iron–phosphorus bonds, thus favoring the molecular conformation which is associated with the high-spin state. The low-spin geometry with "normal" iron–phosphorus bond lengths is favored, on the contrary, by electronic factors.[1] The existence of such opposing factors may account for the fact that the two molecular conformations associated with the different spin states have comparable energies, so that either spin state may become more stable than the other one in the appropriate temperature range.

The large differences in magnetic behavior between the solvated and the unsolvated compounds, however, are not rationalized by the above factors. In particular, the sharp change in μ_{eff} exhibited by the solvated compounds should be attributed to cooperative factors.[18] Since these are sensitive to lattice effects, the following features of the structures of these compounds probably play an important role in determining the magnetic properties: (a) the complex molecules are more regularly packed in the solvated than in the unsolvated compounds (Figure 4; see also footnote *a* to Table II and ref 25 in the companion paper[1]); (b) the shortest contacts in the lattice are established between the solvate molecules and those of the complex. Both factors should favor the propagation through the lattice of the local deformations associated with the change of spin state on a metal center, thus favoring the growth of domains of the alternative spin isomer.[19]

Acknowledgment. Thanks are expressed to Mr. D. Masi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. **1**, 58031-48-4; **2**, 74255-93-9; FeBr$_2$(dppen)$_2$, 58031-47-3; [FeI(dppen)$_2$]BPh$_4$, 78217-10-4.

Supplementary Material Available: Listings of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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[18] Sorai, M.; Ensling, J.; Gütlich, P. *Chem. Phys.* **1976**, *18*, 199; König, E.; Ritter, G.; Irler, W.; Goodwin, H. A. *J. Am. Chem. Soc.* **1980**, *102*, 4681.

[19] A reviewer has suggested that the transition to the low-spin state may occur through a mechanism of the following sort. A small twisting of the FeP$_2$ planes, possibly induced by a phase change in the solid, would cause a new symmetry at the metal center, leading to a new electronic ground state which would in turn bring on the Fe–P bond distance changes. While we consider this to be a likely possibility (in particular, one of the low-lying triplet states, which are more sensitive to geometric distortions than the singlet or the quintet states as shown by calculations on model systems, may become the ground state), we also wish to stress that such an hypothesis is not in contrast with the conclusions draw at the end of this paper. It just goes in more depth into the mechanism of the spin transition. On the other hand, it finds no direct support by the material which is presented here.

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Low-Spin and High-Spin Six-Coordinate Iron(II) Complexes with a P$_4$Cl$_2$ Donor Set. X-ray Structures of FeCl$_2$[(Ph$_2$PCH$_2$CH$_2$)$_2$PPh]$_2$·2(CH$_3$)$_2$CO and of FeCl$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$

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Structural investigations by X-ray diffraction methods have been carried out on two iron(II) chloride complexes formed with the poly(tertiary phosphines) bis[2-(diphenylphosphino)ethyl]phenylphosphine (ppp) and 1,2-bis(dimethylphosphino)ethane (dme). The complexes, with formulas FeCl$_2$(ppp)$_2$·2(CH$_3$)$_2$CO (**1**) and FeCl$_2$(dme)$_2$ (**2**), are, respectively, in the quintet and in the singlet ground state. Crystal data: (**1**) space group $P\bar{1}$, a = 15.786 (12) Å, b = 13.717 (10) Å, c = 10.239 (10) Å, α = 125.6 (1)°, β = 95.1 (1)°, γ = 103.2 (1)°, Z = 1; (**2**) space group $P2_1/n$, a = 9.554 (3) Å, b = 12.012 (5) Å, c = 9.123 (3) Å, β = 92.05 (3)°, Z = 2. Both complexes have a distorted octahedral geometry with the P$_4$Cl$_2$ donor set, the ppp ligand acting as bidentate in **1**. The symmetry-independent Fe–Cl distance is practically identical in the two compounds (2.354 (3) Å in **1** and 2.352 (1) Å in **2**), whereas the Fe–P distances differ dramatically, being in the range 2.66–2.71 Å for the high-spin complex **1** and in the range 2.23–2.24 Å for the low-spin complex **2**. Such large differences in the Fe–P bond lengths account for the different ground-state spin multiplicities of the compounds. Correlations between structural, spectral, and magnetic data for iron(II) complexes with the above donor set and geometry have been performed.

Introduction

It is well-known that the octahedral iron(II) complexes are either in a quintet or in a singlet ground state, depending on the nature of the donor set. Among the pseudooctahedral complexes, those with the P$_4$Cl$_2$ donor set so far reported are low-spin[1] with the exception of the complex FeCl$_2$(dppen)$_2$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene), which exhibits a singlet $\rightleftharpoons$ quintet temperature-dependent equilibrium.[2] To our knowledge no structure of iron(II) complexes with the P$_4$Cl$_2$ donor set has been reported so far.

In the course of investigations on the coordinating behavior of poly(tertiary phosphine) ligands toward first-row transition-metal atoms, the ligand bis[2-(diphenylphosphino)ethyl]phenylphosphine, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)CH$_2$CH$_2$P(C$_6$H$_5$)$_2$, ppp, has generally been found to act as tridentate, yielding low-spin complexes.[3] However, a high-spin compound with formula FeCl$_2$(ppp)$_2$·2(CH$_3$)$_2$CO, whose magnetic and spectral properties could not be rationalized in terms of the possible donor sets and coordination geometries was isolated. Therefore, a structural investigation on this compound was undertaken by X-ray diffraction methods. This study revealed

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[1] Levason, W.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 173.

[2] Levason, W.; McAuliffe, C. A; Mahfooz Khan, M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1975**, 1778.

[3] King, R. B.; Kapoor, R. N.; Saran, M. S.; Kapoor, P. N. *Inorg. Chem.* **1971**, *10*, 1851. Di Vaira, M.; Midollini, S.; Sacconi, L. *Ibid.* **1978**, *17*, 816. Di Vaira, M.; Midollini, S.; Sacconi, L. *Ibid.* **1980**, *18*, 3466.

