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Synthesis, Properties, and Structural Characterization of Novel d^5, d^6, and d^7 Transition-Metal Complexes with Cyclic Diphosphonium Triple-Ylide Anions

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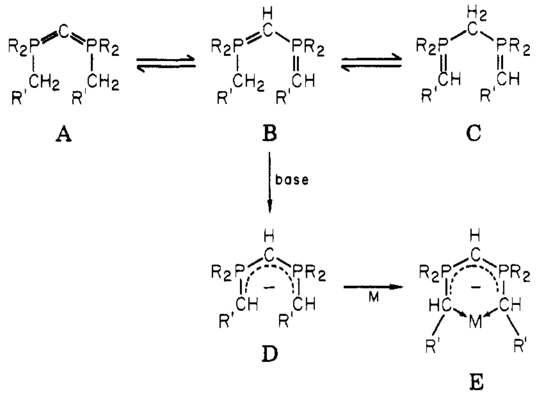
Reaction of the lithiated cyclic double-ylide Li^+L^- (2) with the tetrahydrofuran adducts of $MnBr_2$, $FeCl_2$, and $CoCl_2$ at -78 °C in tetrahydrofuran results in the formation of the novel binary metal ylide complexes MnL_2 (3), FeL_2 (4), and CoL_2 (5), where L^- represents the cylic triple-ylide anion corresponding to the neutral ylide 1 (LH). The deeply colored, air-sensitive compounds crystallize with 2 mol of crystal THF, which can be removed in vacuo. All three complexes are strongly paramagnetic and exhibit Curie–Weiss behavior in susceptibility measurements between 4.2 and 298.5 K. The magnetic moments correspond to a normal high-spin configuration of d^5, d^6, and d^7 metal ions in a tetrahedral environment. The results of a ^{57}Fe Mössbauer investigation of 4 at 4.2 K are also in good agreement with the tetrahedrally coordinated high-spin iron(II) model. The signals in the paramagnetic ^{1}H NMR spectrum of the iron complex 4 in tetrahydrofuran can be assigned on the basis of the proposed structure and are found to follow Curie's law in the temperature range between ca. 300 and 360 K. The single-crystal X-ray diffraction study of the manganese complex 3 established the proposed structure (a = 2848.5 (5) pm, b = 1298.0 (2) pm, c = 1968.9 (2) pm, β = 110.51 (1)°, space group $C2/c$, Z = 4). The manganese cation is surrounded by two symmetry-related, equivalent triple-ylide anions. The seven-membered ylide heterocycles are folded in a boat conformation and have metal–ligand contacts mainly through the benzylide carbon atoms, which form a distorted tetrahedral array around the Mn(II) center. Metal–phenylene interactions are not fully excluded, however, as judged by the Mn–C distance pattern. The crystals of the Co(II) analogue 5 are isomorphous with the crystals of 3.

Introduction

Ylides of phosphorus and sulfur are now recognized as a class of extremely powerful ligand systems that form complexes with both main-group and transition metals.[1-5] For most areas of the periodic table at least some typical examples of the resulting new type of organometallic compounds have been prepared and structurally characterized.[1-12] The unusual features of stoichiometry and charge distribution of these complexes provide structural and mechanistic chemistry with new model systems for pertinent basic and applied research.[13,14] While the coordination chemistry of monofunctional ylides ("monoylides") is already a fairly well-developed area, results on species derived from multifunctional ylides ("double, triple, etc. ylides") are still limited and are restricted to special cases.[3-5]

Thus cumulated double ylides ("carbodiphosphoranes", $R_3P{=}C{=}PR_3$)[15] with various substituents should exhibit specific coordination behavior toward certain metal centers and may react as depicted in the tautomeric forms A, B, or C, but only very few experiments have been carried out to establish the validity of this and analogous schemes.[16-18]



The corresponding anion D, with benzyl substituents ($R' = C_6H_5$), is an efficient ligand system even for alkali metals. Crystal structure data indicate a preferred coordination to the benzylide carbon atoms but also to C1 and C2/6 of the phenyl ring.[19,20] Well-defined complexes can also be formed with an earth alkaline metal, like Ba^{2+}, or a d^{10} transition metal, like Cd^{2+}.[21]

