Conformational equilibria of 2,5-bis(1-phenyliminoethyl)pyrazine anion radical, bpip$^{\bullet -}$. An electron paramagnetic resonance/electron–nuclear double resonance study of bpip$^{\bullet -}$, (bpip$^{\bullet -}$)(RMg$^+$)$_2$, and of the related anion radical of *N*-*tert*-butylpyridine-2-carbaldimine (Bu^t-pyca)

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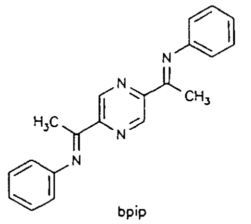
EPR and ENDOR spectra were obtained for the anion radical forms of Bu^t-pyca (*N*-*tert*-butylpyridine-2-carbaldimine) and of the new symmetrical bis-chelate ligand bpip [2,5-bis(1-phenyliminoethyl)pyrazine]. The spin distribution of both species reflects the mixed imine/azine composition of the 'α-diimine' chelate moieties. In the absence of coordinating electrophiles, bpip$^{\bullet -}$ displays ENDOR-detectable conformational equilibria, presumably between s-*cis*/s-*cis*, s-*cis*/s-*trans* and s-*trans*/s-*trans* isomers. Bpip reacts with MgR$_2$, R = 2-tolyl, in an electron-transfer fashion to form an organomagnesium radical complex.

Introduction

Among the most prominent members of the α-diimine ligand family for chelate coordination of metal centres are aromatic 2,2-bipyridine (bpy)[1,2] and non-aromatic 1,4-diorganosubstituted 1,4-diazabutadienes (R-dab).[2–4] As mixed aromatic/non-aromatic 'hybrid' forms, various pyridine-2-carbaldimines (R-pyca) have also been used for some time in stereochemical, photochemical or other studies.[3–7] Owing to their low symmetry, there have not yet been any satisfactory EPR investigations of R-pyca anion radicals although the ligands and their complexes have low lying π* orbitals.[3,4,6]

In this work we describe electron paramagnetic resonance/electron–nuclear double resonance (EPR/ENDOR) studies and the electron-transfer reactivity of a new 'doubled' pyca-type ligand, 2,5-bis(1-phenyliminoethyl)pyrazine (bpip),[8] which is able to bind two equivalent metal centres in a mixed azine/imine chelate fashion.[8,9] There is a continuing interest in new symmetrically bridging ligands[10,11] in the field of metal–metal interactions and 'metallosupramolecular' chemistry;[12,13] bis(pyridine-2-carbaldimine) ligands related to bpip are known.[14,15] In comparison with these previously synthesized ligands,[14,15] bpip contains a smaller π-system, which increases the extent of potential metal–metal interaction in dinuclear complexes.[10] We also report an EPR spectrum of bpip$^{\bullet -}$ in a metal-coordinated form after the electron-transfer reaction[16,17] of bpip with Mg(2-tolyl)$_2$, and a first EPR/ENDOR study of a pyridine-2-carbaldimine anion radical, *i.e.* of the *tert*-butyl derivative Bu^t-pyca$^{\bullet -}$



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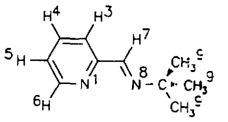


Bu^t-pyca

Results and discussion

2,5-Bis(1-phenyliminoethyl)pyrazine anion radical

Bpip, prepared from the reaction of 2,5-diacetylpyrazine[18] and aniline, can be reduced to an anion radical at −1.42 V *vs.* standard calomel electrode (SCE) in acetonitrile or tetrahydrofuran (THF)/0.1 mol dm^{-3} Bu$_4$NClO$_4$. The green solution displays an EPR spectrum (Fig. 1) which can be simulated assuming a small pyrazine proton coupling *a*(NCH), a larger methyl proton hyperfine splitting, and ^{14}N hyperfine coupling from both the pyrazine and imine nitrogen centres; within the EPR linewidth, both *a*(^{14}N)-values are equivalent (Table 1). This assignment is supported by the results from a Hückel MO calculation of π spin populations[19] which are depicted in Fig. 2 (perturbation parameter[19] h_N = 0.8 for all four nitrogen centres, methyl and *N*-phenyl substituents not included).