0020-1669/81/1320-3430$01.25/0

that the compound possesses a distorted trans-octahedral coordination geometry with the P_4Cl_2 donor set, one phosphorus atom of each ppp ligand being not coordinated to the metal. The four Fe–P bonds are exceptionally long: this may account for the quintet ground state of the complex.

In order to achieve a deeper understanding of the connection between magnetic properties and structure for iron(II) complexes of this type, we have also determined the structures of the low-spin complexes $FeCl_2(dme)_2$ (dme = 1,2-bis(dimethylphosphino)ethane, $(CH_3)_2PCH_2CH_2P(CH_3)_2$) and $FeCl_2(dee)_2$ (dee = 1,2-bis(diethylphosphino)ethane, $(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$), which were attributed the same P_4Cl_2 donor set.[4] On the basis of the structural data obtained for the above compounds and for the similar iron(II) complexes exhibiting a temperature-dependent singlet–quintet transition, which are described in the accompanying paper,[5] it has been possible to derive some correlations between electronic and structural properties for compounds of this type.

Additional iron(II) complexes with formulas $[FeX(ppp)_2]BPh_4$ (X = Br, I) and $Fe(NCS)_2(ppp)_2$ have been synthesized and characterized. Preliminary results of the structural analysis of the compound $FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$ have already been reported.[6]

Experimental Section

All solvents were of reagent quality. The ligand ppp was purchased from Strem Chemicals Inc., Danvers, Mass., and was used without further purification. All reactions and manipulations were carried out in a nitrogen atmosphere.

Synthesis of the Compounds. The compounds $FeCl_2(dme)_2$ and $FeCl_2(dee)_2$ were prepared by literature methods.[4]

$FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$. A solution of anhydrous $FeCl_2$ (130 mg, 1 mmol) in absolute ethanol (15 mL) was added to a solution of the ligand (1.08 g, 2 mmol) in acetone (30 mL). The resulting solution was concentrated by distillation until crystallization was initiated. The pale green crystals which precipitated were filtered and washed with ethanol and then petroleum ether before being dried in a current of nitrogen. Anal. Calcd for $C_{68}H_{66}Cl_2FeP_6 \cdot C_6H_{12}O_2$: C, 67.74; H, 5.99; Fe, 4.26; Cl, 5.40. Found: C, 67.64; H, 6.00; Fe, 4.25; Cl, 5.52. $\mu_{eff}(293\ K) = 5.27\ \mu_B$.

$[FeX(ppp)_2]BPh_4$ (X = Br, I). A solution of anhydrous $FeBr_2$ (216 mg, 1 mmol) or FeI_2 (310 mg, 1 mmol) in ethanol (15 mL) was added to a solution of the ligand (1.08 g, 2 mmol) in acetone (30 mL). After 1 mmol of sodium tetraphenylborate dissolved in 10 mL of ethanol had been added to this solution, the solvent was removed by distillation until crystallization was initiated. The crystals (yellow-orange, X = Br; orange, X = I) were filtered off, washed with ethanol and petroleum ether and dried in a current of nitrogen. Anal. Calcd for $C_{92}H_{86}BBrFeP_6$: C, 72.50; H, 5.69; Fe, 3.66. Found: C, 71.80; H, 5.82; Fe, 3.58. $\mu_{eff}(293\ K) = 3.43\ \mu_B$. Calcd for $C_{92}H_{86}BFeIP_6$: C, 70.33; H, 5.51; Fe, 3.55; P, 11.82. Found: C, 68.92; H, 5.73; Fe, 3.50; P, 12.16. $\mu_{eff}(293\ K) = 3.60\ \mu_B$.

$Fe(NCS)_2(PPP)_2$. Potassium thiocyanate (195 mg, 2 mmol) dissolved in absolute ethanol (15 mL) was added to a solution of $FeCl_2$ (130 mg, 1 mmol) in ethanol (10 mL). The resulting filtered solution was added to a solution of the ligand ppp (1.08 g, 2 mmol) in acetone (30 mL). After concentration by distillation, pale pink crystal precipitated which were filtered off, washed with ethanol, and dried in a current of nitrogen. Anal. Calcd for $C_{70}H_{66}FeN_2P_6S_2$: C, 67.74; H, 5.36; Fe, 4.50; N, 2.25. Found: C, 66.30; H, 5.57; Fe, 4.35; N, 2.37. $\mu_{eff}(293\ K) = 0.99\ \mu_B$.

Physical Measurements. The physical measurements were executed by previously described methods.[7] The electronic spectral data are reported in Table I.

Collection and Reduction of X-ray Data. Diffraction data for the compounds $FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$ (**1**) and $FeCl_2(dme)_2$ (**2**) were collected at 22 ± 2 °C on a Philips PW 1100 automated diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Details on crystal data, intensity collection, and refinement are reported in Table II. Lattice constants were determined by least-squares refinement of the angular positions of 24 reflections for both compounds. The crystal of compound **2** used for data collection was coated with paraffin in order to prevent oxidation by the air. The intensities of three standard reflections measured every 90 min showed small oscillations (≤3%) about their average values but no systematic trend during either data collection. Data sets were processed with use of a 0.04 value for p in the calculation of the $\sigma(I)$'s.[8] The transmission factors approximately ranged 0.87–0.97 (**1**) and 0.63–0.72 (**2**). Corrections for absorption were attempted but failed to give significant improvements in R, probably due to the irregular shapes of the crystals and to the fact that the crystal of **2** was coated with paraffin. The principal computer programs used for the crystallographic calculations are listed in ref 9.

Table I. Electronic Spectra

compd		absorption max,[a] cm^{-1} (ϵ_M for soln)
$FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$	a	8300, 11 800
	b	7200 (80)
$[FeBr(ppp)_2]BPh_4$[b]	a	6500, 8100 sh, 12 200, 19 700 sh, 23 500
	b	6400, 12 000, 15 600 sh, 23 800
$[FeI(ppp)_2]BPh_4$[b]	a	6200, 9500, 12 000, 13 300 sh, 20 400 sh, 23 800
	b	6100, 9500, 11 800, 13 700
$Fe(NCS)_2(ppp)_2$	a	18 500, 22 200
	b	18 800 (200), 22 700 (280)
$FeCl_2(dme)_2$[b]	a	15 200, 27 000 sh
	b	15 100, 26 900
$FeCl_2(dee)_2$[b]	a	14 700, 24 700
	b	14 600, 24 600

[a] Key: a, solid; b, 1,2-dichloroethane solution. [b] The compound decomposes in solution. Bands below 20 000 cm^{-1} have ϵ_M values, estimated before substantial decomposition occurred, in the range 20–80 L mol^{-1} cm^{-1}.