We have reported also, very recently, on the ligand properties of the heterocyclic ylide F and its corresponding anion G, in which the two R′ substituents in B and D are replaced by a phenylene bridge. The preparation and properties of these two new ligands have been described.[22]

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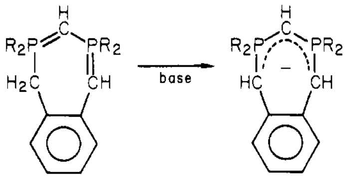
From them, again, complexes with alkali, alkaline earth, and d^{10} transition elements could be obtained and a Cd^{2+} complex has been structurally characterized.[22,23]



F G

In this paper we disclose work on the related compounds of the d^5, d^6, and d^7 metal cations Mn^{2+}, Fe^{2+}, and Co^{2+}. They show an unusual state of bonding not unlike that in related *o*-xylidene complexes[24] and their silyl derivatives. The manganese compound has already been mentioned in a conference report.[5]

Experimental Section

Preparation of Compounds. All manipulations were performed under a dry oxygen-free dinitrogen or argon atmosphere with use of thoroughly degassed solvents and reagents. Tetrahydrofuran was dried over and distilled from sodium wire. Pentane and toluene were dried over calcium hydride. 2,2,4,4-Tetraphenyl-1*H*,2λ^5, 4λ^5-benzodiphosphepin (1) was prepared as described elsewhere.[22] $MnBr_2\cdot 2THF$, $FeCl_2\cdot 1.45THF$, and $CoCl_2\cdot 1.31THF$ are obtained following the general procedure of Soxhlet extraction of the commercially available anhydrous metal dihalides with dry THF.

Bis(2,2,4,4-tetraphenyl-1*H*-2λ^5,4λ^5-benzodiphosphepinyl)manganese(II)-Bis(tetrahydrofuran)(3). A well-stirred solution of 0.90 g of 1 (1.9 mmol) in 10 mL of THF is treated, at −20 °C, with 1.15 mL of a 1.61 M solution of *n*-butyllithium in hexane and then cooled to −78 °C. Addition of 0.34 g of $MnBr_2\cdot 2THF$ (0.90 mmol) to the reaction mixture results in a brown suspension, which is slowly allowed to warm to room temperature. A yellow precipitate forms but redissolves on gentle heating to 40 °C. When the clear yellow-brown solution is cooled to −30 °C, bright-yellow needles of the product 3 separate in a 0.88-g yield (79%); mp 148 °C dec. Anal. Calcd for $C_{74}H_{70}MnO_2P_4$ (1170.21): C, 75.95; H, 6.03; Mn, 4.69. Found: C, 75.53; H, 5.69; Mn, 4.96.

Bis(2,2,4,4-tetraphenyl-1*H*-2λ^5,4λ^5-benzodiphosphepinyl)iron(II)-Bis(tetrahydrofuran) (4). Following a procedure analogous to that described for 3 above, 4 can be obtained from 1.01 g (2.1 mmol) of 1 and 0.24 g (1.0 mmol) of $FeCl_2\cdot 1.45THF$. Brown-orange crystals separate in a 0.80-g yield (74%); mp 153 °C dec. Anal. Calcd for $C_{74}H_{70}FeO_2P_4$ (1171.12): C, 75.89; H, 6.03. Found: C, 75.13; H, 6.05.

Bis(2,2,4,4-tetraphenyl-1*H*-2λ^5,4λ^5-benzodiphosphepinyl)cobalt(II)-Bis(tetrahydrofuran) (5). Following again the above procedure and using 0.90 g of 1 (1.9 mmol) and 0.23 g of $CoCl_2\cdot 1.31$ THF (0.95 mmol), a green precipitate is obtained. This material is extracted with toluene and crystallized by addition of pentane and cooling to −30 °C. Emerald needles form in a 0.23-g yield (21%); mp 112 °C dec. Anal. Calcd for $C_{74}H_{70}CoO_2P_4$ (1174.21): C, 75.70; H, 6.01. Found: C, 75.87; H, 5.93.

