

Synthesis of the Bis(iron) Carbene Complex [Cp*(dppe)FeC(OMe)CHCHC(OMe)Fe(dppe)Cp*][PF₆]₂: A Binuclear Organometallic Compound with a Low-Spin ↔ High-Spin Interconversion

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The new diiron μ -bis(carbene) complex [Cp*(dppe)Fe=C(OCH₃)-CH=CHC-(OCH₃)=Fe(dppe)Cp*][PF₆]₂ (**4**) [Cp* = pentamethylcyclopentadienyl, dppe = ethylenebis(diphenylphosphine)] was obtained by double deprotonation of [Cp*(dppe)Fe=C(OCH₃)CH₂CH₂C(OCH₃)Fe(dppe)Cp*]·2[PF₆] (**2**) with KOBu^t followed by a two-electron oxidation with 2 equiv of ferrocenium (80%). On the basis of the multinuclear NMR spectroscopy the complex **4** appeared as diamagnetic in solution. Temperature-dependent magnetic susceptibility measurements with a microcrystalline sample of **4** showed antiferromagnetic behavior. Isotropic spin-only models of the data derived magnetic exchange coupling constants of $J = -27.4 \text{ cm}^{-1}$. Variable-temperature Mössbauer spectroscopy allowed the observation of both the singlet and triplet spin isomers and their interconversion. The time scale for the spin flipping is larger than 10^{-6} s , suggesting the existence of a thermal barrier between the two spin states.

In a small number of molecular transition metal complexes, the metal ion is capable of undergoing a spin-state interconversion. Depending on the relative values of the ligand-field strength and the mean electron-pairing energy, the ground states are either high-spin or low-spin.^{1–3} The interconversion between the spin states can be induced by an external perturbation such as a variation of the temperature, a variation of the pressure, or an irradiation with light. Interconversion of spin states is generally observed for mononuclear complexes, but it was also observed for a very small number of dinuclear compounds in which the metals are linked by σ -bound bridging atoms.¹

Recently, we found an equilibrium between two spin states for the bimetallic complexes [Cp*(dppe)Fe-C₄-Fe(dppe)Cp*][PF₆]₂ (**1**), in which the metal centers are connected by the π -electron-rich -C₄- chain.⁴ Depending on the cumulenyl (**1a**) versus butadiynediyl (**1b**) structure of the carbon bridge, the metal centers of the two terminal ends are formally 18-electron iron(II) or 17-electron iron(III) ions. Therefore, the complex is either diamagnetic ($S = 0$) or paramagnetic ($S = 1$). Both structures are in equilibrium, and the singlet-triplet energy gap ($J = -18.2 \text{ cm}^{-1}$) is weak enough to render the complex paramagnetic at liquid nitrogen temperature.⁵ This situation is far to be general, and

the closely related rhenium complex [Cp*(NO)(PPh₃)-Re-C₄-Re(PPh₃)(NO)Cp*][PF₆]₂ is diamagnetic at all temperatures.⁶

The spin transition is usually accompanied by a reorganization of the geometry of the metal-ligand distances.⁷ In the case of the CpFe(dppe) unit, it has been noted that the geometries of the coordination spheres of iron(II) and iron(III) are very similar;⁸ therefore one can assume that the reorganization of **1** upon spin conversion might mainly concern the electronic structure of the bridging ligand. However, in such a one-dimensional molecule, when the singlet and triplet interconvert, the position of the atoms in the Fe-C₄-Fe assembly should not be significantly modified. Indeed, the singlet-to-triplet isomerization process might be associated with an increase of the Fe-C _{α} and C β -C β' bond lengths, whereas in the same time, the triple bonds C α ≡C β shorten. Therefore, an increase of the bond length alternation is expected, but the iron-iron distances are thought to become slightly longer, since the total numbers of bonds in the FeC₄Fe linkage are 10 and 9 in the singlet and triplet states, respectively. As a result, the two magnetic states interconvert without detectable thermal barrier.⁴

We thought that replacing the all-carbon bridge in **1** by a two-dimensional butadienediyl spacer, as depicted in Scheme 2, could be a possible way for increasing the thermal barrier between the two spin states. This

