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Contribution from the Chemistry Department,
J. W. Goethe-Universität, D-6000 Frankfurt am Main, West Germany

Deprotonated *p*-Phenylenediamines as Noninnocent Ligands. Metal-to-Ligand Spin Transfer in the Ground State and Ligand-to-Metal Charge Transfer in the Lowest Excited State of Low-Spin Manganese(II) Complexes

Renate Gross[†] and Wolfgang Kaim*[‡]

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Neutral paramagnetic complexes between $(C_5R_5)(CO)_2Mn$ and *p*-phenylenediamines(1−) were obtained via synergistic oxidative deprotonation as labile intermediates between *p*-phenylenediamine precursor complexes and binuclear complexes of the dehydrogenated forms of these ligands. Although the compounds must primarily be regarded as low-spin manganese(II) systems, indicating the capacity of *p*-phenylenediamides(1−) to stabilize metals in relatively high formal oxidation states, the exceptional σ- and π-donor capacity of deprotonated *p*-phenylenediamines causes facile ligand-to-metal charge transfer (LMCT). Spin delocalization is evident from reduced g factors and ^{55}Mn EPR hyperfine coupling and, in particular, from emerging ^{14}N and ^{1}H superhyperfine interaction. Reproduction of these results by HMO/McLachlan spin-density calculations supports the π-type metal/ligand interaction, which is also evident from apparent conformational preferences. LMCT in the lowest excited state is responsible for low-energy transitions d(SOMO) $\leftarrow \pi$ in the near-infrared region; a correlation could be established between LMCT transition energies and the ionization potentials of the protonated ligands, i.e. the corresponding amines. The insensitivity of these transitions to changes of solvent or cyclopentadienyl substituents is a further consequence of the considerably mixed metal/ligand character of the compounds (covalency).

Organometallic coordination chemistry has generally been associated with π-acidic ligands, i.e. with ligands that can compensate for relatively low σ basicity by the ability to accept charge from low-valent metals in low-lying π^* levels (π-back-bonding). Examples include CO, PR_3, and many π-electron-deficient, potentially "noninnocent"[1] organic ligands.[2a] Less familiar in organometallic chemistry are the strongly interacting ligands at the other side of the π-acid/π-base scale, i.e. electron-rich π-systems, where most attenion has been given to complexes of the thiolates[3a] and of deprotonated nitrogen chelate ligands[3b] because of the important coordination chemistry of cysteinate and the dianionic porphyrins in biochemistry.

p-Phenylenediamine (1,4-benzenediamine) and its N-substituted derivatives are among the most electron-rich organic molecules;[4] their propensity to form stable one-electron-oxidation products, the red and blue Wurster's salts, has been established for more than a century.[5] Yet, despite the importance of these compounds and their reactions with metal species, e.g. in photographic processes,[6a] as antioxidants,[6b] or in bioinorganic assay,[7] there is little known about their specific coordination chemistry[8–10] as potentially "noninnocent" ligands. We report here the remarkably electronic structure of coordinatively simple, i.e. nonchelate, 1:1 complexes between dicarbonylcyclopentadienylmanganese(II) fragments and singly deprotonated *p*-phenylenediamines. These complexes can be characterized by IR, EPR, and electronic spectroscopy as systems with close-lying frontier orbitals of considerably mixed metal/ligand character in the ground state and first major excited state.

Experimental Section

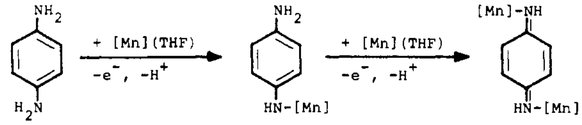
Instrumentation and spectra analysis were described before.[11a]

Preparations. Ligand exchange of the photogenerated solvates[12] $(\eta^5\text{-}C_5R_5)(CO)_2Mn(THF)$ (R = H, CH_3) with $1,4\text{-}H_2N\text{-}C_6H_4\text{-}NH_2$ or $1,4\text{-}Me_2N\text{-}C_6H_4\text{-}NH_2$ in a 1:1 ratio yields orange-colored Mn(I)/amine complexes[9b,13a] (cf. **2**), which can be isolated and purified, albeit under considerable loss by column chromatography on silica at −20 °C (eluents were hexane, toluene, and diethyl ether). These complexes are highly susceptible to oxidative deprotonation, e.g. by aerial oxygen or lead dioxide,[11,13] yielding deep blue or green solutions that contain the paramagnetic intermediates $R_2N\text{-}C_6H_4\text{-}NH\text{-}Mn(CO)_2(C_5R_5)$. These oxidations have to be carried out very carefully, e.g. by monitoring the conversion by electronic spectroscopy (cf. Table I), in order to ensure complete reaction to these intermediates without allowing a second oxidative deprotonation to occur (eq 1 and 2). Chromatography of the

Table I. Spectroscopic Data for Compounds **1**–**4** from Eq 2 (Cp = $\eta^5\text{-}C_5H_4CH_3$)[a]