Table I. Regression Parameters *C* and θ of Magnetic Susceptibility Data (Figure 1) and Effective Magnetic Moments of Complexes 3-5

	3	4	5
C, $cm^3\ K\ mol^{-1}$	4.35 (1)	3.13 (1)	2.21 (1)
θ, K	−1.8	2.0	−0.8
$\mu_{eff} = (8C)^{1/2}\ \mu_B$	5.9	5.0	4.2
no. of unpaired electrons	5	4	3
calcd spin-only values	5.92	4.90	3.87

Physical Measurements. Susceptibility measurements were performed on a modified Faraday balance between 4.2 and 298.5 K as described in ref 25. The resulting susceptibility data were corrected for the diamagnetic ylide anions following the increment procedure given in ref 26.

The ^1H NMR spectrum of compound 4 was recorded on a Bruker CXP 200 instrument at 200 MHz in the Fourier transform mode. The ^{57}Fe Mössbauer spectrum was obtained with a ^{57}Co source in rhodium metal at 4.2 K. The isomeric shifts were corrected to achieve compatibility with literature values based on the α-Fe matrix by subtraction of 0.108 $mm\cdot s^{-1}$.

X-ray Crystal Structure Determination of MnL_2 (3). Crystals of $Mn(C_{33}H_{27}P_2)_2\cdot 2THF$ were obtained by crystallization from a tetrahydrofuran solution. A crystal (0.3 × 0.27 × 0.23 mm) was mounted on a Nonius CAD4 automatic four-circle diffractometer equipped with a graphite monochromator and a scintillation counter (ω-scan mode). All measurements were carried out by using Mo K_α radiation (λ = 71.069 pm). The unit-cell dimensions of a = 2848.5 (5) pm, b = 1298.0 (2) pm, c = 1968.9 (2) pm, β = 110.51 (1°), and $V = 6819.10^6$ pm^3 were obtained by centering and refinement of 15 reflections from different parts of the reciprocal space. Precession photographs and systemetic absences indicated the monoclinic space group *C*2/*c* (No. 15, Z = 4, d_{calcd} = 1.19 g/cm^3).

Intensities were measured by a coupled Ω–2θ technique with scan speeds varying from 1.3 to 10.0° min^{-1}, depending on the standard deviation to intensity ratio of a preliminary 10° min^{-1} scan. The intensity of the reflection and its standard deviation were calculated from INT − BGL + BGR and $(INT + 4\ (BGL + BGR))^{1/2}$ respectively, where INT, BGL, and BGR are the peak intensity and the left and the right backgrounds, and the time spent measuring the background was half that taken to measure the peak. A Zr filter was inserted in front of the detector if the peak count was greater than 50 000 counts s^{-1}. The intensities of the three monitor reflections remeasured after every 90 min of X-ray exposure showed no significant variation during the course of data collection. (Pertinent crystal data is given in Table IV.) The cell parameters were obtained by least-squares fit to the θ values of 75 automatically centered reflections.

A test solution on the basis of space group *Cc* had revealed that the manganese atom is located on a twofold axis, and therefore the data processing was continued with space group *C*2/*c*. The remaining atoms were correlated by appropriate symmetry operations.

A total of 6197 reflections were collected ($1° \leq 2\theta \leq 50°$). Intensity data were corrected for Lorentz and polarization effects; absorption correction was not applied. The crystal was stable in the X-ray beam. The structure was solved by the Patterson method (SHELX). Elemental analysis and IR absorptions indicated the presence of two THF molecules per formula unit, and difference Fourier synthesis showed indeed two groups of electron densities to be interpreted as solvent species. Only one of the two groups could be refined, however, with an occupational factor 0.5, although refinement improved on inclusion of the remaining peaks as constants. The coordinates were also added to the list of atomic parameters (Table II, C81–C95). Positions of some of the hydrogen atoms were calculated according to the idealized geometry and included as fixed-atom contributions (B_{iso} = 9.0 $Å^2$) to refinement calculations. Least-squares refinement (SHELX) of 221 parameters with 2177 structure factors ($I \geq 2\sigma(I)$) resulted

