[10] Both complexes are paramagnetic with a similar temperature dependence of μ_{eff} as found for the monomers (cf. Figure 2).

Because of the symmetry of the tetranuclear TCNE complex the two coupling constants J_1 and J_2 are sufficient to analyze the
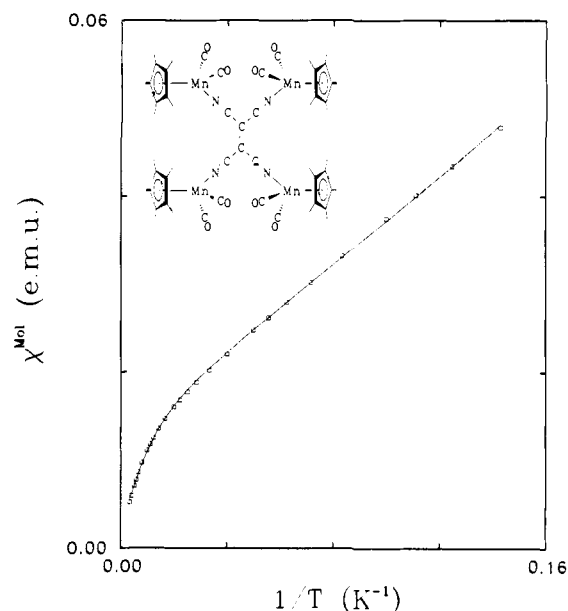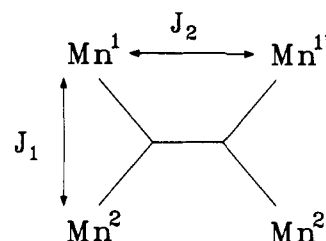

Figure 3. Molar susceptibility of the tetranuclear TCNE complex **7** versus reciprocal temperature. Experimental data are shown as open squares. The theoretical fit with the parameters given in the text is represented by the continuous line.

temperature variation of the magnetic susceptibility, as shown below.

On the basis of previous electronic arguments[10] we consider that $J_2 \ll J_1$ and the J_2 term is therefore set equal to zero. The tetranuclear complex **7** can then be considered as formed by two separate and identical dinuclear units.

The magnetic behavior has been interpreted in terms of an isotropic magnetic exchange interaction (J_1 term) between two $S_1 = S_2 = 1$ ions, Mn^1 ($Mn^{1'}$) and Mn^2 ($Mn^{2'}$), and of a Bleany–Bowers equation (J term) that accounts for the singlet and triplet states present at each manganese center. This leads to the following energy levels above the ground state: $J - 2J_1$ (multiplicity of 1), $J - J_1$ (multiplicity of 3), and $J + J_1$ (multiplicity of 5).

The equation for the molar magnetic susceptibility has been derived from the analytical expression (2) given by Belorizky et al.,[17] where $x_1 = (-J + J_1)/kT$, $x_2 = (-J - J_1)/kT$, and $x_3 = (-J + 2J_1)/kT$. The other symbols have their usual meaning.

$$X = 4N\mu_B^2g^2/kT[2\exp(-x_1) + 10\exp(-x_2)]/[1 + 1 + \exp(-x_3) + 3\exp(-x_1) + 5\exp(-x_2)] \quad (2)$$

J, J_1, and g values were determined by least-squares fitting[18] of the experimental data. A very good agreement is obtained (see Figure 3) for the values $g = 1.64$, $J = 16.3 \text{ cm}^{-1}$, and $J_1 = 11.4 \text{ cm}^{-1}$. As for the mononuclear complex **6**, the g factor is distinctly smaller than 2. The quality of the fit confirms the adequacy of the phenomenological model chosen and the antiferromagnetic nature of the interaction.