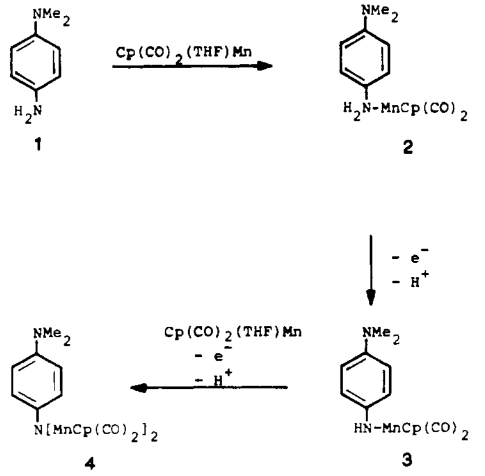
compd	ν_{CC}, cm^{-1}	ν_{CO}, cm^{-1}	λ_{max}, nm
1	1510		
2	1518	1907 1835	385
3	1580	1937 1882	860
4	1550	1915 1838	626

[a] Measurements in toluene solution; all infrared bands are very strong.



(1)

[Mn] = $(\eta^5\text{-}C_5Me_5)(CO)_2Mn$



(2)

[†] Present address: Battelle-Institut, D-6000 Frankfurt am Main, West Germany.

[‡] Karl Winnacker Fellow, 1982–1987.

(1) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer-Verlag: Berlin, 1969, p 291.

(2) Cf.: Cotton, F. A.; Wilkinson, G. *Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980: (a) pp 61–194; (b) p 237.

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Table II. ESR and Electron Spectroscopic Data for Arylamide Complexes $(\eta^5\text{-}C_5(CH_3)_nH_{5-n})(CO)_2(4\text{-}XC_6H_4NH)Mn^a$

n	X	g	$a_{^{55}Mn}$, mT	a_{NH}, mT	$\nu_{max}{}^{LMCT}$, cm^{-1}
5	H	2.0150	5.27	*b*	16 000
1	H	2.0136	5.05	*b*	16 000
5	CH_3	2.0140	5.09	*b*	14 640 14 530 (DMF)
5	NH_2	2.0114	4.51	0.6 (^{14}N) 0.7 (^1H)	11 320
5	NMe_2	2.0120	4.55	0.5 (^{14}N) 0.6 (^1H)	11 600
1	NMe_2	2.0086	4.24	0.65 (^{14}N) 0.77 (^1H)	11 630 11 800 (DMF)

[a] Measurements at room temperature in toluene solution, except where indicated. Values from computer simulated and second order-corrected spectra. [b] No superhyperfine splitting observed.

labile oxidized complexes proved to be unsuccessful; binuclear complexes have been described (*p*-quinonediimine complexes)[13a] or shall be subject of forthcoming reports (nitrene complexes).[11b,c]

With *N*,*N*-dimethyl-*p*-phenylenediamine (*Caution*: This ligand is mutagenic!)[14] and $(C_5H_4CH_3)(CO)_2Mn(THF)$, a relatively pure paramagnetic intermediate (eq 2) could be isolated and characterized by elemental analysis and EPR, electronic, and vibrational spectroscopy (Tables I and II). A toluene solution of the orange Mn(I)/amine complex was treated with an excess (50%) of lead dioxide at 0 °C in an ultrasonic bath for about 1 h. The blue-green solution was then filtered under argon; removal of the solvent and two washings with hexane gave 82% of a dark green material that was very sensitive toward further oxidative deprotonation. Anal. Calcd for $C_{16}H_{18}MnN_2O_2$: Mn, 16.89; N, 8.62; H, 5.54. Found: Mn, 15.6; N, 8.33; H, 4.90.

With *p*-phenylenediamine or the (pentamethylcyclopentadienyl)dicarbonylmanganese fragment, the mononuclear paramagnetic complexes were similarly obtained as deeply colored intermediates that were too labile to be completely purified; however, their unambiguous spectroscopic characterization was possible by correlating EPR, vibrational, and electron spectroscopic informations (eq 1 and 2 and Tables I and II).

N-deuteriation of *N*,*N*-dimethyl-*p*-phenylenediamine was accomplished by three dissolution/evaporation cycles using D_2O at ambient temperature.

Results and Discussion

Formation and Reactivity. The 1:1 complexes of the organometallic manganese(I) fragments $(C_5R_5)(CO)_2Mn$ with *p*-phenylenediamines have a very strong tendency to simultaneously lose protons and electrons. Single oxidative deprotonation creates, to a first approximation, labile manganese(II) complexes of *p*-phenylenediamide(1−) ligands, as is evident from EPR spectroscopy of the paramagnetic reaction products (Tables I and II and Figure 1). While arylamide complexes of the $(C_5R_5)(CO)_2Mn^+$ fragments could be isolated in favorable instances,[9b,13,15a] the mononuclear complexes with the extremely electron-rich *p*-phenylenediamide(1−) ligands tend to lose a second proton easily to form eventually binuclear species, either *p*-quinone diimine complexes[13a] (from unsubstituted phenylenediamine precursors) or (4-(dimethylamino)phenyl)nitrene-bridged dimers,[11b,15b] if one nitrogen center is blocked against deprotonation (eq 1 and 2). We have now observed the paramagnetic, mononuclear precursor in the former reaction (eq 1) and demonstrate the relative stabilization of these species by blocking one amino function against deprotonation (eq 2).