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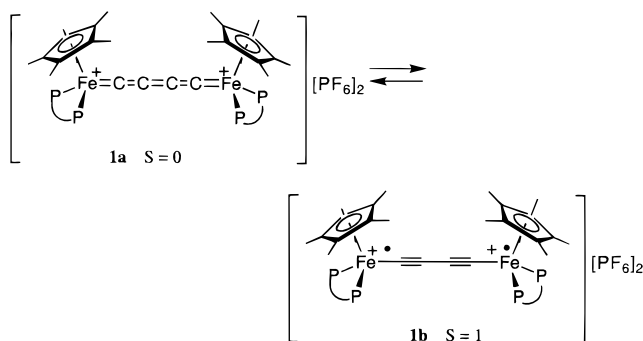
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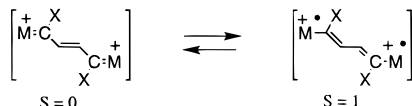
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Scheme 1



Scheme 2



hydrocarbon spacer is no longer linear, and if the singlet–triplet still interconvert, the two-dimensional reorganization of the spacer should be more entropy demanding. Therefore, the lifetime of the two spin states could be long enough to allow the observation of the two discrete states of the molecule.

With this ultimate goal, we have synthesized the iron bis(carbene) complex $[\text{Cp}^*(\text{dppe})\text{Fe}=\text{C}(\text{OCH}_3)\text{CH}=\text{CHC}(\text{OCH}_3)\text{Fe}(\text{dppe})\text{Cp}^*][\text{PF}_6]_2$ (**4**). On the basis of the NMR and magnetic susceptibility measurements, the complex **4** appeared as diamagnetic in solution. In the solid state, a spin-crossover was observed by magnetic susceptibility measurements and variable-temperature Mössbauer spectroscopy.

The binuclear μ -bis(carbene) complex $[\text{Cp}^*(\text{dppe})\text{Fe}=\text{C}(\text{OCH}_3)\text{CH}=\text{CHC}(\text{OCH}_3)\text{Fe}(\text{dppe})\text{Cp}^*] \cdot 2[\text{PF}_6]$ (**4**) was obtained in a two-step one-pot procedure starting from the previously described bis(carbene) $[\text{Cp}^*(\text{dppe})\text{Fe}=\text{C}(\text{OCH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{OCH}_3)\text{Fe}(\text{dppe})\text{Cp}^*] \cdot 2[\text{PF}_6]$ (**2**).⁹ In the first step, a double proton abstraction was carried out by treatment of an orange solution of **2** with 2.4 equiv of KO^tBu . After removal of the solvent under vacuum, the salmon pink crude solid was washed with pentane. This very unstable species was supposed to be the bis(vinyl)-bridged diiron complex **3** (see Scheme 3) and was used without further purification and characterization. Addition of 1.95 equiv of ferrocenium salt to a CH_2Cl_2 solution of **3** induced a fast color change from fuchsia to dark blue. After concentration of the solution, a deep blue powder corresponding to the dimethoxybutadienediyl-bridged bis(carbene) **4** was precipitated by addition of pentane. The crude solid isolated in 80% yield was crystallized from a CH_2Cl_2 /diethyl ether mixture (2:1) at -20°C . Analytically pure and thermally stable microcrystals of **4** were collected and characterized by multinuclear NMR spectroscopy. The ^1H NMR spectrum of **4** allowed the observation of a single set of proton resonances, indicating the presence of only one geometric isomer. The hydrogen atoms of the Cp^* and C_βH were observed at δ 1.22 and 5.48, respectively. The carbene carbon atoms resonate almost 40 ppm downfield lower than in the parent bis(carbene) **2**.⁹ Surprisingly, the ^{31}P NMR spectrum displays a broad singlet for the phosphorus atom resonance.¹⁰ This signal, more than