In contrast to **1–4**, the similar yet more robust[5a,11] complex **8** with the more basic pyridine ligand (Figure 1) and the dinuclear

(16) Carlin, R. L.; van Duyneveldt, A. J. *Magnetic Properties of Transition Metal Compounds*; Springer-Verlag: New York, 1977; Chapter 8.
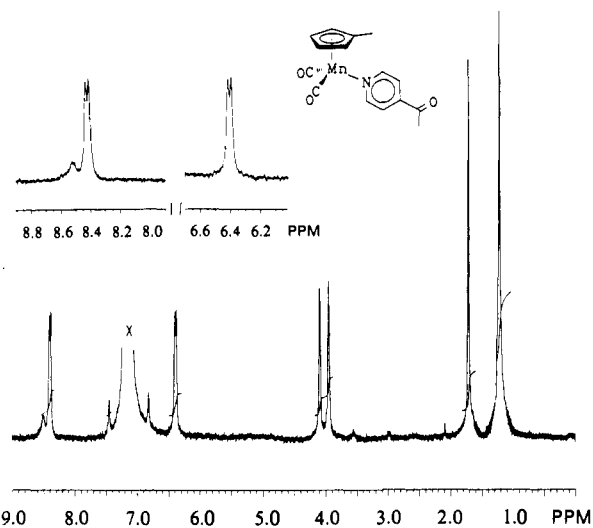
(17) Belorizky, E.; Fries, P. H.; Gojon, E.; Latour, J. M. *Mol. Phys.* 1987, 61, 661.

(18) Variable monomeric $S = {}^1/{}_2$ impurity and temperature-independent paramagnetism (TIP) were also included in the fit (Figure 3). Their values settled at %(impurity) = 8.5% and TIP = 1.03×10^{-3}.

5696 *J. Am. Chem. Soc., Vol. 114, No. 14, 1992*

Kaim et al.

Figure 4. ¹H NMR spectrum of complex 2 in C_6D_6 solution (x: solvent signal).
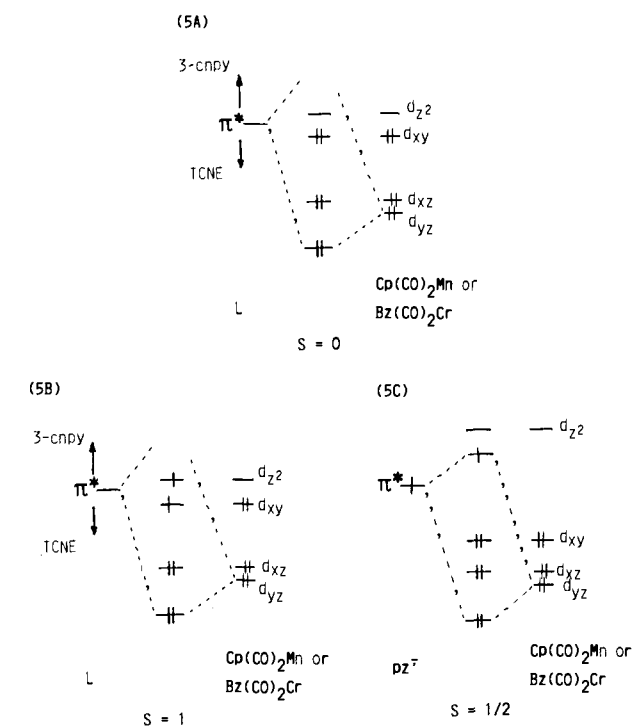
arylbis(dialkylphosphine) complex 9[12] show much less paramagnetism with $\mu_{eff} < 0.7$ μ_B at 300 K (Table I). On the other hand, the electron-rich chromium(0) analogue of 8, (C_6H_6)-$(CO)_2Cr(py)$ (10), long known to be quite labile,[7] exhibits sizable paramagnetism (Figure 1), as does the dinuclear pyrazine complex 11 (Table I).