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Table II. Final Positional and Isotropic Thermal Parameters (with Esd's) for Non-Hydrogen Atoms of the Manganese Complex 3

atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	0.0	0.2317 (3)	0.25	0.050 (3)	0.051 (3)	0.038 (2)	0.0	0.0	0.02 (19)
P1	−0.0996 (2)	0.1186 (4)	0.1283 (3)	0.051 (3)	0.045 (3)	0.039 (3)	0.000 (3)	0.010 (2)	−0.007 (3)
P2	−0.0313 (2)	0.2508 (4)	0.0757 (2)	0.061 (3)	0.057 (3)	0.036 (3)	0.004 (3)	0.013 (2)	−0.007 (3)
C6	−0.0816 (6)	0.1925 (13)	0.2070 (9)	0.05 (1)	0.04 (1)	0.04 (1)	−0.01 (1)	0.010 (9)	−0.002 (9)
C7	−0.0763 (6)	0.1593 (12)	0.0629 (9)	0.05 (1)	0.05 (1)	0.04 (1)	−0.01 (1)	0.02 (1)	−0.02 (1)
C5	−0.0198 (7)	0.3337 (14)	0.1507 (9)	0.06 (1)	0.07 (1)	0.05 (1)	0.00 (1)	0.02 (1)	0.03 (1)
C51	−0.0980 (7)	0.3059 (15)	0.1868 (9)	0.04 (1)	0.07 (1)	0.02 (1)	−0.01 (1)	−0.02 (1)	0.00 (1)
C52	−0.0675 (8)	0.3720 (16)	0.1586 (9)	0.08 (2)	0.04 (1)	0.02 (1)	−0.00 (1)	−0.02 (1)	−0.02 (1)
C53	−0.0818 (8)	0.4786 (16)	0.1465 (11)	0.07 (2)	0.04 (1)	0.08 (2)	−0.01 (1)	0.01 (1)	0.00 (1)
C54	−0.1225 (11)	0.5156 (16)	0.1599 (12)	0.11 (2)	0.03 (1)	0.07 (2)	−0.01 (1)	0.00 (2)	0.00 (1)
C55	−0.1529 (8)	0.4537 (20)	0.1865 (12)	0.07 (2)	0.07 (2)	0.07 (2)	−0.0 (2)	0.01 (1)	0.03 (1)
C56	−0.1393 (8)	0.3494 (17)	0.1989 (10)	0.05 (1)	0.07 (2)	0.05 (1)	−0.02 (1)	0.01 (1)	−0.01 (1)

	x/a	*y/b*	*z/c*	U_{iso}, Å²		*x/a*	*y/b*	*z/c*	U_{iso}, Å²
C1[a]	−0.0469 (6)	0.3185 (14)	−0.0107 (9)	−0.05 (1)	C35	−0.192 (1)	0.134 (2)	0.012 (1)	0.10 (1)
C11	−0.085 (1)	0.385 (2)	−0.026 (1)	0.08 (1)	C4	−0.0824 (6)	−0.0108 (13)	0.1591 (9)	0.05 (1)
C12	−0.099 (1)	0.445 (2)	−0.092 (1)	0.10 (1)	C41	−0.069 (1)	−0.037 (1)	0.233 (1)	0.06 (1)
C13	−0.070 (1)	0.432 (2)	−0.135 (1)	0.08 (1)	C42	−0.060 (1)	−0.142 (2)	0.252 (1)	0.09 (1)
C14	−0.032 (1)	0.370 (2)	−0 (1)	0.09 (1)	C43	−0.066 (1)	−0.219 (2)	0.199 (1)	0.09 (1)
C15	−0.021 (1)	0.309 (2)	−0.056 (1)	0.08 (1)	C44	−0.079 (1)	−0.194 (2)	0.127 (1)	0.08 (1)
C2	0.0293 (7)	0.1979 (15)	0.0896 (9)	0.06 (1)	C45	−0.087 (1)	−0.089 (2)	0.109 (1)	0.07 (1)
C21	0.071 (1)	0.259 (2)	0.100 (1)	0.09 (1)	C81	0.285	0.263	0.974	0.15
C22	0.122 (1)	0.214 (2)	0.110 (1)	0.10 (1)	C82	0.284	0.199	0.024	0.15
C23	0.125 (1)	0.114 (2)	0.108 (1)	0.09 (1)	C83	0.243	0.295	−0.056	0.15
C24	0.084 (1)	0.050 (2)	0.095 (1)	0.10 (1)	C84	0.275	0.317	−0.003	0.15
C25	0.036 (1)	0.091 (2)	0.086 (1)	0.08 (1)	C85	0.298	0.181	0.998	0.15
C3	−0.1677 (6)	0.1061 (13)	0.085 (1)	0.06 (1)	C91	0.211 (2)	0.107 (4)	0.712 (3)	0.10 (1)
C31	−0.195 (1)	0.075 (2)	0.124 (1)	0.10 (1)	C92	0.245 (2)	0.157 (3)	0.768 (2)	0.08 (1)
C32	−0.248 (1)	0.065 (2)	0.095 (2)	0.13 (1)	C93	0.236 (3)	0.253 (5)	0.755 (3)	0.13 (2)
C33	−0.267 (1)	0.090 (2)	0.025 (2)	0.11 (1)	C94	0.193 (2)	0.259 (5)	0.724 (3)	0.25 (2)
C34	−0.245 (1)	0.125 (2)	−0.018 (1)	0.15 (1)	C95	0.184 (2)	0.175 (4)	0.678 (3)	0.12 (2)