40 times broader than the peak of the PF_6^- anion, was suggestive of a paramagnetic character for complex **4**.¹¹ Indeed, in the $[\text{Cp}^*(\text{dppe})\text{Fe}(\text{III})\text{L}]^+$ series, as in other organometallic paramagnetic series, the ^{31}P NMR resonances are generally not observed.¹² However, the determination of the magnetic moment of **4** in solution (CD_2Cl_2 and $\text{CD}_3\text{C}(\text{O})\text{CD}_3$) by the Evans methods^{13,14} ($\mu_{\text{eff}} = 0.0 \pm 0.1 \mu_{\text{B}}$) indicated that the binuclear complex **4** is essentially diamagnetic in solution, in agreement with its biscarbene structure. Note that the closely related compound $[(\text{C}_5\text{H}_5)(\text{dppm})\text{Fe}(\text{=CH-CH=CH-CH=})\text{Fe}(\text{dppm})(\text{C}_5\text{H}_5)][\text{PF}_6]_2$ was X-ray characterized and also identified as diamagnetic.¹⁵

The paramagnetic character of **4** was definitely established by ESR spectroscopy at low temperature. The spectrum of a solid sample of **4** recorded at 74 K displayed an unresolved broad signal with a peak-to-peak field difference $\Delta H_{\text{pp}} = 530$ G at $g = 2.10$. This g value is typical of low-spin Fe(III) complexes.⁸ The broadening of the signal is characteristic of the presence of two unpaired electrons in the same molecule, which greatly shortens the relaxation time.¹⁶ Moreover, the triplet state character of the ESR-active species was probed by the observation a sharp $\Delta m_s = 2$ transition ($g = 4.31$). The spectrum recorded at 4 K under the same conditions displayed a much weaker signal without variation of the g tensor and line broadening, suggesting that the triplet was not the ground state.

The spin ground state of **4** was further probed on a SQUID magnetometer with a recrystallized sample over the temperature range 5–300 K. The temperature dependence of the magnetic susceptibility is shown in Figure 1 in the form of $\chi_{\text{m}}T$ versus T . At room temperature, $\chi_{\text{m}}T$ equals $1.77 \text{ emu K mol}^{-1}$, a value much larger than what is expected for two $S = 1/2$ local spins. As T is lowered, $\chi_{\text{m}}T$ first decreases as a linear function of T down to *ca.* 100 K, then decreases more and more rapidly, and tends to zero as T approaches absolute zero. For such a binuclear system in which the metal ions are both pseudooctahedral Fe(III), with a single unpaired electron located on each metal atom, the dependence of the magnetic susceptibility on temperature can be modeled by using the modified Bleaney–Bowers expression (eq 1).² In this equation, \bar{g} is the averaged g

$$\chi = \frac{2N\bar{g}^2\mu_{\text{B}}^2}{kT[3 + \exp(-J/kT)]}(1 - \rho) + \frac{N\bar{g}^2\mu_{\text{B}}^2}{2kT}\rho + C \quad (1)$$

value and ρ is the molar fraction of the noncoupled species. It is assumed that the “impurity” follows the

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(10) It was checked that the broad ^{31}P NMR signal was not due to adventitious traces of the mixed-valence $[\text{Cp}^*(\text{dppe})\text{Fe}=\text{C}(\text{OCH}_3)\text{CHCHC}(\text{OCH}_3)\text{Fe}(\text{dppe})\text{Cp}^*][\text{PF}_6]$ complexes in the solution by addition of a minute amount of ferrocenium.

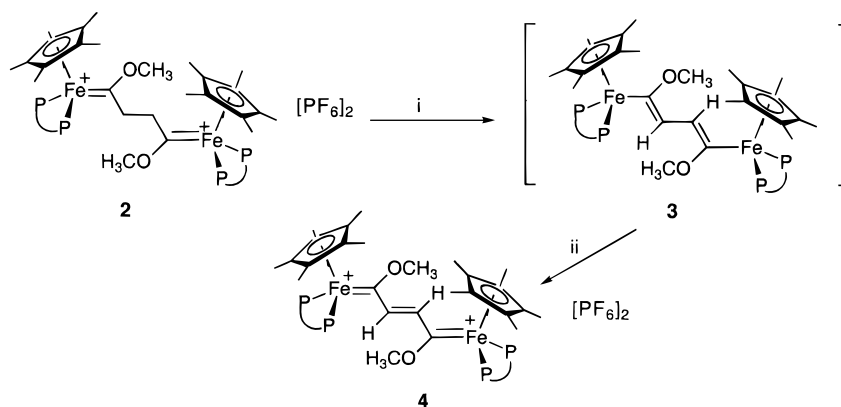
(11) From a theoretical approach it was previously stated that in dinuclear dications connected by conjugated bridges the HOMO–LUMO gaps are very small. As a consequence, it was suggested that some of these species might have open-shell ground states.