Magnetic resonance data proved to be less useful for the detection of strong paramagnetism in these 18 VE complexes, as evidenced by the absence of characteristic EPR signals down to 4 K. ¹H NMR Spectra of freshly prepared solutions of the complexes in noncoordinating C_6D_6 exhibit just slightly broadened lines with no unusual shifts as illustrated in Figure 4.[5c,6,8,9,19]

Discussion

A first cause of the unexpected paramagnetism at higher temperatures (>50 K) for most of the complexes (1–11) lies in the generally small ligand field splitting of low-valent chromium and manganese, which favors spin crossover.[2,3] Other factors are the ligand strength and the coordination geometry;[16] Reduction of the C_{3v} symmetry of the $CpMn(CO)_3$ parent to C_s in $CpMn$-$(CO)_2(L)$[4,9d] and weakening of the bond to L leads to an arrangement of d orbitals (5A,B) that favors the occupation of magnetically excited states such as the triplet configuration (5B). Specifically, the d_{xy} orbital should be destabilized and the d_{z^2} orbital strongly stabilized as a result of the replacement of CO by weaker ligands.[20] A similar line of reasoning starts from pseudo-O_h symmetry for the tricarbonyl[5a] and involves a perturbation to pseudo-C_{4v} symmetry by weakening one ligand interaction (→ square pyramid), which should also lead to a stabilized d_{z^2} and a destabilized d_{xy} orbital.[21]

Whereas weak, i.e., neither very basic nor strongly π-accepting, nitrogen ligands such as TCNE (in partially reduced form[9a,b]), 3-cnpy (acidity of conjugated acid $pK_{BH^+} = 1.36$),[8b] or pyrazine ($pK_{BH^+} = 0.65$)[8a] give rise to strong paramagnetism at temperatures above 100 K (Figures 1 and 2), the pyridine ($pK_{BH^+} = 5.3$) monomer 8 and the dinuclear complex 9 of a strongly π-accepting arylbis(dialkylphosphine) ($pK_{BH^+} \approx 6.4$)[22] do not exhibit significant thermal population of higher spin states up to 300 K ($\mu_{eff} < 0.7$ μ_B). It is even possible to obtain an approximately linear correlation between ligand basicities and magnetic moments of complexes ($C_5H_4R)(CO)_2Mn(L)$ 1, 4, 8, and 9 with $\mu_{eff}(300\ K) =$

(19) Preliminary studies with J. Heck, University of Nijmegen, The Netherlands. Slow exchange between $S = 0$ and paramagnetic species could be responsible for the observation of little affected NMR signals.

(20) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(21) Cf.: Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill: New York, 1984; p 436.

(22) Cf. data in: Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

7.42 − 2.76pK_{BH^+} (in μ_B, $r = 0.981$).

Following a similar argument, the exchange of C_5H_4Me by the more electron rich, "stronger" C_5Me_5 ligand on going from 2 to 3 is expected to lead to a decrease of paramagnetism (cf. Table I).

As the comparison between mononuclear $(C_5R_5)(CO)_2Mn$ complexes 1–4 of conventional ligands with high-lying π^* orbitals (5 A,B: 3-cnpy) and of the complex 6 with a strongly stabilized π^* level (5A,B: TCNE) demonstrates, the observed solid-state paramagnetism of the latter is probably not explainable by the anion radical formulation of the TCNE ligand.[9c] The TCNE complexes 6 and 7[9,10] contain spin-paired TCNE[·−] (charge aspect),[9,23] however, the d orbital involved in spin pairing (d_{yz} in the coordinate system adopted here[20]) is different from the d_{xy} and d_{z^2} orbitals that are responsible for the *metal-based* spin crossover (5). For metal complexes of TCNE it is important to strictly distinguish between charge and spin formulations.[10,23]

The interpretation of the paramagnetism as a metal-based phenomenon is in agreement with the result that magnetic exchange coupling between ligand-bridged metal centers reduces μ_{eff}/Mn in polynuclear compounds 5 and 7 relative to the monomers 4 and 6 (Table I).