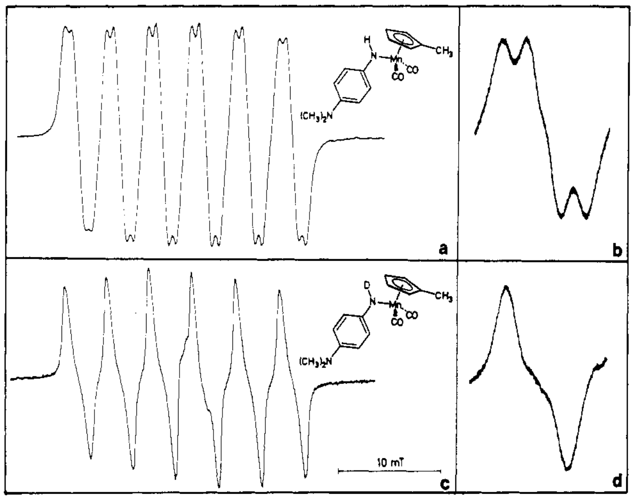

Figure 1. EPR spectra of the N-protonated (A) and N-deuteriated complex (C) at 300 K in toluene solution. Expanded representation of individual sextet lines ($I(^{55}Mn) = {}^5/_2$) reveals a partly resolved four-line pattern (B) for the former case ($a_N \sim a_H$) and a triplet (D) for the latter situation ($a_N > a_D = 0.15a_H$).

Whereas the low carbonyl stretching frequencies and typical metal-to-ligand charge-transfer (MLCT) characteristics suggest that the diamagnetic binuclear complexes contain "normal" $Cp(CO)_2Mn^I$ fragments[9b,13a] that stabilize the two different dehydrogenated forms of the *p*-phenylenediamine ligands (eq 1 and 2) by efficient back-bonding,[16] the paramagnetic mononuclear intermediates are of particular interest because they exhibit a special electronic structure.

As the CO stretching frequencies and the EPR data from Tables I and II suggest, it is mainly the metal fragment that is oxidized in the first step, while the otherwise extremely basic ligands are deprotonated in a *synergistic process*. Flow of electron density from the σ- and π-donating phenylenediamine ligand to the metal center is evident by the high-energy shift of the "aromatic" CC stretching bands from the typical low value of 1510 cm^{-1} for free *p*-phenylenediamines to 1580 cm^{-1} (Table I).

EPR Spectroscopy. The set of strong ligands stabilizes the less common low-spin manganese(II) configuration ($S = {}^1/_2{}^{13b}$) and allows detection of EPR spectra at room temperature because of slow relaxation.[17] In contrast, cationic organometallic Mn(II)

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(3) (a) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121. (b) Cf., e.g.: Levason, W.; Spicer, M. D. *Ibid.* **1987**, *76*, 45.

(4) (a) Nakato, Y.; Ozaki, M.; Egawa, H.; Tsubomura, H. *Chem. Phys. Lett.* **1971**, *9*, 615. (b) Streets, D. G.; Hall, W. E.; Caesar, G. P. *Ibid.* **1972**, *17*, 90. (c) Kaim, W.; Bock, H. *Chem. Ber.* **1978**, *111*, 3843.

(5) Weber, A. *Ber. Dtsch. Chem. Ges.* **1975**, *8*, 714. Wurster, C. *Ibid.* **1879**, *12*, 522. Wurster, C.; Sendtner, R. *Ibid.* **1879**, *12*, 1803.

(6) (a) Cf.: Tong, L. K. J. In *The Theory of the Photographic Process*, 4th ed.; James, T. H., Ed.; Macmillan: New York, 1977; p 339. (b) *Chem. Eng. News* **1987**, *65* (May 18), 29.

(7) For *p*-phenylenediamine oxidase activity of iron and copper systems, cf.: Gad, A.; Sylven, B. *J. Histochem. Cytochem.* **1969**, *17*, 156. Schechinger, T.; Hartmann, H. J.; Weser, U. *Biochem. J.* **1986**, *240*, 281.

(8) For coordination compounds employing merely the amine basicity of *p*-phenylenediamines, cf.: Strohmeier, W.; Schönauer, G. *Chem. Ber.* **1962**, *95*, 1767.

(9) (a) Joss, S.; Bigler, P.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 3487. (b) Gross, R.; Kaim, W. *Angew. Chem.* **1985**, *97*, 869; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 856.

(10) Nesmeyanov, A. N.; Perevalova, E. G.; Fedin, V. P.; Slovokhotov, Yu. L.; Struchkov, Yu. T.; Lemenovskii, D. A. *Dokl. Akad. Nauk SSSR* **1980**, *252*, 1141.

(11) (a) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 4865. (b) Gross, R.; Kaim, W. *J. Chem. Soc., Faraday Trans.*, in press. (c) Gross, R, Ph.D. Thesis, University of Frankfurt, 1987.

(12) Strohmeier, W.; Gerlach, K. *Chem. Ber.* **1961**, *94*, 398, 2031. Cf. also: Fischer, E. O.; Herberhold, M. *Experientia, Suppl.* **1964**, *9*, 259.