Table II. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$ (**1**) and $FeCl_2(dme)_2$ (**2**)

	1	**2**
formula	$C_{74}H_{78}Cl_2Fe_1O_2P_6$	$C_{12}H_{32}Cl_2Fe_1P_4$
fw	1312.04	427.04
space group	$P\bar{1}$	$P2_1/n$
a, Å	15.786 (12)	9.554 (3)
b, Å	13.717 (10)	12.012 (5)
c, Å	10.239 (10)	9.123 (3)
α, deg	125.6 (1)	90
β, deg	95.1 (1)	92.05 (3)
γ, deg	103.2 (1)	90
V, $Å^3$	1685.1	1046.3
Z	1	2
density, g cm^{-3}	1.293 (calcd), 1.27 (obsd)	1.355 (calcd), 1.33 (obsd)
cryst size,[a] mm	0.2 × 0.2 × 0.5	0.3 × 0.3 × 0.5
μ(Mo Kα), cm^{-1}	4.86	12.7
scan speed, deg/min	4.8	4.8
scan range, deg	$(1.2 + 0.3 \tan\theta)°$	$(1.2 + 0.3 \tan\theta)°$
bkgd	$t_{b1} = t_{b2} = {}^1/_2 t_s$[b]	$t_{b1} = t_{b2} = {}^1/_2 t_s$[b]
2θ limits, deg	4–44	4–66
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	2616	2388
no. of variables	186	102
R	0.082	0.055
R_w	0.090	0.057

[a] Irregularly shaped crystals. [b] t_{b1} and t_{b2} = background count times; t_s = total scan time.

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(4) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507.

(5) Cecconi, F.; Di Vaira, M.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.*, companion paper in this issue.

(6) Di Vaira, M.; Midollini, S.; Sacconi, L. *Cryst. Struct. Commun.* **1980**, *9*, 407.

(7) Sacconi, L.; Morassi, R. *J. Chem. Soc. A* **1968**, 2997. Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* **1968**, *7*, 1417.

(8) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

Table III. Atomic Parameters for the Structure of $FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO^{a,b}$

atom	x/a	y/b	z/c	U, Å^2	atom	x/a	y/b	z/c	U, Å^2
Fe	0.5000	0.5000	0.5000		C32	0.518 (1)	0.297 (1)	0.692 (1)	0.064 (3)
Cl	0.5577 (2)	0.4420 (3)	0.2699 (3)		C33	0.516 (1)	0.256 (1)	0.793 (1)	0.068 (3)
P1	0.3376 (2)	0.3582 (3)	0.2633 (3)		C34	0.462 (1)	0.138 (1)	0.727 (2)	0.077 (4)
P2	0.4787 (2)	0.2653 (3)	0.3985 (3)		C35	0.411 (1)	0.057 (1)	0.567 (2)	0.084 (4)
P3	0.7366 (2)	0.1819 (3)	0.3290 (4)		C36	0.413 (1)	0.092 (1)	0.465 (2)	0.070 (4)
C1	0.354 (1)	0.203 (1)	0.123 (1)	0.052 (3)	C41	0.761 (1)	0.190 (1)	0.163 (1)	0.047 (3)
C2	0.373 (1)	0.157 (1)	0.227 (1)	0.055 (3)	C42	0.819 (1)	0.124 (1)	0.079 (1)	0.057 (3)
C3	0.560 (1)	0.195 (1)	0.294 (1)	0.052 (3)	C43	0.838 (1)	0.116 (1)	−0.056 (2)	0.079 (4)
C4	0.658 (1)	0.270 (1)	0.405 (1)	0.054 (3)	C44	0.799 (1)	0.173 (1)	−0.104 (2)	0.076 (4)
C11	0.305 (1)	0.391 (1)	0.120 (1)	0.047 (3)	C45	0.742 (1)	0.233 (1)	−0.033 (2)	0.074 (4)
C12	0.244 (1)	0.451 (1)	0.139 (1)	0.059 (3)	C46	0.724 (1)	0.245 (1)	0.108 (1)	0.064 (3)
C13	0.226 (1)	0.486 (1)	0.038 (2)	0.072 (4)	C51	0.840 (1)	0.302 (1)	0.500 (1)	0.056 (3)
C14	0.271 (1)	0.458 (1)	−0.082 (2)	0.074 (4)	C52	0.886 (1)	0.417 (1)	0.534 (1)	0.062 (3)
C15	0.331 (1)	0.400 (1)	−0.103 (1)	0.069 (3)	C53	0.964 (1)	0.506 (1)	0.671 (2)	0.080 (4)
C16	0.350 (1)	0.363 (1)	−0.004 (1)	0.059 (3)	C54	0.995 (1)	0.479 (1)	0.771 (2)	0.091 (4)
C21	0.228 (1)	0.306 (1)	0.292 (1)	0.044 (3)	C55	0.951 (1)	0.369 (2)	0.741 (2)	0.098 (5)
C22	0.151 (1)	0.221 (1)	0.162 (1)	0.065 (3)	C56	0.873 (1)	0.278 (1)	0.607 (2)	0.081 (4)
C23	0.071 (1)	0.178 (1)	0.183 (2)	0.082 (4)	C61	0.040 (2)	0.155 (3)	0.693 (5)	0.347 (9)
C24	0.066 (1)	0.227 (1)	0.343 (2)	0.087 (4)	C62	0.177 (2)	0.089 (3)	0.566 (5)	0.347 (9)
C25	0.139 (1)	0.317 (1)	0.475 (2)	0.094 (5)	C63	0.108 (2)	0.083 (3)	0.663 (5)	0.347 (9)
C26	0.222 (1)	0.359 (1)	0.457 (1)	0.068 (3)	O	0.108 (2)	0.021 (3)	0.715 (5)	0.347 (9)
C31	0.469 (1)	0.213 (1)	0.528 (1)	0.049 (3)					