The lower oxidation state and hence more destabilized d_{xy} orbital (5) of the metal in the chromium(0) complexes 10 and 11 relative to the manganese(I) analogues 8 and 5 is evident from the low oxidation potentials (see Experimental Section) and is presumably responsible for more pronounced paramagnetism (Table I) and lability of 10 and 11.

Complexes of $(C_5R_5)(CO)_2Mn$ and $(C_6H_6)(CO)_2Cr$ with singly reduced and, consequently, much more basic[24] nitrogen ligands such as pyrazine and pyridyl- or nitrile-containing anion radicals[8] may exhibit an orbital ordering (5C) different from that of 5A,B. EPR measurements[8] of several reduced manganese complexes have shown that the additional electron usually occupies a ligand-entered π^* orbital and that the coordinated metal centers are clearly low-spin d⁶ with an "18 + δ" VE configuration;[25] however, the

(23) See: Rettig, M. F.; Wing, R. M. *Inorg. Chem.* **1969**, *8*, 2685.

(24) Kaim, W.; Olbrich-Deussner, B. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 173.

(25) (a) Olbrich-Deussner, B.; Kaim, W. *J. Organomet. Chem.* **1988**, *340*, 71. (b) Kaim, W.; Olbrich-Deussner, B.; Gross, R.; Ernst, S.; Kohlmann, S.; Bessenbacher, C. In *Importance of Paramagnetic Organometallic Species in Activation, Selectivity and Catalysis*; Chanon, M., Ed.; Kluwer Academic Publishers: Dordrecht, 1989; p 283.
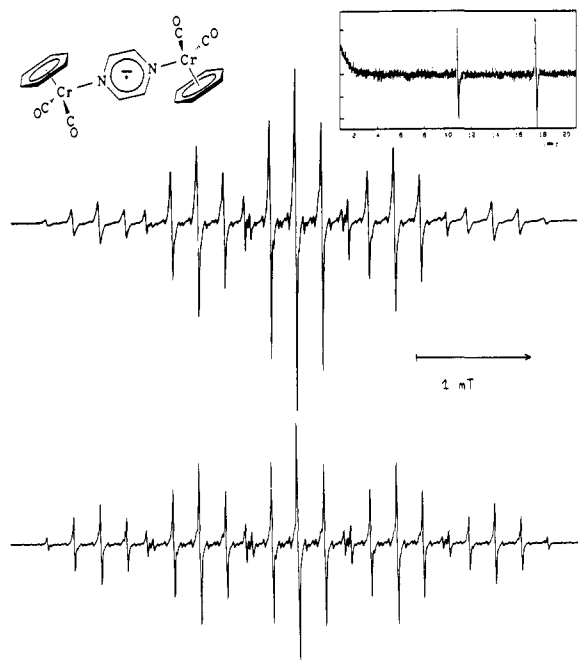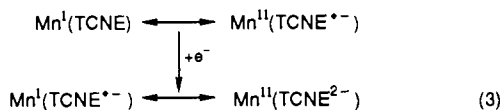
Figure 5. EPR and ^{1}H ENDOR spectrum of **11**$^{·-}$, generated with K, in 1,2-dimethoxyethane solution at 293 K (top) and computer-simulated spectrum with the data given in the text and a line width of 0.012 mT (bottom).

relation g(radical complex) $<$ g(electron) $=$ 2.0023 $<$ g(ligand radical) indicates the presence of low-lying ligand-field excited states.[8] The new anion radical of the dichromium(0) complex **11** in 1,2-dimethoxyethane shows a centering of the unpaired electron on the pyrazine ring with EPR/^{1}H ENDOR coupling constants $a(^{14}N)$ = 0.863 mT, $a(^{13}C)$ = 0.268 mT, and $a(^1H)$ = 0.228 mT (Figure 5). The ^{53}Cr isotope coupling of 0.136 mT is about twice as large as in the dinuclear bis(pentacarbonylchromium) radical complex (pz$^{·-}$)[Cr(CO)$_5$]$_2$,[8] which in conjunction with the slightly lowered pyrazine proton coupling constant (0.246 $\rightarrow$ 0.228 mT) points to a certain increase of metal/ligand orbital mixing. The low isotropic g of 2.0017 for **11**$^{·-}$ relative to that of 2.0035 for (pz$^{·-}$)[Cr(CO)$_5$]$_2$[8] is again indicative of close-lying LF excited states.