(13) (a) Sellmann, D.; Müller, J. *J. Organomet. Chem.* **1985**, *281*, 249. (b) Sellmann, D.; Müller, J.; Hofmann, P. *Angew. Chem.* **1982**, *94*, 708; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 691.

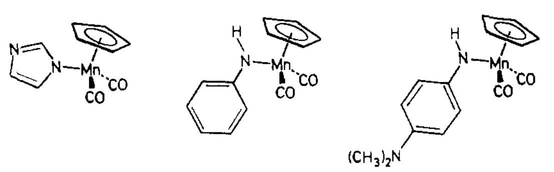
(14) Chung, K. T.; Fulk, G. E.; Andrews, A. E. *Appl. Environ. Microbiol.* **1981**, *42*, 641.

(15) (a) Considering that oxidative deprotonation fails to yield sufficiently stable complexes with less electron-rich nitrogen bases,[11] it seems that persistence is at an optimum with moderately electron-rich arylamides;[9b,13] the use of the extremely electron-rich *p*-phenylenediamides(1−) as well as the combination between the least electron-rich metal fragment $(C_5H_5)(CO)_2Mn$ and *p*-tolylamide[13a] have resulted in difficulties in isolating mononuclear paramagnetic complexes. (b) Complexes with (4-aminophenyl)nitrene ligands (cf. ref 10) can be viewed as phenylogues of aminonitrene complexes: Wiberg, N.; Häring, H. F.; Huttner, G.; Friedrich, P. *Chem. Ber.* **1978**, *111*, 2708. See also ref 11b.

(16) Gross, R.; Kaim, W. *Angew. Chem.* **1984**, *96*, 610; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 614.

(17) Cf.: Pohl, K.; Wieghardt, K.; Kaim, W.; Steenken, S., submitted for publication in *Inorg. Chem.*

Chart I. HMO/McLachlan-Calculated π-Spin Populations ρ for Paramagnetic Manganese Complexes[a]



ρ_{Mn}^{HMO}:	0.904	0.833	0.759
ρ_{N}^{HMO}:	0.017	0.254	0.270
a_{Mn}:	6.1	5.27	4.24 [mT]
a_N:	not observed	not observed	0.65 [mT]

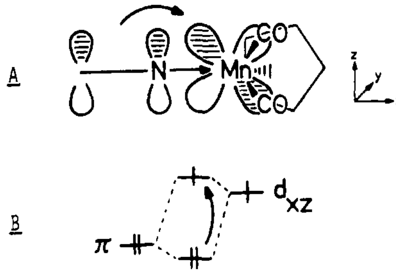
[a] Parameters: $h_C = h_{Mn} = 0.0$, $h_N = 1.0$, all $k = 1.0$; McLachlan parameter $\lambda = 1.2$. Coligands at manganese and methyl substituents at amine nitrogen were disregarded.

complexes that contain only "weaker" ligands such as isocyanides[18a] or phosphanes[18b] have exhibited no or little resolved EPR spectra at room temperature, presumably due to fast relaxation.[19] Whereas +II is a fairly high oxidation state for a carbonyl-containing metal center, the *p*-phenylenediamides(1−) constitute extremely strong σ- and π-electron-rich ligands. Anilide, $C_6H_5NH^-$, already has $pK_{BH^+} = 27.7$,[20a] so that the *p*-amino derivatives can be expected to exhibit an even higher basicity,[20b] approaching, e.g., that of the oxide ion with $pK_{BH^+} = 36$.[2b] On the other hand, the already π-electron-excessive *p*-phenylenediamines with ionization potentials around 7 eV[4] must become even more π-electron donating upon anion formation,[21] thereby allowing the stabilization of an apparently high metal oxidation state by charge transfer from the ligand to appropriate incompletely filled orbitals at the metal.

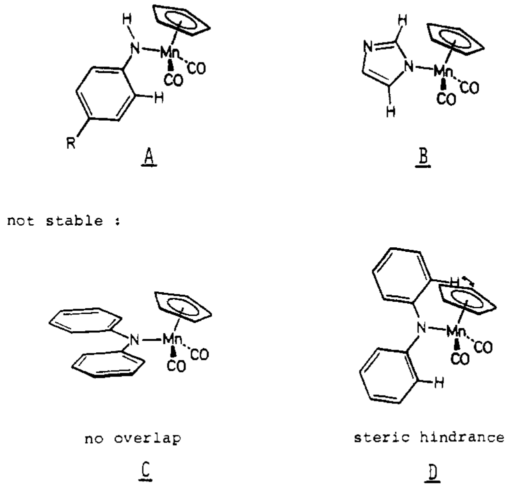
In contrast to the situation for related complexes with less electron-rich anionic ligands such as imidazolates, alkoxides, or deprotonated malonodinitriles,[11] the ESR data do now reveal considerable ligand participation in the distribution of the unpaired electron. The isotropic metal coupling constant is reduced to about two-thirds of the ~6 mT value recorded for related complexes with weakly interacting ligands;[11] correspondingly, the distinct, positive deviation of $\langle g \rangle$ from the free electron value of 2.0023[9b,11] has been markedly reduced.