[a] Disordered solvent ($G = 0.5$).

Table III. Selected Interatomic Distances (Å) and Angles (Deg) for the Manganese Complex 3

Bond Distances			
Mn-C6	2.235 (16)	P1-C3	1.833 (17)
Mn-C5	2.263 (17)	P1-C4	1.794 (17)
Mn-C51	2.798 (19)	P2-C7	1.701 (15)
Mn-C52	2.798 (20)	P2-C5	1.763 (17)
P1-C6	1.741 (16)	P2-C2	1.788 (18)
P1-C7	1.723 (16)	P2-C1	1.825 (17)
Bond Angles			
C5-Mn-C6	84.0 (7)	P1-C7-P2	124.8 (1.0)
C7-P1-C6	115.2 (8)	C5-P2-C7	117.3 (9)
C3-P1-C6	113.2 (8)	C2-P2-C7	113.1 (9)
C3-P1-C7	107.7 (8)	C2-P2-C5	102.7 (9)
C4-P1-C6	104.8 (8)	C1-P2-C7	106.0 (8)
C4-P1-C7	114.1 (8)	C1-P2-C5	113.5 (8)
C4-P1-C3	101.2 (8)	C1-P2-C2	103.5 (9)

Table IV. Details of X-ray Data Collection

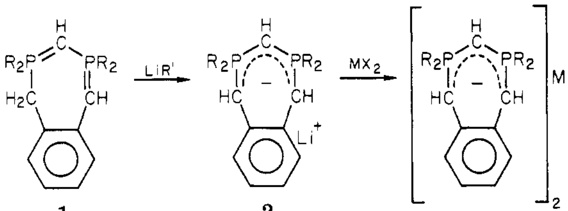
monochromated (graphite) MoKα X radiation	$\lambda = 0.71069$ Å
reflections measd	6197 [$\pm h,k,l$]
takeoff angle	$\theta = 3.6°$
θ limits	$1 < \theta < 25$
Ω-2θ scan technique	96 steps
horizontal detector aperture	$(5 + 1.25 \tan \theta)$ mm
vertical aperture	4.0 mm
Ω scan range	$0.7 + 0.35 \tan \theta$
$\sigma(F)$	$(\sigma(I)^2(\text{poisson}) + (Ik)^2)^{1/2}/2F$; $k = 0.02$

in a final R_1 of 0.113 and R_2 of 0.104 ($[\sum W||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$; $w = 1.8985/(\sigma^2(F))$).

The final positional and thermal parameters are listed in Table II. Table III contains interatomic distances and angles. Table V, observed and calculated structure factors, is available as supplementary material. The thermal parameter expression is defined as $U = \exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$.