The situation is different for the complexes of the superior π acceptor TCNE where the low basicity of reduced forms and the contribution from orbital mixing according to formulation (3) result in nonobservability of EPR signals of reduced forms even at low temperatures.[9a,10]

$$\begin{array}{ccc}
\text{Mn}^{I}(\text{TCNE}) & \longleftrightarrow & \text{Mn}^{II}(\text{TCNE}^{·-}) \\
& \Big\downarrow {\scriptstyle +e^-} & \\
\text{Mn}^{I}(\text{TCNE}^{·-}) & \longleftrightarrow & \text{Mn}^{II}(\text{TCNE}^{2-})
\end{array} \qquad (3)$$

The MO ordering presented in (5) in order to rationalize magnetic behavior also allows now a better understanding of the extraordinary photolability[5,7,8] of many complexes of the type $(C_6R_6)(CO)_2Cr(L)$ and $(C_5R_5)(CO)_2Mn(L)$. The presence of low-lying ligand-field transitions in the visible of thermally stable carbonyl complexes is quite uncommon,[5,26] it is more reminiscent of classical complexes with their photodissociative d $\rightarrow$ d transitions. While the virtually diamagnetic pyridine complex **8** undergoes effective photosubstitution only at rather short wavelengths,[5a] i.e., in the "typical" region of LF bands,[5b,26] the paramagnetic 18 valence electron complexes such as **3** or **11** show quite effective photobleaching in daylight as evident from the disappearance of negatively solvatochromic long-wavelength MLCT bands (see Experimental Section and supplementary material). This photolability stands in contrast to that of related complexes such as dinuclear $(CO)_5Cr(pz)Cr(CO)_5$, which exhibit rather low photochemical quantum yields.[26] Attempts to detect absorptions from Laporte-forbidden ligand-field transitions on the long-wavelength tail of the very intense charge-transfer band (λ_{max} 415 nm in THF) of **1** were unsuccessful, probably due to the expected $>10^3$-fold difference in intensity.

In conclusion, we have demonstrated that seemingly conventional organometallic 18 VE complexes can exhibit sizable paramagnetism in the solid state because of a particular low-symmetry situation and the presence of one weak ligand. The electronic structure (5) deduced from the clearly metal-based paramagnetism also explains the pronounced photolability of some of these complexes. The particular electronic structure of $(C_5R_5)(CO)_2Mn(L)$ is thus responsible for a remarkably dichotomy; *weak* ligands L lead to unprecedented high- or intermediate-spin Mn(I) $=$ d^6 complexes whereas *strong* anionic ligands stabilize low-spin Mn(II) $=$ d^5 systems.[9b,27]

Supplementary Material Available: Nine figures containing absorption spectra and cyclic voltammograms of complexes **10** and **11**; ^{1}H NMR spectra of complexes **1** and **3** in C$_6$D$_6$; effective magnetic moment of complex **1** as a function of temperature; temperature dependence of the molar magnetic susceptibility of complex **6**, experimental data and calculated curve; and photobleaching of complex **3** (10 pages). Ordering information is given on any current masthead page. A listing of experimental magnetic data is available from the authors on request.

(26) (a) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711. (b) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1989**, *28*, 85. (c) Rawlins, K. A.; Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1990**, *29*, 3866.

(27) Gross, R.; Kaim, W. (a) *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 856; (b) *Inorg. Chem.* **1986**, *25*, 4865; (c) *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3549.