Most notably, however, is the appearance of *p*-phenylenediamine ligand superhyperfine structure as illustrated in Figure 1. The superhyperfine splitting (SHFS) pattern could be analyzed by using N-deuteriated species. The coordinating ^{14}N nucleus and the attached proton exhibit similar coupling constants as would be expected for planar nitrogen configuration.[22] No further hyperfine coupling from other nuclei in the *p*-phenylenediamine π system could be detected, which disfavors an aminyl radical complex formulation;[9b,23] there is also a significant anisotropy of g and $a(^{55}Mn)$ in frozen-solution EPR spectra with the most prominent component at $g_1 = 2.014$ and $a_1 = 8.5$ mT for the complex depicted in Figure 1.[24]

The distinct anisotropy of a and g values as well as the steric requirements for complex formation are compatible with a special conformation in which the plane of the π ligand coincides with the mirror plane of the metal fragment (IA).[25,26] While complexes with primary amides[13] such as the ones presented here are formed without apparent steric strain (IIA), deprotonated secondary amines can adopt the necessary conformation (IA) only in the case of imidazolate (IIB)[11a] and related biochemically relevant heterocyclic systems[11b] but not in the case of the sterically more demanding diarylamides (IIC,D).



I



II

Conformations IA, IIA, IIB, and IID allow maximum π interaction between the singly occupied d_{xz} orbital of the metal and the π system of the ligand (IA,B); in fact, the metal center may even be treated as a π center in a simple Hückel molecular orbital approach.[11b] HMO/McLachlan spin-density calculations[27] for the imidazolate, anilide, and *p*-phenylenediamide(1−) complexes with nonoptimized Coulomb integral parameters $h_C = h_{Mn} = 0.0$ and $h_N = 1.0$[27] and all resonance integral parameters $k = 1.0$ reproduce the observed spin distribution surprisingly well (Chart I).

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(18) (a) Nielsen, R. M.; Wherland, S. *Inorg. Chem.* **1985**, *24*, 3458. (b) Connelly, N. G.; Kitchen, M. D. *J. Chem. Soc., Dalton Trans.* **1977**, 931.

(19) Bencini, A.; Gatteschi, D. In *Transition Metal Chemistry*; Melson, G. A., Figgis, B. N., Eds.; Marcel Dekker: New York, 1982; Vol. 8, p 1.

(20) (a) Cf. data in: Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic: New York, 1985. (b) p*K* value of 25.6 for *N,N*-dimethyl-*p*-phenylenediamine in liquid ammonia: Takemoto, J. H.; Lagowski, J. J. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 315.

(21) For a recent discussion of the π-donor ability of dialkylamide ligands cf.: Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 905. See also: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, England, 1980; pp 19, 500.

(22) Johnson, C. S., Jr.; Gutowsky, H. S. *J. Chem. Phys.* **1963**, *39*, 58. Bolton, J. R.; Carrington, A.; dos Santos-Veiga, J. *Mol. Phys.* **1962**, *5*, 465.

(23) (a) *Spin delocalization in N,N-dimethyl-p-phenylenediamine* radical cation: Grampp, G.; Stiegler, G. *Z. Phys. Chem. (Munich)* **1984**, *141*, 185. (b) Spin delocalization in arylaminyl radicals: Neugebauer, F. A. In *Landolt-Börnstein, Physical and Chemical Tables*; Springer-Verlag: West Berlin, 1981; New Series, Vol. II/9c 1, p 9.

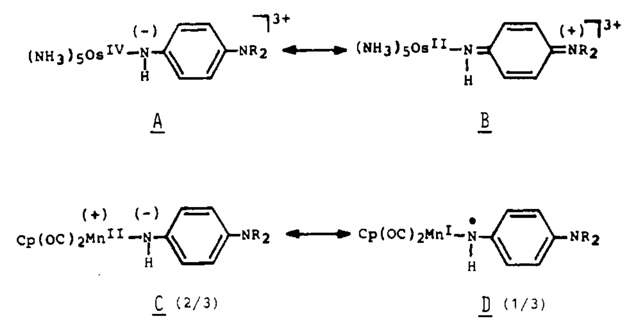
(24) More detailed information could not be obtained due to considerable overlap in the central region of the frozen-solution spectra. Comparable g and metal hfs anisotropy were reported for the related species $(\eta$-$C_4H_6)_2Mn(L)$ (Harlow, R. L.; Krusic, P. J.; McKinney, R. J.; Wreford, S. S. *Organometallics* **1982**, *1*, 1506), for $(\eta$-$C_5H_5)Cr(CO)_2(L)$ (Morton, J. R.; Preston, K. F. *Abstracts of Papers*, 19th Annual International EPR Conference, York, England, 1987), and for $(\eta$-$C_5Ph_5)(CO)_2Co^-$ (Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219); L = CO, PR_3.

(25) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. Cf. also: Marynick, D. S.; Kirkpatrick, C. M. *Ibid.* **1985**, *107*, 1993.

(26) Structural data for a thiolate complex: Winter, A.; Huttner, G.; Zsolnai, P.; Kroneck, P.; Gottlieb, M. *Angew. Chem.* **1984**, *96*, 986; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 975. Cf. also: Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1.