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.0512 (14)	0.0393 (13)	0.0342 (12)	0.0098 (10)	0.0147 (10)	0.0250 (11)
Cl	0.0600 (18)	0.0528 (17)	0.0396 (15)	0.0151 (14)	0.0207 (13)	0.0318 (14)
P1	0.0454 (17)	0.0423 (16)	0.0374 (15)	0.0097 (13)	0.0099 (13)	0.0268 (14)
P2	0.0469 (17)	0.0404 (16)	0.0418 (16)	0.0111 (13)	0.0124 (13)	0.0286 (14)
P3	0.0580 (20)	0.0581 (20)	0.0610 (20)	0.0205 (16)	0.0254 (16)	0.0451 (17)

[a] Standard deviations on the last significant digits are in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2 \theta)/\lambda^2]$ and anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [b] Atoms C61–O belong to the acetone molecule.

Table IV. Atomic Parameters for the Structure of $FeCl_2(dme)_2{}^{a,b}$

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0	0	0	0.0347 (3)	0.0309 (3)	0.0322 (3)	0.0010 (2)	−0.0028 (2)	0.0024 (2)
Cl	−0.0641 (1)	0.1402 (1)	−0.1695 (1)	0.0626 (5)	0.0495 (5)	0.0554 (5)	0.0079 (4)	−0.0075 (4)	0.0181 (4)
P1	0.1341 (1)	0.1245 (1)	0.1222 (1)	0.0528 (5)	0.0462 (5)	0.0519 (5)	−0.0076 (4)	−0.0127 (4)	−0.0039 (4)
P2	0.1880 (1)	−0.0323 (1)	−0.1316 (1)	0.0559 (6)	0.0635 (6)	0.0568 (6)	0.0116 (5)	0.0165 (5)	0.0081 (5)
C1	0.296 (1)	0.142 (1)	0.034 (1)	0.080 (4)	0.0304 (12)	0.262 (11)	−0.100 (6)	0.070 (5)	−0.197 (10)
C2	0.323 (1)	0.075 (1)	−0.077 (1)	0.098 (4)	0.136 (6)	0.202 (8)	−0.066 (4)	0.078 (5)	−0.062 (6)
C3	0.084 (1)	0.268 (1)	0.133 (1)	0.115 (5)	0.060 (3)	0.201 (8)	−0.004 (3)	−0.056 (5)	−0.043 (4)
C4	0.197 (1)	0.099 (1)	0.304 (1)	0.311 (12)	0.110 (5)	0.108 (5)	−0.095 (7)	−0.128 (7)	0.024 (4)
C5	0.181 (1)	−0.015 (1)	−0.328 (1)	0.160 (7)	0.205 (9)	0.071 (4)	0.091 (6)	0.056 (4)	0.038 (5)
C6	0.288 (1)	−0.160 (1)	−0.106 (1)	0.063 (3)	0.079 (3)	0.105 (4)	0.029 (2)	0.015 (3)	0.002 (3)

[a] Standard deviations on the last significant digits are in parentheses. Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [b] Hydrogen atom parameters are listed in Table V.[14]

Solution and Refinement of the Structures. The structure of compound **1** was solved by standard heavy-atom procedures. The positions of all nonhydrogen atoms were determined from Fourier syntheses. The iron atom resides on an inversion center so that the molecule possesses $\bar{1}$ crystallographic symmetry. In the full-matrix least-squares refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(F_o)$. The scattering factors of the neutral atoms were taken from ref 10, and anomalous dispersion terms for Fe, Cl, and P were included in F_c.[11] The acetone molecule was refined as a rigid group with idealized geometry (C–C = 1.55 Å, C–O = 1.24 Å, C–C–C = C–C–O = 120°) with application of an overall temperature factor. Hydrogen atoms of the ppp ligand were introduced in calculated position (C–H = 0.95 Å) by the procedure described previously,[12] and their fixed contribution was added to F_c. In the final set of cycles anisotropic thermal parameters were used for the Fe, Cl, and P atoms. The final values of the discrepancy indices, defined by $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ are shown in Table II. The final difference Fourier map showed a peak with height 0.8 e Å^{-3} in the proximity of the metal atom position.

The structure of compound **2** was solved by procedures analogous to those followed for **1**. Also the molecule of compound **2** possesses $\bar{1}$ crystallographic symmetry. After the first stages of the refinement the temperature factors of the carbon atoms had reached very large values. The aspect of difference maps indicated that this fact was to be ascribed to large thermal vibrations, rather than to disordering in the structure. Consequently, the refinement was continued with application of anisotropic temperature factors to all nonhydrogen atoms. The methylenic hydrogens were introduced in calculated positions (C–H = 0.95 Å) whereas the methyl hydrogen atoms were treated as part of rigid CH_3 groups with idealized geometry (C–H = 0.95 Å, H–C–H = 109.5°). Overall temperature factors were separately assigned to the CH_2 and to the CH_3 hydrogen atoms, and their values were refined. The final R and R_w values are listed in Table II. A difference Fourier calculated at the end of the refinement

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(9) (a) Stewart, J. M.; Kundall, F. A.; Baldwin, J. C. "x-Ray 72 System of Programs", Technical Report TR 192; University of Maryland: College Park, Md., 1972. (b) Sheldrick, G. "SHELX 76 System of Computing Programs", University of Cambridge: Cambridge, England, 1976. (c) Johnson, C. K. "ORTEP", Report ORNL 3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965. These programs have been adapted to a CII 10070 and to a SEL 32/70 computer by Dr. C. Mealli.

(10) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 71 ff.

(11) Reference 10, p 148 ff.

(12) Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 1518.