Fig. 1 shows, however, that the experimental spectrum is not perfectly reproduced by the computer simulation. While the typical[19,20] anisotropic EPR line-broadening of large radical ions with ^{14}N hyperfine splitting precluded a more detailed investigation at lower temperatures, the low radical concentrations necessary for high-resolution studies led to low signal-to-noise ratios (Fig. 1). For further analysis, we therefore resorted to ^{1}H-ENDOR spectroscopy which produced distinctly temperature-dependent spectra (Fig. 3, Table 1). Although ^{14}N-ENDOR signals of pyrazine radical ions with a_N-values of ~0.8 mT are usually well detectable, particularly at temperatures around 275 K,[21] the much smaller ^{14}N hyperfine coupling of ~0.16 mT for bpip anion radical results in poorly defined features in the low-frequency region (< 3 MHz) where possible artifact signals and baseline problems did not allow us to assign signals with the necessary confidence.

At 243 K and below, there are two pairs of ^{1}H-ENDOR signals visible for the two kinds of protons mentioned above; the hyperfine coupling constants are consistent with the assignment made in Table 1. No phenyl proton coupling is observed, which suggests a close-to-perpendicular arrangement between the phenyl rings and the heterocyclic imine functions; on the other hand, the large ^{14}N and CH$_3$ coupling constants are in agreement with a close-to-planar π-system involving the 10 π centres depicted in Fig. 2.

Additional lines appear at higher temperatures (Fig. 3), which are attributed to an interconversion of s-*cis*/s-*cis*, s-*cis*/s-*trans* and s-*trans*/s-*trans* rotamers **I**, **II** and **III** (Scheme 1) and which are a consequence of the partially restricted rotation around the pyrazine/imine bonds.

In fact, at least three different pairs of small (pyrazine CH) and large ^{1}H coupling constants (methyl) can be identified (Fig. 3, Table 1); hence the unsatisfactory computer

Table 1 EPR/ENDOR data[a] of bpip$^{\bullet-}$ and its bis(2-tolylmagnesium) complex

Radical	a(mT)			g
	^{1}H(CH$_3$)	^{1}H(NCH)	^{14}N	
bpip$^{\bullet-}$ (EPR, 293 K)[b]	0.186[c]	0.018[c]	0.159[c,d]	2.0033
bpip$^{\bullet-}$ (ENDOR, 243 K)[b]	0.193	0.020	n.d.	
(ENDOR, 273 K)[b]	0.193[c]	0.020[c]	n.d.	
	0.233[e]	0.069[e]		
		0.049[e]		
(ENDOR, 283 K)[b]	0.198[e]	0.020[e]	n.d.	
	0.184[e]			
	0.233[e]	0.069[e]		
	0.141[c]	0.049[c]		
(bpip$^{\bullet-}$)(RMg$^+$)$_2$[f]	0.12	$<$0.08	0.24[d]	2.0035

[a] Measurements in THF solution, no phenyl proton hyperfine coupling observed. [b] From electrolysis in THF/0.1 mol dm^{-3} Bu$_4$NClO$_4$. [c] Main component. [d] Equivalent hyperfine splitting of pyrazine and imine nitrogen centres. [e] Minor component, for assignments see text. [f] From electron-transfer reaction between bpip and R$_2$Mg (R = 2-tolyl) in THF.