Results and Discussion

The cyclic double-ylide 1 is easily metalated in tetrahydrofuran solution by reaction with *n*-butyllithium at −20 °C. The resulting deep orange solution containing the lithium salt 2, when treated, at −78 °C with a 0.5 M amount of $MnBr_2 \cdot 2THF$, $FeCl_2 \cdot 1.45THF$, and $CoCl_2 \cdot 1.31THF$, respectively, according to eq 1 affords the complexes 3 and 4 in good yield (70–80%) as highly air-sensitive orange-red crystals containing 2 mol of solvent. The yield of 5 is unexpectedly low (20%). Cooling down the moss green reaction mixture gives emerald crystals of 5 together with a water-soluble brown byproduct, the identity of which has not been established. Extraction with toluene and crystallization at −30 °C gives pure 5.



(1)

1 2

3, M = Mn
4, M = Fe
5, M = Co

R = C_6H_5

The new complexes 3–5 are strongly paramagnetic and show Curie–Weiss behavior in susceptibility measurements between 4.2 and 298.5 K (Figure 1). The resulting magnetic moments μ_{eff} are listed in Table I together with Curie–Weiss constants. The magnetic moments are in good agreement with spin-only values for d^5, d^6, and d^7 cations in a tetrahedral crystal field. The somewhat higher

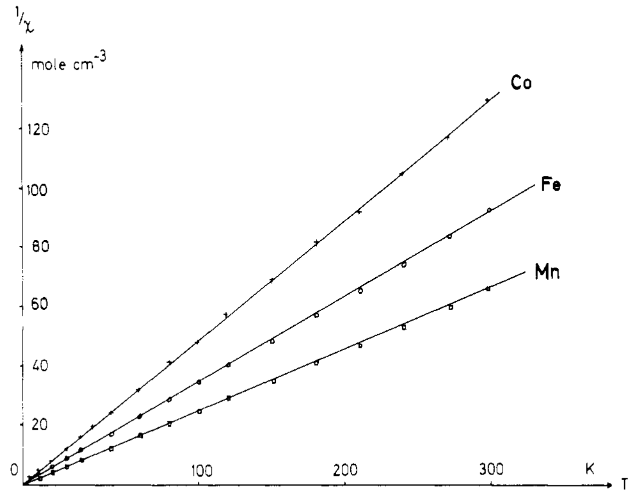


Figure 1. Reciprocal molar susceptibility $1/\chi$ of the complexes **3**–**5** as a function of temperature.

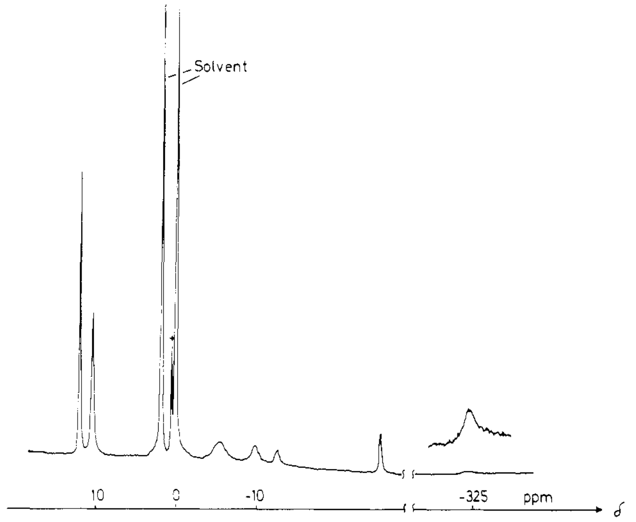
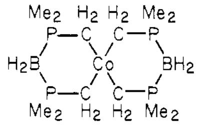


Figure 2. ^1H NMR spectrum of the iron complex **4** in tetrahydrofuran at 56.2 °C (+, diamagnetic impurity).

values for **4** and **5** are not unusual. Other homoleptic organometallic compounds, e.g., **6**, which has been synthesized in the Munich Laboratories[27] show similar behavior.



6

$\mu_{eff} = 4.1\ \mu_B$

Magnetic resonance spectroscopy should also provide information about the magnetic properties. However, we were unable to detect an ESR signal for **4** down to 77 K. Instead, paramagnetic ^1H NMR spectra could be obtained. As shown in Figure 2, there are seven broad signals outside the diamagnetic range. This is expected for a stereochemically rigid ligand in **4** if the unpaired spin is delocalized predominantly through the chemical bonds. The experimental shifts at 325.5 K are as follows: −11.7, −10.3, 4.9, 9.3, 11.7, 24.9, and 325 ppm (negative shifts to low-field relative to THF-H_β). The relative intensities allow assignments of the phenyl protons: δ (H ortho) −11.7, δ(H meta) 4.9, and δ(H para) −10.3; ortho and meta protons are distinguished on the basis of shift sign alternation. Since reference data are lacking, further assignments are uncertain. This precludes the determination of isotropic shifts. All shifts decrease and broaden upon lowering of the temperature except for the small signals denoted with X. We believe that these arise from a diamagnetic impurity.