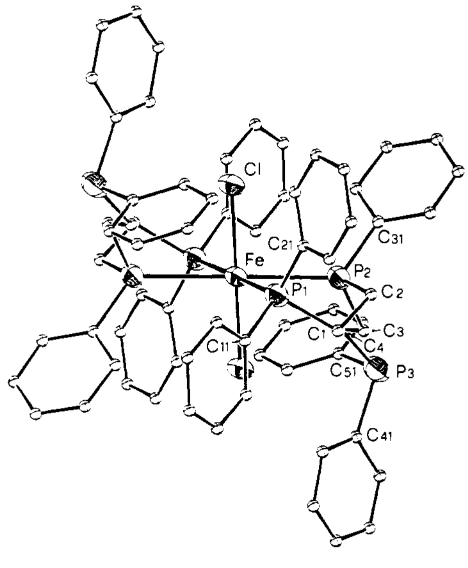

Figure 1. Perspective view of the $FeCl_2(ppp)_2$ molecule.

was featureless. Although effects of high thermal motion prevented the accurate determination of the carbon atom positions in this structure, the positions of the heavier atoms should have been determined with sufficient accuracy to the purposes of the present investigation. In fact, (a) the thermal factors of the metal and ligand atoms are in the normal range and (b) the values of the metal–ligand distances found for compound **2** are comparable to those existing in the similar complex $FeCl_2(dee)_2$.[13] It is also significant (c) that possible errors in the data due to the effects of thermal motion did not prevent the refinement of minor features of this structure such as the orientation of the CH_3 groups.

The final positional and thermal parameters for the nonhydrogen atoms in the structures of compounds **1** and **2** are listed in Tables III and IV, respectively. Parameters for the hydrogen atoms of **2** are reported in Table V, which is included in the supplementary material.[14] Listings of the observed and calculated structure amplitudes are available.[14]

Ligand Field Calculations. In the calculations, based on the angular overlap model (AOM),[15] the tensor operator techniques outlined by Gerloch[16] were used. Details on the procedures have been reported previously.[17] The model systems referred to in the calculations were based on the geometries experimentally determined for the complexes described in this paper and in the companion paper.[5] All states of the d^6 configuration were included in the calculations, spin–orbit coupling being neglected in view of the facts that the spin transition dealt with here is of the $\Delta S = 2$ type and that quasi-degeneracy of the ground state with excited states of different spin multiplicity does not seem to occur for the systems investigated.

Table VI. Selected Bond Lengths (Å) and Angles (Deg) for the Structure of $FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$

Fe–Cl	2.354 (3)	P2–C3	1.83 (1)
Fe–P1	2.713 (3)	P2–C31	1.84 (2)
Fe–P2	2.665 (3)	P3–C4	1.84 (1)
P1–C1	1.84 (1)	P3–C41	1.84 (2)
P1–C11	1.83 (2)	P3–C51	1.83 (1)
P1–C21	1.84 (1)	C1–C2	1.56 (2)
P2–C2	1.84 (1)	C3–C4	1.52 (1)
Cl–Fe–P1	83.4 (1)	Fe–P2–C31	126.1 (3)
Cl–Fe–P2	86.1 (1)	C2–P2–C3	100.6 (5)
P1–Fe–P2	77.4 (1)	C2–P2–C31	102.7 (6)
Fe–P1–C1	100.8 (3)	C3–P2–C31	100.6 (7)
Fe–P1–C11	121.1 (3)	C4–P3–C41	104.2 (7)
Fe–P1–C21	126.4 (4)	C4–P3–C51	99.4 (5)
C1–P1–C11	102.5 (6)	C41–P3–C51	101.1 (6)
C1–P1–C21	100.2 (5)	P1–C1–C2	108.2 (7)
C11–P1–C21	101.3 (6)	P2–C2–C1	112.6 (8)
Fe–P2–C2	107.1 (5)	P2–C3–C4	113.1 (6)
Fe–P2–C3	116.4 (5)	P3–C4–C3	114.4 (7)

Table VII. Selected Bond Lengths (Å) and Angles (Deg) for the Structure of $FeCl_2(dme)_2$

Fe–Cl	2.352 (1)	P1–C4	1.78 (1)
Fe–P1	2.241 (1)	P2–C2	1.88 (1)
Fe–P2	2.230 (1)	P2–C5	1.80 (1)
P1–C1	1.78 (1)	P2–C6	1.82 (1)
P1–C3	1.80 (1)	C1–C2[a]	1.33 (1)
Cl–Fe–P1	88.9 (1)	Fe–P2–C2	107.3 (2)
Cl–Fe–P2	88.1 (1)	Fe–P2–C5	120.9 (2)
P1–Fe–P2	85.8 (1)	Fe–P2–C6	120.3 (2)
Fe–P1–C1	110.3 (2)	C2–P2–C5	101.0 (4)
Fe–P1–C3	121.2 (2)	C2–P2–C6	100.9 (3)
Fe–P1–C4	121.3 (2)	C5–P2–C6	103.1 (3)
C1–P1–C3	98.6 (4)	P1–C1–C2[a]	117.7 (5)
C1–P1–C4	99.8 (5)	P2–C2–C1[a]	118.1 (5)
C3–P1–C4	101.5 (4)		

[a] Values outside the normal range, due to effects of thermal motion (see text).

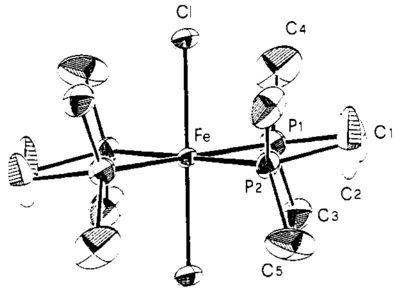

Figure 2. Perspective view of the $FeCl_2(dme)_2$ molecule.

Results and Discussion

The structure of $FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$ consists of isolated $FeCl_2(ppp)_2$ molecules and of acetone molecules. The metal atom is in a six-coordinate environment, formed by two chlorine and four phosphorus atoms, one terminal phosphorus atom of each ppp ligand being uncoordinated. The arrangement of the donor atoms is trans octahedral, with approximate D_{2h} symmetry and crystallographic C_i symmetry. Figure 1 shows a perspective view of the $FeCl_2(ppp)_2$ molecule. Selected values of bond distances and angles are listed in Table VI.