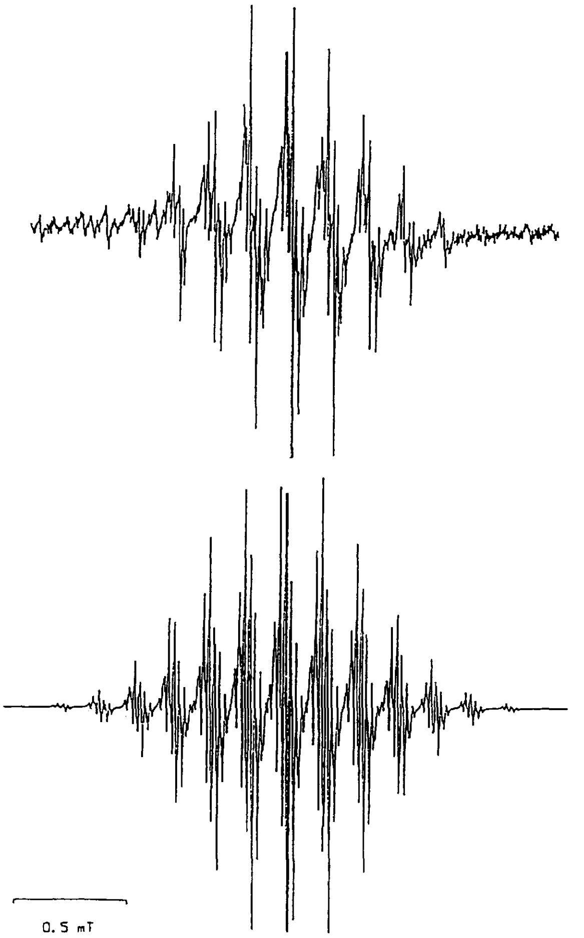


Fig. 1 EPR spectrum (top) of bpip$^{\bullet-}$, generated by electrolysis at a Pt cathode in THF/0.1 mol dm^{-3} Bu$_4$NClO$_4$ at 293 K, and simulation with the coupling constants of Table 1 (0.065 mT linewidth)

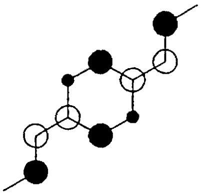


Fig. 2 Hückel MO representation of the singly occupied π MO of bpip anion radical (h_N = 0.8 for all nitrogen centres; methyl and phenyl substituents not included)

simulation of the EPR spectrum which accounts only for the main species.

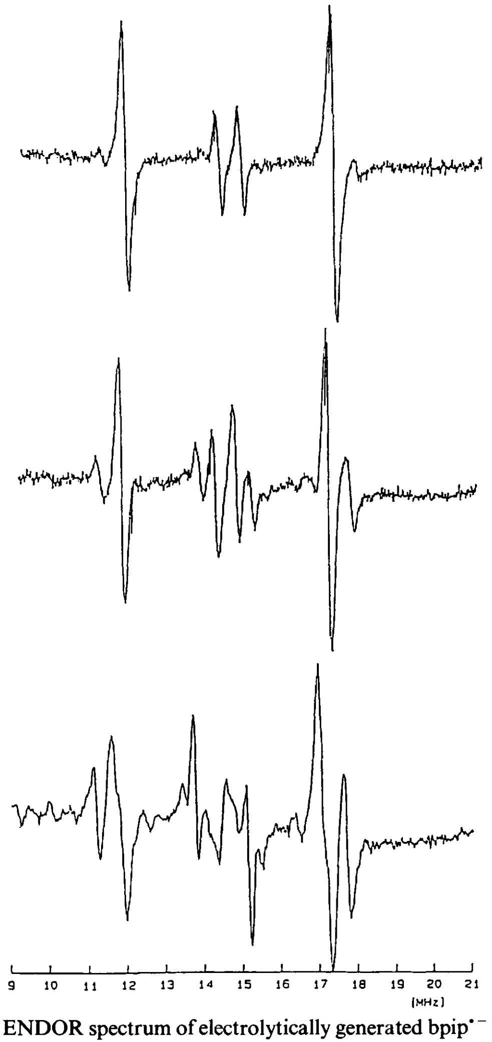
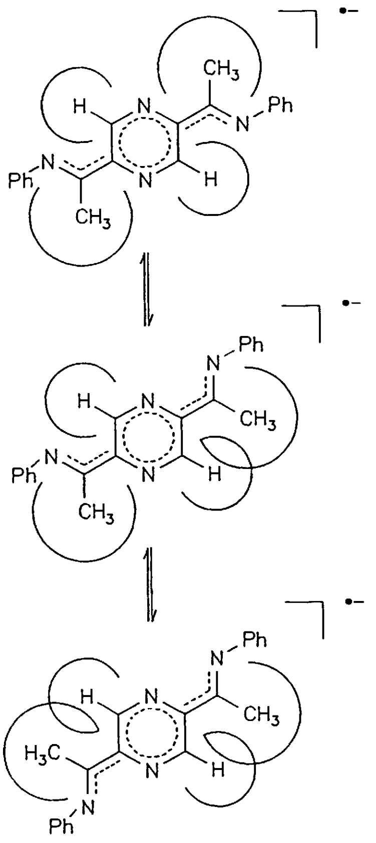