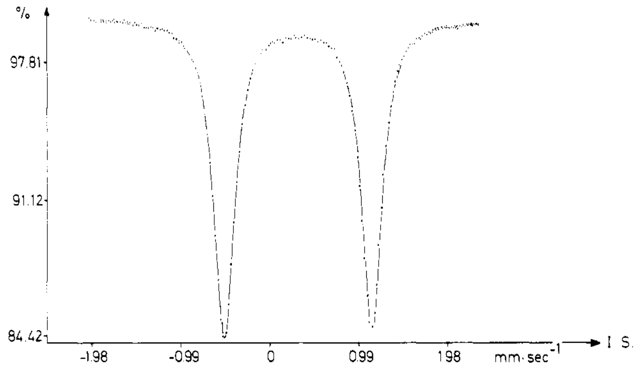


Figure 3. ^{57}Fe Mössbauer spectrum of the iron complex **4** at 4.2 K. (ordinate, transmission).

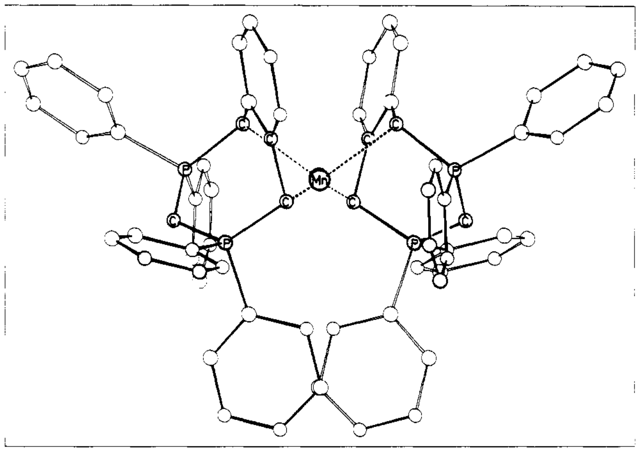


Figure 4. Molecular structure of the manganese complex **3** as determined by X-ray diffraction analysis. (Disordered solvent molecules are omitted.)

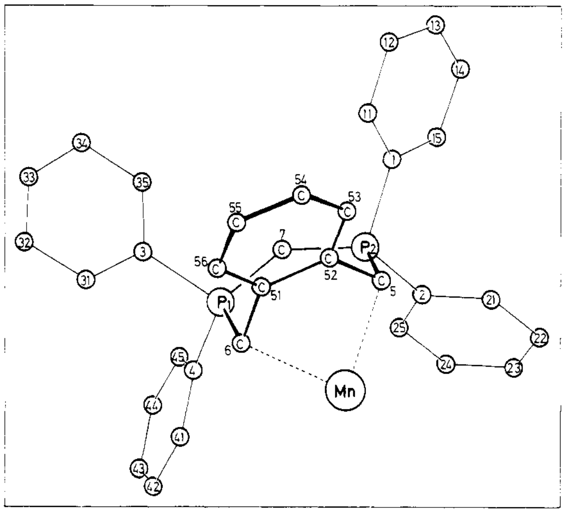


Figure 5. Metal–ligand interaction in the manganese complex **3**, as determined by X-ray diffraction, with atomic numbering.