The most notable feature of this structure consists in the extremely large Fe–P distances, equal to 2.713 (3) and 2.665 (3) Å. These are indicative of relatively weak metal–ligand interactions, so that they account for the unexpectedly high spin multiplicity of the gound state of this compound. Such long metal–phosphorus bonds may be ascribed to combined effects of electronic factors (see below) and of steric repulsions due to the phenyl groups attached to the phosphorus atoms.

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(13) Unpublished results of this laboratory. The structure of the compound $FeCl_2(dee)_2$ (monoclinic, space group $P2_1/c$, $a = 10.213$ (6) Å, $b = 13.529$ (9) Å, $c = 10.719$ (7) Å, $\beta = 108.72$ (8)°, $Z = 2$) has been solved and refined by procedures analogous to those described for compounds **1** and **2** to $R = 0.054$ (1180 observed reflections, 125 parameters, anisotropic temperature factors for all nonhydrogen atoms). The coordination geometry (C_i crystallographic symmetry) is similar to that of compound **2**. The thermal motion of the carbon atoms in the room-temperature structure of the dee derivative is even larger than in the case of compound **2**, consistent with the low melting point of the former compound.[4] On the other hand, the temperature factors of the metal and ligand atoms are only slightly larger than in the structure of **2**. The Fe–P bonds, measuring 2.260 (2) and 2.268 (3) Å, are a little longer (by ca. 0.03 Å) than those in compound **2**, as would be expected in view of the increased steric hindrance of the substituent groups on the phosphorus atoms. The Fe–Cl distance, of 2.349 (2) Å, matches that of 2.352 (1) Å in compound **2**. It has not been considered important to report here more details about this structure determination because reference to the above values of metal–ligand distances is sufficient for the purposes of the present discussion.

(14) Supplementary material.

(15) Schäffer, C. E.; Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1958**, *8*, 143; Schäffer, C. E. *Struct. Bonding (Berlin)* **1968**, *5*, 68; **1973**, *14*, 69.

(16) Gerloch, M.; McMeeking, R. F. *J. Chem. Soc., Dalton Trans.* **1975**, 2443. Gerloch, M.; McMeeking, R. F.; White, A. M. *Ibid.* **1975**, 2452.

(17) Di Vaira, M. *Inorg. Chim. Acta* **1980**, *38*, 21.

The importance of nonbonded interactions is suggested by the existence of numerous short interligand contacts and by the fact that the peripheral phosphorus atom of the ppp ligand, having two phenyl substitutents, forms a longer bond to the metal than the central phosphorus atom, which bears only one phenyl group. No other unusual feature is present in this structure.

The structure of the low-spin compound $FeCl_2(dme)_2$ is formed by isolated molecules, in which the metal atom has a P_4Cl_2 environment as in the previous compound. The symmetry of the coordination polyhedron is close to D_{4h}, although it is rigorously C_i also in this case. Figure 2 shows a perspective view of the $FeCl_2(dme)_2$ molecule. Values of bond distances and angles involving the nonhydrogen atoms are listed in Table VII. The abnormally short C–C distance and the large P–C–C angles in the ligand molecule reveal the effects of thermal motion that have been described in the experimental section. Indeed, according to the time-averaged picture provided by X-ray diffraction, the chelate ring appears to be almost planar. However, as has been stressed above, the positions of the heavier atoms are affected by thermal motion to a much lesser extent than those of the light ones, so that the values derived for bond distances and angles about the metal atom may be referred to with some confidence in the following discussion.

The Fe–P distances of 2.241 (1) and 2.230 (1) Å in $FeCl_2(dme)_2$ are dramatically shorter than those existing in the high-spin compound, quoted above. Such differences in bond lengths should be determined by (a) the large rearrangement in the d electron density distribution on the metal center accompanying the change of spin state, the orbitals of e_g octahedral parentage being empty in the low-spin state but occupied in the high-spin state, (b) the different steric requirements of the ppp and of the dme ligand molecules, and (c) the different electronic inductive properties of the phosphorus atoms of the two ligand molecules.[18] Factor a seems to be the most effective one in determining the Fe–P bond distances, according to the results of structural investigations on the different spin isomer of the same compound.[5] Although factors b and c probably have a less significant direct influence on the bond lengths, they should have an important indirect effect as they contribute to control the spin state of the metal atom and the associated electron density distribution. At variance with the Fe–P distances, the Fe–Cl bond length of 2.352 (1) Å in the compound $FeCl_2(dme)_2$ is practically identical with that (2.354 (3) Å) found for the ppp derivative. It has to be emphasized that the Fe–Cl bond length is remarkably constant for all of the compounds considered in this study, irrespective of the nature of their ground state.[5,13] This is surprising since in the singlet ⇌ quintet transition a large rearrangement of the d-electron density distribution should occur along the directions of the axial as well as of the equatorial bonds. Hoever, closer consideration reveals that in the axial direction the above effect, essentially involing σ bonding, may be counterbalanced by the following: the chlorine atoms, which are π donors unlike the phosphorus atoms, in the low-spin state undergo four-electron destabilizing interactions with the filled metal t_{2g} orbitals. Such interactions are released in the high-spin state, in which the t_{2g} orbitals are only partially occupied.

A short discussion of the properties of the compounds reported in this paper follows. All of the compounds slowly decompose in air, both in the solid state and in solution. The $[FeX(ppp)_2]BPh_4$ (X = Br, I) complexes decompose faster than the other ones. All compounds are sparingly soluble at room temperature in deoxygenated organic solvents like acetone, 1,2-dichloroethane, and methylene chloride, the $[FeX(ppp)_2]BPh_4$ complexes being more soluble than the others. The $[FeX(ppp)_2]BPh_4$ complexes behave as 1:1 electrolytes in 1,2-dichloroethane, whereas all of the others do not conduct in such solution.

The compound $FeCl_2(ppp)_2\cdot 2(CH_3)_2CO$ is paramagnetic with a μ_{eff} value of 5.27 μ_B, corresponding to the quintet ground state. The compounds $[FeX(ppp)_2]BPh_4$ have μ_{eff} values ranging from 3.43 to 3.60 μ_B, consistent with a triplet ground state. All of the above magnetic moments are practically constant over the 90–300 K temperature range. The compounds $Fe(NCS)_2(ppp)_2$, $FeCl_2(dme)_2$, and $FeCl_2(dee)_2$ are diamagnetic.