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Scheme 3^a

^aReagents and conditions: (i) THF, KOBu^t (2.4 equiv), 20 °C, 3 h; (ii) CH₂Cl₂, [(C₅H₅)₂Fe][PF₆] (1.95 equiv), 20 °C.

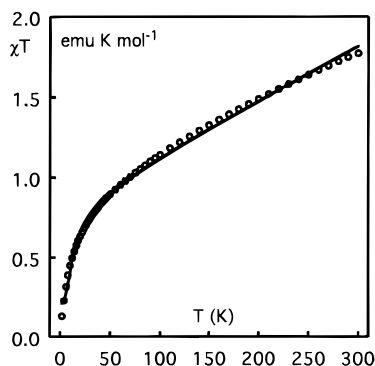


Figure 1. χT versus T plot for **4**. Solid line is the theoretical curve calculated with eq 1.

Curie law and has the same molecular weight and the same g factor as the actual compound. The parameter C describes the temperature-independent contribution from angular momentum (spin–orbit coupling).² Similar treatments were successfully used to evaluate the extent of magnetic exchange between paramagnetic Cp*(dppe)-Fe(III) sites in related complexes.^{5,16} In this case, the spin–orbit coupling is rather large and produces the linear variation of $\chi_m T$ versus T in the range 100–300 K.

The line drawn through the data points in Figures 1 is the best fit of parameters obtained with eq 1 using the experimental g value ($g = 2.10$): $J/k = -39.1 \pm 0.2$ K (-27.4 ± 0.2 cm⁻¹), $\rho = 0.12 \pm 0.01$, and $C = 0.0027 \pm 0.0002$ emu mol⁻¹.¹⁷ From these data, three important conclusions may be drawn: (i) the complex **4** is paramagnetic in the solid state, (ii) the singlet–triplet transition is smooth, and the triplet lies above the singlet in agreement with an antiferromagnetic exchange between the two $S = 1/2$ iron centers, (iii) the dependence of the magnetic susceptibility on temperature could be modeled by the Bleaney–Bowers expression, indicating that the spin states are in equilibrium. Moreover, as the transition is very smooth, we assume that the structural changes associated with the spin conversion upon cooling or warming should be short-

range ones inside the dimer or concerning the closest neighbors, but not affecting all the solid.²

Among the physical methods that have been used to follow the spin transition as a function of temperature, Mössbauer spectroscopy has proven to be a very efficient tool.¹⁸ The zero-field ⁵⁷Fe Mössbauer spectra of the microcrystalline samples of complex **4** were recorded in the range 4.5–293 K. Spectral features were least-squares fit to Lorentzian line shapes, and the fitting parameters are given in Table 1. The spectrum recorded at 4 K, which can be considered as representative of the ground state, displays a unique doublet, as illustrated in Figure 2 (bottom). The isomeric shift (δ) and quadrupole splitting (QS) parameters are suggestive of the bis(carbene) structure **4a** (Scheme 5). Indeed, the parameters determined at 80 K for the related mononuclear carbene [Cp*(dppe)Fe=C(OCH₃)CH₃][PF₆] (**5**, $\delta = 0.216$ mm s⁻¹ vs Fe, QS = 1.223 mm s⁻¹) are not very different from those obtained for **4**.¹⁹ Moreover, it seems likely that in a binuclear μ -bis(carbene) compound in which the metal centers are linked by a conjugated π -system, the participation of the oxygen atom in the stabilization of the complex should be less efficient than in the mononuclear Fischer-type carbene complex **5** as depicted in Scheme 4. To evaluate the possible influence of the oxygen atom on the QS, the known ethylidene iron complex [Cp*(dppe)Fe=C(H)-CH₃][PF₆] (**6**) was taken as a model.⁹ The synthesis of the stable iron carbene **6** has been previously reported by our group. The Mössbauer spectrum of **6** displayed a single doublet ($\delta = 0.148$ mm s⁻¹ vs Fe, QS = 1.081 mm s⁻¹). As expected, the Mössbauer parameters obtained for **6** are closer to those observed for **4** than those found for **5**.