Fig. 3 ENDOR spectrum of electrolytically generated bpip$^{\bullet-}$ at 243 K (top), 273 K (middle) and 283 K (lower spectrum). 20 mW microwave power, 316 W rf power, 12.5 kHz modulation frequency.

On reduction, the single bonds between the aromatic heterocycle and the imine double bonds acquire some partial double-bond character with increased barrier to rotation.[19,22] At low temperatures, there is only one rotamer observable by ENDOR spectroscopy (0.193 and 0.020 mT hyperfine splitting) which we tentatively identify as species **I** because of the least interference between (pyrazine-C)H and (imino)CH$_3$ groups (Scheme 1). At temperatures above 243 K, the fraction of high-energy rotamers **II** and eventually **III** should increase, the exact assignment of hyperfine coupling being somewhat uncertain



Scheme 1 Rotamers of bpip anion radical with coplanar 10-centre π-systems

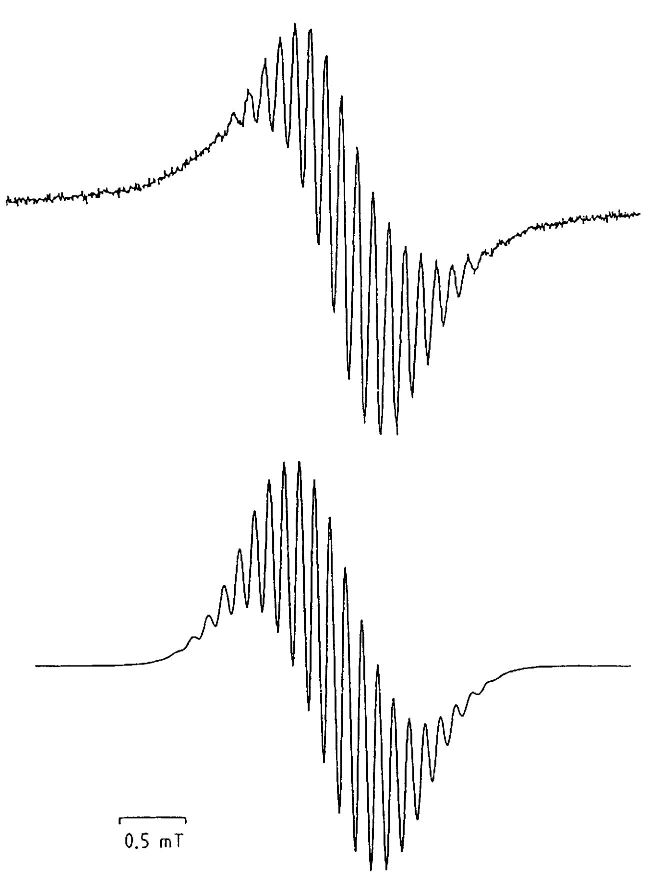


Fig. 4 EPR spectrum (top) of the paramagnetic reaction product of bpip with $Mg(2\text{-tolyl})_2$ in 1,2-dichloroethane at 293 K; lower spectrum: computer simulation with the data from Table 1 and 0.098 mT linewidth

due to the low symmetry of the presumed intermediate rotamer **II**. Tentatively, we assign the ^1H coupling constants of 0.233, ≈0.193, 0.069 and 0.020 mT to rotamer **II** and values of 0.141 and 0.049 mT to rotamer **III**. The larger (pyrazine-C)H coupling constants in comparison with that of conformer **I** can be attributed to interference with the methyl group as illustrated in Scheme 1.