The reflectance spectrum of $FeCl_2(ppp)_2\cdot 2(CH_3)_2CO$, showing two bands in the region 8000–12 000 cm^{-1} (Table I), is typical of the tetragonal high-spin d^6 chromophores.[20] It differs drastically from the spectrum in 1,2-dichloroethane solution, which shows an intense absorption at ca. 7200 cm^{-1}, being indicative of a high-spin, possibly tetrahedral, species. Probably the ppp ligand acts as monodentate in such solution. Alternatively, equilibrium 1 may exist, similar to that indicated

$$\underset{\text{six-coordinate}}{FeCl_2(ppp)_2} \rightleftharpoons \underset{\text{tetrahedral}}{FeCl_2(ppp)} + ppp \qquad (1)$$

for the compound $FeCl_2(dppen)_2$, where dppen is the bidentate ligand *cis*-1,2-bis(diphenylphosphino)ethylene.[2] The reflectance spectra of the $[FeX(ppp)_2]BPh_4$ complexes, showing numerous and relatively weak bands (Table I), are essentially similar to the spectra recorded in 1,2-dichloroethane solution, before substantial decomposition takes place. Such spectra are consistent with the existence of the triplet ground state, since many triplet–triplet transitions are expected to occur, even at low energies, for low-symmetry coordination geometries. The intensities of the bands in these spectra, which are lower than those usually found for phosphorus-containing iron(II) complexes in the triplet ground state,[21] may be rationalized considering that long Fe–P bonds are probably present, as found in the structure of the chloride described above. It is reasonable to assign a five-coordinate geometry with a P_4X donor set to these complexes, assuming that one terminal phosphorus atom of each ppp ligand is uncoordinated, as in the $FeCl_2(ppp)_2$ molecule. Support to this assumption is provided by the similarity in the spectral and magnetic properties of the present complexes with those of $[FeI(dppen)_2]BPh_4$.[5] Unfortunately the structures of these compounds could not be investigated by X-ray diffreaction, owing to the fact that suitable crystals were not obtained. The spectra of the diamagnetic compounds are similar to those previously reported for pseudooctahedral d^6 low-spin complexes.[20] Their assignment is discussed below.

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(18) A reviewer has pointed out to us that the differences in electronic inductive properties between the phosphorus atoms of the ppp and dme ligands may be as important as the steric effects in determining the spin state of the metal atom. The importance of the former factor is not disputed here. However, it should be noted that the nucleophilicity $n°$ values (generally considered to be good indicators of the low-spin character of donor atoms), which are reported by Basolo and Pearson[19] for aryl- and alkyl-substituted phosphorus, are very close to each other (PPh_3 8.79, PEt_3 8.85). As to the role of steric repulsions within the $Fe_2L_2(ppp)_2$ (L = Cl, NCS) molecules, it has to be streesed that, owing to the flexibility of the ppp ligand, such interactions should not be capable of preventing the low-spin state from being attained: they *favor* the high-spin state by favoring the associated coordination geometry, with long Fe–P bonds. Therefore, the fact that the compound $Fe(NCS)_2(ppp)_2$ is low spin (see text) whereas the chloride is high spin is easily rationalized in view (a) of the higher field strength and lower steric requirements of the NCS group compared to chlorine and (b) of the ligand field parametrization described in the text for these compounds, which indicates that the chloride lies close to the singlet ⇌ quintet crossover.

(19) Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions"; Wiley: New York, 1967; p 399.

(20) Lever, A. B. P. "Inorganic Electron Spectroscopy"; Elsevier: Amsterdam, 1968.

(21) Sacconi, L.; Di Vaira, M. *Inorg. Chem.* **1978**, *17*, 810 and references therein.

Table VIII. Structural and Spectral Data for the High-Spin Compounds[a]

				assignment a[b]		assignment b[b]	
compd	⟨Fe-P⟩	ν_1	ν_2	e_σ(P)	e_σ(Cl)	e_σ(P)	e_σ(Cl)
$FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$[c]	2.68	8.3	11.8	2.76, 2.97	4.42	3.96, 4.28	2.00
$FeCl_2(dppen)_2$[d,e]	2.60	9.7	13.9	3.05, 3.78	5.20	4.25, 5.27	2.45
$FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$[e,f]	2.58	10.1	13.2	3.55	4.80	4.61	2.71

[a] ⟨Fe-P⟩ is the mean (Å) of two symmetry-independent bond distances; ν_i are spectral frequencies (10^3 cm^{-1} units). The ⟨Fe-P⟩, ν_1, and ν_2 values for the compound $FeBr_2(dppen)_2$[2,25] are in the order 2.65, 9.2, and 11.6. [b] See text for assignments a and b and definitions of the AOM e_λ parameters (10^3 cm^{-1} units). The pairs of e_σ(P) values reported for the first two compounds in the table refer to the Fe-P1 and Fe-P2 interactions, in that order; such e_σ(P) parameters were linked to each other in the calculations via the squared-overlap ratio.[26] [c] Present work. [d] Reference 2. [e] Reference 5. [f] High-spin isomer, 295 K structure.

Table IX. Structural and Spectral Data for the Low-Spin Compounds[a]

compd	⟨Fe-P⟩	ν_1	ν_2	e_σ(P)	e_π(P)	e_σ(Cl)	e_π(Cl)
$FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$[b]	2.30	14.4	21.7	8.5	−0.2	3.7	0.4
$FeCl_2(dee)_2$[c]	2.26	14.7	24.7	8.5	−1.0	3.7	1.2
$FeCl_2(dme)_2$[c]	2.24	15.2	27.0	8.8	−1.2	3.7	1.2

[a] ⟨Fe-P⟩, ν_i, and e_λ defined as in Table VIII; values of $B = 500$ cm^{-1} and $C = 3000$ cm^{-1} used in the calculations. [b] Reference 5; low-spin isomer, 130 K structure. [c] Reference 4 and present work.