Further evidence for a tetrahedral ligand arrangement is provided by the ^{57}Fe Mössbauer spectrum of crystalline **4** at 4.2 K. The spectrum consists of a doublet (Figure 3) centered at 0.204 (1) mm s^{-1} with a quadrupole splitting of 1.644 (1) mm·s^{-1}. High-spin Fe(II) compounds differ

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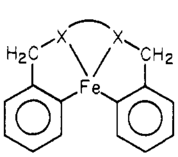
[27] Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287–306.

from low-spin Fe(II) compounds mainly by their large quadrupole splitting of 0.8–3.2 mm·s^{-1}.[28,29]

Hence the value found for FeL_2 is in good agreement with the results of the susceptibility measurements. The relatively low isomeric shift (IS) seems to be a characteristic feature of organoiron(II) compounds like **7**[30] or **4**, but further data are necessary to allow a generalization of this finding.

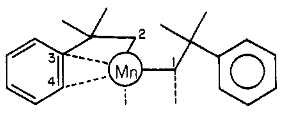


7

IS(mm·s^{-1}) = 0.44 (4) (X = N) and 0.68 (4) (X = O)

Crystal Structure of 3. **3** crystallizes in the space group $C2/_c$. The monoclinic cell contains discrete molecules, in which each manganese cation is coordinated by two equivalent ylide anions. Two THF molecules are found as interstitial solvate but have no contact to the metal centers.

Only very few dialkylmanganese(II) complexes have been structurally characterized. The dimer $[Mn(CH_2C(CH_3)_2C_6H_5)_2]_2$ provides useful reference data, however.[31] In this compound one of the 2-methyl-2-phenylpropyl ligands acts as a bridge between the Mn atoms. The distances Mn–C_1 and Mn–C_2 differ accordingly, and only the Mn–C_2 value is a suitable standard for the Mn–C(alkyl) two-center two-electron single bond. The agreement with the Mn–C(5,6) distances in **3** is quite satisfactory and characterizes the metal–ligand interaction in **3** as basically a set of four Mn–C σ bonds. There is also a phenyl–metal contact in both **3** and the reference compound,[31] as shown by distances in the range between 268 and 280 pm. The resulting trapezoidal ligand contact in **3–5** resembles the geometry in metal complexes with *o*-xylylidene ligands[24] described recently in the literature. Fundamental differences between these and the ylide ligands arise mainly from their relative steric requirements and the effect of the onium centers in the latter. Further work on related complexes and on multiple ylides with smaller ring sizes is in progress.



8

half of the dimer $[Mn(CH_2C(CH_3)_2C_6H_5)_2]_2$

Acknowledgment. This work has been generously supported by Fonds der Chemischen Industrie, Frankfurt/Main, and by Deutsche Forschungsgemeinschaft, Bonn - Bad Godesberg. Thanks are expressed to Professor J. Voitländer for providing the facilities for magnetic measurements.

Supplementary Material Available: Table V, observed and calculated structure factors, and thermal parameters for **3** (23 pages). Ordering information is given on any current masthead page.

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Synthesis and Stereochemistry of Some (Silylamino)phosphinimines

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A series of *P*-alkyl-*P*-halo-substituted (silylamino)phosphinimines, $(Me_3Si)_2NP(R)(X){=}NSiMe_3$, are obtained either by oxidative addition of RI (R = Et, *i*-Pr, *t*-Bu) to $(Me_3Si)_2NP{=}NSiMe_3$ or by treatment of $[(Me_3Si)_2N]_2PMe$ with I_2 or Br_2. Reaction of the iodophosphinimines with MeLi affords the dialkyl derivatives $(Me_3Si)_2NP(R)(Me){=}NSiMe_3$ (R = Et, *i*-Pr, *t*-Bu). Alcoholysis of the *t*-BuI product in the presence of Et_3N yields the N–H compounds $Me_3SiN(H)P(t\text{-Bu})(OR){=}NSiMe_3$ (R = Me, CH_2CF_3). Variable-temperature ^1H NMR studies of these (silylamino)phosphinimines demonstrate that, depending on what substituents are present, they may be fluxional via [1,3]-silyl exchange, hindered rotation about the amino P–N bond, or [1,3]-proton exchange. The results are discussed in terms of the electronic and steric effects of the phosphorus substituents.

Introduction

Several recent studies have focused on the preparative chemistry and dynamic stereochemistry of compounds containing the Si–N–P linkage. For example, their importance as polyphosphazene precursors[1,2] is now well established and their use in organophosphorus[3–5] and organometallic chemistry[6–8] is beginning to develop. Investigations of stereochemical features of these compounds,

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