(27) (a) Heilbronner, E.; Bock, H. *The HMO Model and its Application*; Wiley/Verlag Chemie: London/Weinheim, FRG, 1976; Vol. 1. (b) McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.

(i) The unpaired electron is predominantly centered at the metal, even in the *p*-phenylenediamide(1−) complexes. (ii) Delocalization in the arylamide systems occurs almost exclusively to the coordinating nitrogen center (superhyperfine coupling), ruling out a radical ligand formulation. (iii) This delocalization is greater for the *p*-phenylenediamide(1−) system than for the anilide complex, reflecting the LMCT situation (IA). (iv) Even the magnitudes of hyperfine and superhyperfine splitting are reproduced by applying a McConnell-type equation $a = Q\rho$ with reasonable parameters Q_N = 2.4 mT[22] and Q_{Mn} = 6.8 mT,[11] thus indicating the validity of a σ/π separation approach (IA). Incidentally, Ludi and coworkers have recently reported a diamagnetic osmium/*p*-phenylenediamide(1−) system with the two resonance forms IIIA and IIIB,[9a] yet the paramagnetic manganese complexes allow a much better assessment of contributions from resonance structures such as IIIC,D via the EPR spectroscopically accessible spin distribution.



III

While there is no detectable solvent dependence of the EPR parameters, the characteristic changes on replacement of η^5-C_5Me_5 by the more electron deficient η^5-C_5H_4Me coligand supports the interpretation given by IA,B. Reduction of g and $a(^{55}Mn)$ values and increasing $a(^{14}N)$ and $a(H)$ superhyperfine couplings are consistent with a more pronounced ligand-to-metal charge transfer and enhanced metal-to-ligand spin transfer from the more electron deficient $(C_5R_5)(CO)_2Mn^+$ fragment to the electron-rich arylamide ligand.

Electronic Spectroscopy. Consistency of EPR and calculational data suggests that the *p*-phenylenediamide(1−) complexes from Table I lie in the theoretically and experimentally interesting intermediate region between a paramagnetic transition-metal system and a "radical" complex.[28] Such arrangements have received special attention recently because the biochemically important and spectroscopically conspicuous copper(II)/thiolate systems,[29,30] including "blue" copper species,[29a,b] were characterized as having the unpaired electron in an orbital of mixed metal/ligand character.[30] In addition to considerable reduction of metal coupling[29,30] and emergence of appreciable ligand superhyperfine features,[31] the copper/thiolate systems are distinguished by intense ligand-to-metal charge-transfer (LMCT) transitions in the visible region.[29,30,32] Similar phemomena are observed for the $Cp(CO)_2(anion)Mn^{II}$ complexes; in fact, the corresponding absorption maxima of amide complexes span the whole area from the near-UV to the near-IR region of the spectrum,[9b,11] while alkanethiolate complexes absorb around 20 000 cm^{-1}.[26]

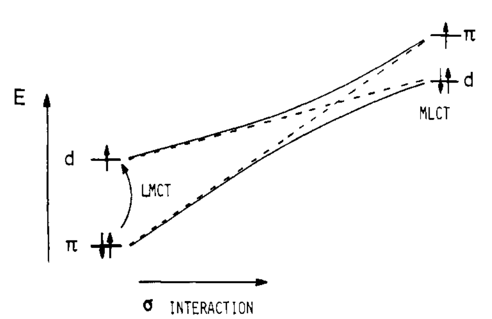


Figure 2. Effect of increasing σ-interaction between metal and ligand on the orbital difference and on the character of the charge-transfer transition.

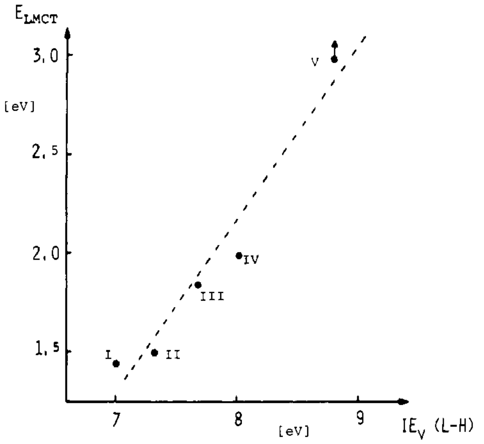


Figure 3. Correlation between LMCT absorption energies (in eV; 1 eV = 8066 cm^{-1}) of complexes $(C_5Me_5)(CO)_2(L)Mn$ with anionic ligands L^- in toluene solution and photoelectron spectroscopically determined[4,38] ionization energies of the protonated ligands L–H = *N*,*N*-dimethyl-*p*-phenylenediamine (I), *p*-phenylenediamine (II), 4-methylaniline (III), aniline (IV), and imidazole (V).[9b,11] Least-squares fit: E_{LMCT} = 0.88IE − 4.85 eV; r = 0.969.