The structural data reported in this paper and in the companion paper[5] for several pseudooctahedral iron(II) compounds with a P_4Cl_2 donor set offer the opportunity to investigate possible correlations between the spectral properties and the structures of such compounds. In particular, it was interesting to verify whether angular-overlap parameters could be approximately transferred between the high-spin and the low-spin compounds. Transferability of such parameters between related chromophores has often been assumed, but, to our knowledge, it has never been tested for the different spin isomers of the same compound or for structurally related chromophores in different spin states. The structural and spectral data for the high-spin compounds, which are relevant to the present part of the discussion, are summarized in Table VIII. The order of energy levels for these d^6 high-spin chromophores having approximate D_{4h} symmetry, may be either (a) $^5B_{2g} < {}^5E_g \ll {}^5B_{1g} < {}^5A_{1g}$ or (b) $^5B_{2g} < {}^5E_g \ll {}^5A_{1g} < {}^5B_{1g}$, depending on whether (a) $e_\sigma(P) < e_\sigma(Cl)$ or (b) $e_\sigma(P) > e_\sigma(Cl)$.[22-24] Assignment a is preferred for the following reasons. First, a lower equatorial rather than axial field strength is suggested by the existence of very long Fe–P distances in the compounds (Table VIII). Second, according to scheme a, the first transition in the 8000–13 000-cm^{-1} region is assigned as $^5B_{2g} \rightarrow {}^5B_{1g}$, with energy proportional to the equatorial field strength $E(^5B_{2g} \rightarrow {}^5B_{1g}) = 10\,Dq^{eq}$;[23,24] in agreement with this, the values of ν_1 in Table VIII increase with decreasing Fe–P distances. Also the spectral and structural data obtained for the compound $FeBr_2(dppen)_2$ conform to the above trend reasonably well (see footnote *a* to Table VIII and ref 25). Two sets of e_σ(P) and e_σ(Cl) parameters,[22] corresponding to assignments a and b, have been derived by the procedure of extensive scans through parameter space:[16,17] such values are listed in Table VIII. The e_σ(P) values are inversely proportional to the Fe–P bond lengths so that they are proportional, as may be readily verified, to the squares to the metal–ligand overlaps, in agreement with the assumptions of the simple AOM approach for weak metal–ligand interactions.[15,26] Although the e_σ(Cl) values do not follow such a simple trend, the entries in Table VIII do provide an indication of the range of values to be compared with those of the low-spin chromophores.

The two bands not obscured by CT excitations in the spectra of the low-spin compound have been assigned to the transitions $^1A_{1g} \rightarrow {}^1E_g{}^a$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ involving components of the cubic $^1T_{1g}$ term split in D_{4h} symmetry.[23] An analogous assignment had been previously made for d^6 tetragonal chromophores with the As_4X_2 donor sets.[27] It was soon evident that, in order to fit the spectra of the present low-spin compounds, the e_π parameters should not be neglected. Indicative values of parameters from the broad region of good fit (reasonable values for the Racah *B* and *C* parameters being taken from the literature[24,27]) are listed in Table IX. Such values are quite different from those obtained for the high-spin compounds (Table VIII) according to assignment a and cannot be related to the latter even accounting by usual procedures[26] for changes in bond lengths. Although the agreement with the values from assignment b is better, we do not believe that this suffices to substantiate scheme b for the high-spin compounds. We rather draw the conclusion that parameters cannot be transferred between the two spin states.

Finally, it has been verified that with the values of parameters listed in Tables VIII and IX and with values of the Racah parameters confined within reasonable ranges, the correct ground state is calculated for each of the compounds considered in this study. The separation between the ground state and the lowest excited state of different spin multiplicity (generally a spin triplet) is found to be definitely larger for the low-spin than for the high-spin compounds, which have states with $S = 0-2$ bunched within 1000–3000 cm^{-1}. This is further evidence for the fact that the quintet ground state may be stabilized for these tetragonal iron(II) complexes with the P_4Cl_2 donor set only if special, essentially geometric, requirements are fulfilled by the ligands.

Acknowledgment. Thanks are expressed to Mr. F. Cecconi and Mr. D. Masi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. 1, 74255-95-1; **2**, 27316-95-6; $[FeBr(ppp)_2]BPh_4$, 78217-06-8; $[FeI(ppp)_2]BPh_4$, 78217-02-4; $Fe(NCS)_2(ppp)_2$, 78217-07-9; $FeCl_2(dee)_2$, 22920-46-3; $FeBr_2(dppen)_2$, 58031-47-3.

Supplementary Material Available: Table V (hydrogen atom parameters for the structure of $FeCl_2(dme)_2$) and listings of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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(22) The e_λ parameters have the usual meaning of the AOM approach.[16] The e_π(P) parameter may be safely neglected for the present high-spin chromophores; the e_π(Cl) one should not be ignored but, being conceivably close to a fixed fraction of e_σ(Cl), its exclusion from the model has no major effect on the trends which are derived. The fact that $e_\pi(Cl) > e_\pi(P)$ is at the asis of the choice of the $^5B_{2g}$, rather than the ^5E_g, ground state for these systems.

(23) Lever, A. B. P. *Coord. Chem. Rev.* **1968**, *3*, 119.

(24) Dabrowiak, J. C.; Merrel, P. H.; Busch, D. H. *Inorg. Chem.* **1972**, **11**, 1979.

(25) Preliminary results of this laboratory. The structure of $FeBr_2(dppen)_2$ (space group $P\bar{1}$, $a = 12.33$ Å, $b = 11.65$ Å, $c = 10.30$ Å, $\alpha = 118.5°$, $\beta = 103.2°$, $\gamma = 105.1°$, $Z = 1$) has been determined and refined from 2145 observations to $R = 0.064$. Values of symmetry-independent bond distances (Å) and angles (deg) about the metal atom are Fe–Br = 2.49, Fe–P1 = 2.67, Fe–P2 = 2.64, Br–Fe–P1 = 84.8, Br–Fe–P2 = 86.5, and P1–Fe–P2 = 78.8.

(26) Hitchman, M. A. *Inorg. Chem.* **1972**, *11*, 3387.

(27) Felthan, R. D.; Silverthorn, W. *Inorg. Chem.* **1968**, *7*, 1154.