In order to provide additional evidence for this assignment we obtained a dinuclear bis(chelate) complex of $bpip^{\bullet -}$ which then has to exist in the sterically less favourable conformation **III**. The driving force for this high-energy arrangement is provided by formation of the coordinative bonds. The bis(chelate) complex chosen was obtained *via* a single-electron-transfer reaction with bis(2-tolyl)magnesium. It is well known that π-electron-accepting α-diimine ligands such as bpy, 1,10-phenanthroline[16] or R-dab[16,17] react with diorgano-magnesium or -zinc compounds to form radical complexes under loss of one alkyl radical (chelate-assisted inner-sphere electron transfer) [eqn. (1)].[16,17] For the dinuclear bpip system we

$$\text{bpip} + 3R_2Mg \longrightarrow (\text{bpip}^{\bullet -})(^+MgR)_2 + R_3Mg^- + R^\bullet \quad (1)$$

assume two-fold organomagnesium coordination with only one electron-transfer step; triorganomagnesiate anions are known species.[23]

Unfortunately, the bis(organomagnesium) complex could not be studied by ENDOR due to difficulties in saturating EPR signals; the less well resolved EPR spectrum (Fig. 4) may be simulated by assuming the typically[16,17,24] increased ^{14}N hyperfine splitting and a methyl proton coupling of 0.12 mT (Table 1) which would support our assignments for the conformer **III**.

N-tert-Butylpyridine-2-carbaldimine anion radical

Although Bu^t-pyca, like Bu^t-dab,[17] is reduced only irreversibly at ~ −1.9 V *vs.* $Fc^{+/0}$ in cyclic voltammetry (MeCN/0.1 mol dm^{-3} Bu_4NClO_4; 295 K), it could be converted into a relatively persistent anion radical with potassium in THF at 200 K. The achievable concentration at high-resolution conditions was fairly low; nevertheless, we could obtain EPR and ENDOR spectra. Although we have no direct evidence from EPR or ENDOR spectroscopy, we assume the formation of an ion pair between K^+ and $Bu^t\text{-pyca}^{\bullet -}$ in its chelating conformation;[3] without such co-ordination the pyca systems probably prefer the *trans* conformation with respect to the imine moieties.

Owing to the large number of coupling parameters (2 × ^{14}N, 6 × ^1H coupling constants, Table 2), we had to resort to ENDOR spectroscopy in order to obtain at least the $a(^1H)$-values. Fig. 5 shows that there are indeed six such signal pairs, of which we attribute the smallest value to the *tert*-butyl protons and the largest ^1H coupling to the proton at the imine group. The remaining four $a(^1H)$-values are tentatively assigned to the 2-pyridine group in the typical[24] order $a(H^5) > a(H^3) > a(H^4) > a(H^6)$. This ordering is not only supported by a Hückel MO calculation but also by comparison with the related symmetrical species $bpy^{\bullet -}$ and $Bu^t\text{-dab}^{\bullet -}$ (Table 2).[24,25] The ^{14}N coupling constants could not be determined accurately from the EPR spectrum; using the spectral width and the ^1H-ENDOR information, we arrived at the reasonable estimates listed in Table 2.