Low-lying LMCT excited states have rarely been established for organometallic complexes[33] because unfilled metal d orbitals are not readily available in closed-shell systems with "strong" ligands. However, open-shell species may provide a possibility for low-lying LMCT as has been demonstrated by analysis of the ferrocenium ion;[33] a low-spin iron(III) complex with a dialkylamide ligand and LMCT absorption in the visible has been characterized only recently.[17] The incompletely filled t_{2g} subshell of a low-spin d^5 configuration is also present in the manganese(II) species described here; furthermore, the well-known tendency of Mn(II) to form complexes with unusually small ligand field splitting[34] has been established also for organometallic species.[35,36]

Since arylamines are already very electron rich,[4] their deprotonated forms must have even higher lying occupied π MOs that are available for interaction with a half-filled metal d orbital of appropriate symmetry (IA,B).[13b] The transition between both levels is spin-allowed for only one electron so that the extinction coefficients for these absorption bands lie well below[13b,17,26,33] the "normal" value for charge-transfer bands of 5000–15 000 M^{-1} cm^{-1};[33,36] estimations for the sensitive *p*-phenylenediamide(1−)

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(28) Von Zelewsky, A.; Daul, C.; Schläpfer, C. W. In *Landolt Börnstein, Physical and Chemical Tables*; Springer-Verlag: West Berlin, 1981; New Series Vol. II/17a, p 199. Cf. also: Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

(29) (a) Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 168. (b) Sykes, A. G. *Chem. Soc. Rev.* **1985**, *14*, 283. (c) Stevens, T. H.; Martin, C. T.; Wang, H.; Brudvig, G. W.; Scholes, C. P.; Chan, S. I. *J. Biol. Chem.* **1982**, *257*, 12106.

(30) Penfield, K. W.; Gewirth, A. A.; Solomon, E. I. *J. Am. Chem. Soc.* **1985**, *107*, 4519.

(31) Roberts, J. E.; Cline, J. F.; Lum, V.; Freeman, H.; Gray, H. B.; Peisach, J.; Reinhammar, B.; Hoffmann, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 5324.

(32) (a) Schugar, H. *Adv. Bioinorg. Chem.* **1986**, *1*. (b) John, E.; Bharadwaj, P. K.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1986**, *25*, 3065.

(33) Geoffroy, G. L.; Wrighton, M. S.; *Organometallic Photochemistry*; Academic: New York, 1979; p 18.

(34) Cf. data in: *Landolt-Börnstein, Physical and Chemical Tables*; Springer-Verlag: West Berlin 1981; New Series, Vol. II/8, pp 185–211, or New Series Vol. II/12b, pp 93–104. See also: Manoharan, P. T.; Gray, H. B. *Inorg. Chem.* **1966**, *5*, 823.

(35) High-spin/low-spin equilibria in manganocenes: (a) Switzer, M. E.; Wang, R.; Rettig, M. F.; Maki, A. H. *J. Am. Chem. Soc.* **1974**, *96*, 7669. (b) Ammeter, J. H.; Bucher, R.; Oswald, N. *Ibid.* **1974**, *96*, 7833; *Helv. Chim. Acta* **1975**, *58*, 671. (c) Hebendanz, N.; Köhler, F. H.; Müller, G.; Riede, J. *J. Am. Chem. Soc.* **1986**, *108* 3281.

(36) Gross, R.; Kaim, W. *Inorg. Chem.* **1985**, *24*, 498.

complexes also yield values of approximately 3000 M^{-1} cm^{-1}.

The extraordinary decrease of the LMCT absorption energy from >24 000 cm^{-1} for imidazolate and related complexes[9b,11] of the Cp(CO)$_2$Mn fragments to values below 12 000 cm^{-1} for the *p*-phenylenediamide(1–) complexes (Table II) may be rationalized by considering the simplified diagram in Figure 2. Increasing electron donation from ligand to metal corresponds to a strong destabilization of the occupied ligand π level and causes a less pronounced, indirect destabilization of the interacting metal orbital (ligand field effect).

Convergence of both levels in this model, which, among other factors, neglects Franck–Condon contributions, leads to a point of maximum orbital mixing and minimum excitation energy, from which on the transitions may be viewed as MLCT processes.[37] Convincing evidence for the LMCT character (IA,B) of the transitions summarized in Table II and against their formulation as $\pi^* \leftarrow$ d processes[13b] comes from a correlation between the absorption energies (in eV) and the ionization potentials of the protonated nitrogen ligands;[4,38] both processes involve the loss of one electron from the highest occupied π level of the ligand (Figure 3).

There is a reasonable correlation between both sets of data, justifying the use of the simple orbital scheme (IA,B). The deviation of the slope from unity can be attributed to the ligand field effect on the half-filled metal level in the case of the LMCT process (Figure 2). The absolute ligand field effect is by no means small as can be seen by the enormous cathodic shift in the oxidation potential of more than 2 V from complexes Cp(CO)$_3$Mn[39] to $[(C_5Me_5)(CO)_2(L)Mn]^-$, L = –S-*t*-Bu or –NHC$_6$H$_4$Me.[9b,26]

The *p*-phenylenediamide(1–) complexes do not show the pronounced solvatochromism that is often typical for charge-transfer transitions.[37b,40] The reason lies presumably in the considerably mixed metal/ligand character of the frontier orbitals (IA,B) so that external perturbations affect *both* levels and leave the difference little changed. This virtual insensitivity pertains also to the change from η-C$_5$H$_4$Me to η-C$_5$Me$_5$ coligands; in an MLCT situation there is a clear bathochromic shift on destabilization of the metal level by introducing methyl groups at the cyclopentadienyl ring.[36]

Summary. Despite preparative difficulties due to the intermediate nature of the species, we have succeeded in defining coordinatively simple, i.e. nonchelate, 1:1 complexes between the extremely σ- and π-electron-rich *p*-phenylenediamides(1–) and $[Cp(CO)_2Mn^{II}]^+$ fragments by EPR and electronic spectroscopy as systems with close-lying frontier orbitals of mixed metal/ligand character. These paramagnetic mononuclear species may be viewed as intermediates in reactions leading to diamagnetic binuclear *p*-quinone diimine or nitrene complexes. Notable metal-to-ligand spin transfer in the ground state as evidenced by reduced metal hyperfine splitting and detectable ligand superhyperfine splitting suggests the further use of the *p*-phenylenediamides(1–) as potentially noninnocent ligands in the fascinating intermediate area between paramagnetic transition-metal-centered species and genuine "radical" complexes, i.e., in the synthesis of truly delocalized open-shell coordination compounds. If a second oxidative deprotonation and binucleation can be avoided, e.g. by steric measures, the *p*-phenylenediamides(1–) may be considered as very suitable monodentate ligands for the stabilization of metals in high formal oxidation states.

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Registry No. 1, 99-98-9; 2, 110116-27-3; 3, 110095-89-1; 4, 110095-90-4; [Mn](THF), 86155-78-4; (η^5-C$_5$H$_4$Me)(CO)$_2$Mn(THF), 51922-84-0; [Mn](PhNH), 110095-91-5; (η^5-C$_5$H$_4$Me)(CO)$_2$(PhNH)Mn, 110095-92-6; [Mn](4-CH$_3$C$_6$H$_4$NH), 98104-74-6; [Mn](4-NH$_2$-C$_6$H$_4$NH), 110095-93-7; [Mn](4-NMe$_2$C$_6$H$_4$NH), 110095-94-8; (η^5-C$_5$H$_4$Me)(CO)$_2$(4-NMe$_2$C$_6$H$_4$NH)Mn, 98104-73-5; Cp(CO)$_2$(THF)Mn, 12093-26-4; Cp(CO)$_2$(Im)Mn, 110116-28-4; Cp(CO)$_2$(PhNH)Mn, 97695-95-9; 4-NH$_2$C$_6$H$_4$NH$_2$, 106-50-3; PhNH$_2$, 62-53-3; 4-MeC$_6$H$_4$NH$_2$, 106-49-0.

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(37) For the ambivalence of LMCT/MLCT, cf.: (a) Gross, R.; Kaim, W. *Angew. Chem.* **1987**, *99*, 257; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 251. (b) Kaim, W.; Ernst, S.; Kohlmann, S. *Chem. Unserer Zeit* **1987**, *21*, 50.

(38) (a) Kobayashi, T.; Nagakura, S. *Chem. Lett.* **1972**, 1013. (b) Cradock, S.; Findlay, R. H.; Palmer, M. H. *Tetrahedron* **1973**, *29*, 2173.

(39) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61.

(40) Cf. the argumentation concerning MLCT solvatochromism in: Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3306. Kaim, W.; Kohlmann, S.; Ernst, S.; Olbrich-Deussner, B.; Bessenbacher, C.; Schulz, A. *J. Organomet. Chem.* **1987**, *321*, 215.

Contribution from the Department of Chemistry,
National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

Kinetics of Acid-Catalyzed Dissociation of Copper(II) Diamino Diamide Complexes

Min-Shiun Chao and Chung-Sun Chung*

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The dissociation kinetics of the copper(II) complexes of 4,7-diazadecanediamide (L-2,2,2), 5-methyl-4,7-diazadecanediamide (5-Me-L-2,2,2), 4,8-diazaundecanediamide (L-2,3,2), and 6-hydroxy-4,8-diazaundecanediamide (6-OH-L-2,3,2) have been studied at 25.0 °C and μ = 4.0 M (NaClO$_4$ + HClO$_4$) by the stopped-flow method. These reactions are specific-acid catalyzed; however, the rate constants of these reactions do not depend on the concentrations of acetic, chloroacetic, and dichloroacetic acids. At pH values below 1.4 both the proton-assisted and the direct protonation pathways make contributions to the rates. The ratios of the rate constant of dissociation by the direct protonation pathway to the rate constant by the proton-assisted pathway for the complexes with the 6,5,6-membered ring system are larger than those for the complexes with the 6,6,6-membered ring system. The reactions exhibit associative character.

Introduction

The kinetics of the reactions of copper(II) polyamine complexes are receiving considerable attention at present.[1] The earlier studies have been reviewed,[2] and recent work has focused on the acid-catalyzed dissociation of copper(II) polyamine complexes[3-12] and

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(1) Durmhiller, J. A.; Montavon, F.; Lehn, J. M.; Taylor, R. W. *Inorg. Chem.* **1986**, *25*, 3751-3757.

(2) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; Vol. 2.

(3) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* **1981**, *20*, 2152-2155.

0020-1669/87/1326-3600$01.50/0