Summarizing, the R-pyca anion radical exhibits a spin distribution which resembles that of both $bpy^{\bullet -}$ and $R\text{-dab}^{\bullet -}$. Although pyca is thus a true 'hybrid' system, the better π-acceptor capability of the imine function in comparison with that of 2-pyridyl[2] causes a higher spin population at the non-

Table 2 EPR/ENDOR data[a] of α-diimine anion radicals

		K$^+$/(Bu^t-pyca$^{\bullet-}$)		
a	K$^+$/(bpy$^{\bullet-}$)[b]	Exp.[c]	Calc.[d]	K$^+$/(Bu^{t}dab$^{\bullet-}$)[e]
N^1	0.261	0.29	0.313	
H^3	0.122	0.224	0.165	
H^4	0.106	0.068	0.085	
H^5	0.470	0.369	0.286	
H^6	0.057	0.046	0.003	
H^7 (imine)		0.488	0.575	0.43
N^8 (imine)		0.55	0.649	0.56
H^9 (Bu^t)		0.013		0.015
g	2.0030	2.0032		2.0035[e]

[a] Coupling constants a in mT; for numbering see structural formulae. [b] In THF solution, from ref. 22. [c] In THF solution, ^{1}H-values from ENDOR spectroscopy at 200 K, ^{14}N-values from EPR spectrum at 293 K. [d] From Hückel MO calculations ($h_N = 0.5$, all $k = 1$) and application of the McConnell equation $a = Q \times \rho = Q \times c^2$, $Q = 2.3$ mT (ref. 19). [e] In THF solution, from ref. 23.

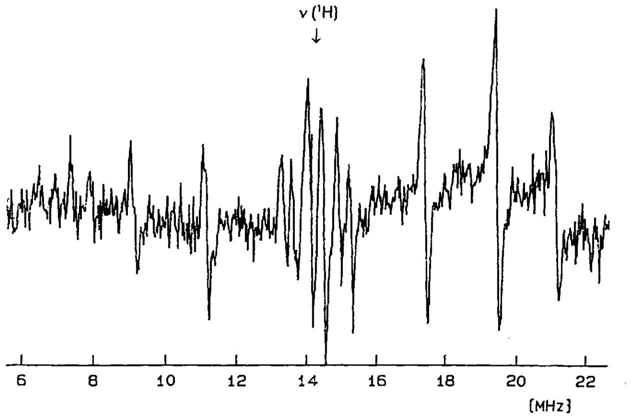


Fig. 5 ENDOR spectrum of Bu^t-pyca$^{\bullet-}$ in THF at 200 K, generated by reduction with potassium

aromatic arm of this unsymmetrical α-diimine. In bpip, on the other hand, the stronger π-acceptor character of pyrazine leads to an even distribution of spin between the imine and heterocyclic nitrogen centres, rendering this molecule a promising bifunctional ligand system for co-ordination chemistry.[8-13]

Experimental

EPR and ENDOR spectra were recorded in the X band on a Bruker System ESP 300 equipped with an ENI A500 RF amplifier, a Bruker ER033 field-frequency lock, a Bruker ER035M gaussmeter and a HP 5350B microwave counter. IR spectra were obtained using Perkin-Elmer 684 and 283 instruments; NMR spectra were recorded with a Bruker AC250 spectrometer. Cyclic voltammetry was carried out using a three-electrode configuration (glassy carbon electrode, Pt counter electrode Ag/AgCl reference) and a PAR 273 potentiostat and function generator.

Bu^t-pyca[3-6] was obtained following standard literature procedures. All reactions involving the generation of radicals were carried out in dried solvents under argon or high vacuum.

2,5-Bis(1-phenyliminoethyl)pyrazine (bpip)

A mixture containing 2,5-diacetylpyridine (264 mg, 1.61 mmol),[18,26] freshly distilled aniline (310 mg, 3.33 mmol), molecular sieve 4 Å (3 g) and acidic alumina (Woelm A-super-I, 20 mg) were heated in hexane (70 cm^3) under reflux for 24 h. The hot solution was filtered, condensed to 30 cm^3, and the pale-yellow crystals were collected. Washing with hexane, recrystallization from diethyl ether, and drying under vacuum yielded a pale-yellow product (201 mg, 40%), mp 165 °C (Found: C, 76.0; H, 5.8; N, 17.6. Calc. for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82%); ν_{max}/cm^{-1}(KBr) 1640 (C=N); δ_H(250 MHz; [$^2H_6$]acetone 2.36 (6 H, s, Me), 6.19 (4 H, dd, J 1.1 and 8.4, *o*-H), 7.15 (2 H, t, J 1.1, 7.5, *p*-H), 7.42 (4 H, m, *m*-H) and 9.43 (2 H, s, pyrazine CH).

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References

1 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.
2 H. tom Dieck, K. D. Franz and F. Hohmann, *Chem. Ber.*, 1975, **108**, 163; R. W. Balk, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta*, 1978, **28**, 133.
3 G. van Koten and K. Vrieze, *Rec. Trav. Chim. Pays-Bas*, 1981, **100**, 129; *Adv. Organomet. Chem.*, 1982, **21**, 152; K. Vrieze and G. van Koten, *Inorg. Chim. Acta*, 1985, **100**, 79.
4 G. van Koten, J. T. B. H. Jastrzebski and K. Vrieze, *J. Organomet. Chem.*, 1983, **250**, 49.
5 H. Brunner and W. A. Herrmann, *Chem. Ber.*, 1972, **105**, 770; *J. Organomet. Chem.*, 1973, **57**, 183.
6 D. J. Stufkens, *Coord. Chem. Rev.*, 1990, **104**, 39; M. Maruyama, H. Matsuzawa and Y. Kaizu, *Inorg. Chem.*, 1995, **34**, 3232.
7 D. P. Drolet, L. Chan and A. J. Lees, *Organometallics*, 1988, **7**, 2502.
8 W. Kaim, S. Ernst and V. Kasack, *J. Am. Chem. Soc.*, 1990, **112**, 173.
9 V. Kasack, S. Hasenzahl, R. Reinhardt and W. Kaim, unpublished results.
10 W. Kaim and S. Kohlmann, *Inorg. Chem.*, 1987, **26**, 68; 1986, **25**, 3442.
11 W. Kaim and J. Fees, *Z. Naturforsch., Teil B*, 1995, **50**, 123.
12 E. Constable, *Chem. Ind. (London)*, 1994, 56.
13 S. Campagna, A. Giannetto, S. Serroni, G. Denti, S. Trusso, F. Mallamace and N. Micali, *J. Am. Chem. Soc.*, 1995, **117**, 1754.
14 M. B. Lawson and E. B. Fleischer, *J. Coord. Chem.*, 1972, **2**, 79.
15 H. Haga and K. Koizumi, *Inorg. Chim. Acta*, 1985, **104**, 47; S. C. F. Maloney, M. R. McDevitt and F. L. Urbach, *Inorg. Chim. Acta*, 1989, **164**, 123.
16 W. Kaim, *J. Am. Chem. Soc.*, 1982, **104**, 3833 and 7385; *Top. Curr. Chem.*, 1994, **169**, 231.
17 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, 1991, **113**, 5606; S. Hasenzahl, W. Kaim and T. Stahl, *Inorg. Chim. Acta*, 1994, **225**, 23.
18 T. Caronna, G. Fronza, F. Minisci and O. Porta, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2035.
19 F. Gerson, *High Resolution ESR Spectroscopy*, Wiley, London, 1970.
20 C. S. Johnson and R. Chang, *J. Chem. Phys.*, 1965, **43**, 3183.

21 W. Lubitz and T. Nyrönen, *J. Magn. Reson.*, 1980, **41**, 17; W. Kaim and W. Lubitz, *Angew. Chem.*, 1983, **95**, 915; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 892; *Angew. Chem. Suppl.*, 1983, 1209.

22 K. Scheffler and H. B. Stegmann, *Elektronenspinresonanz*, Springer, Berlin, 1970.

23 A. D. Pajerski, M. Parvez and H. G. Richey, Jr., *J. Am. Chem. Soc.*, 1988, **110**, 2660.

24 W. Kaim, *Chem. Ber.*, 1981, **114**, 3789.

25 P. Clopath and A. von Zelewsky, *Helv. Chim. Acta*, 1972, **55**, 52.

26 C. Bessenbacher, S. Ernst, S. Kohlmann, W. Kaim, V. Kasack, E. Roth and J. Jordanov, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 4075.

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