Above 4.5 K, a second doublet appeared in the spectrum (Figure 2), indicating a partial transformation of the complex **4** and the presence of a second iron site. The intensity of this doublet reversibly increases with the temperature, and its parameters are significantly different from those of the ground-state, indicating significant changes at the iron nuclei. One can note both an increase of δ and a decrease of the QS values (Table 1). According to the investigation of the iron–carbon bonding by Mössbauer spectroscopy that we previously

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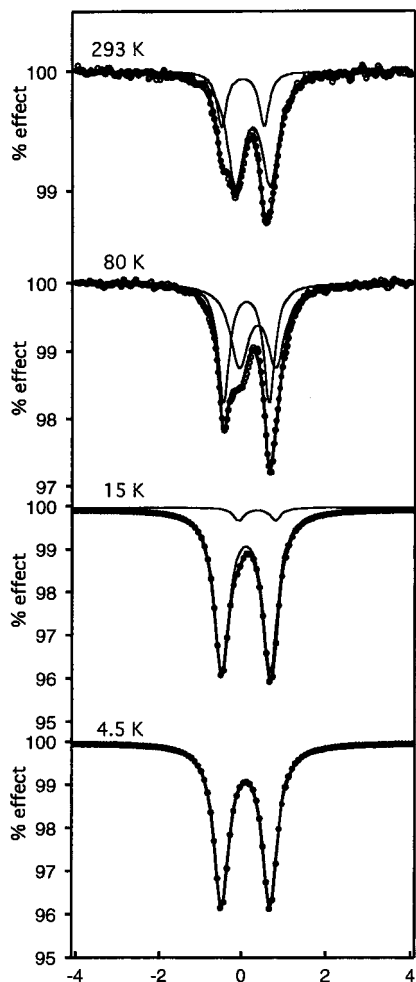
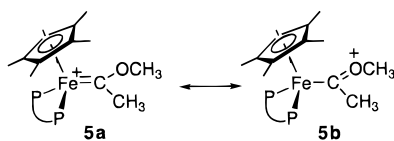
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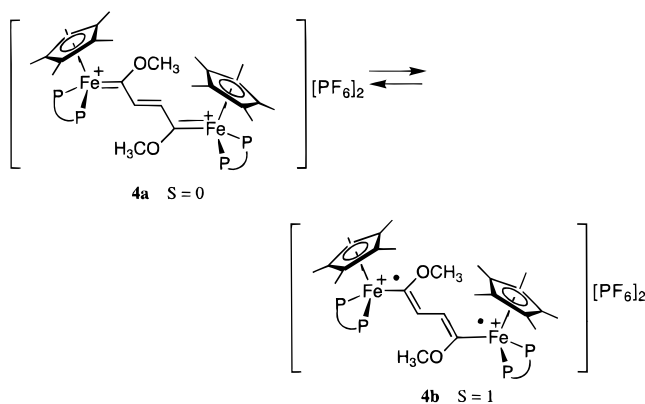
Table 1. ^{57}Fe Mössbauer Fitting Parameters Determined for Compounds **4**

T (K)	$S = 1$			$S = 0$			α^a	α^b
	δ (mm/s)	γ (mm/s)	QS (mm/s)	δ (mm/s)	γ (mm/s)	QS (mm/s)		
4.5				0.216	0.163	1.117	0.00 ± 0.05	0.00 ± 0.01
10	0.46		0.95	0.216	0.170	1.124	0.05 ± 0.05	0.06 ± 0.01
15	0.46	0.15	0.94	0.21	0.21	1.13	0.15 ± 0.05	0.18 ± 0.01
20	0.49	0.19	0.96	0.22	0.23	1.10	0.36 ± 0.05	0.29 ± 0.01
40	0.47	0.23	0.85	0.22	0.16	1.07	0.50 ± 0.05	0.53 ± 0.01
80	0.48	0.21	0.83	0.23	0.15	1.06	0.58 ± 0.05	0.64 ± 0.01
150	0.46	0.21	0.81	0.22	0.15	1.04	0.64 ± 0.05	0.69 ± 0.01
220	0.42	0.21	0.80	0.19	0.15	1.01	0.69 ± 0.05	0.71 ± 0.01
293	0.38	0.24	0.81	0.15	0.17	0.99	0.77 ± 0.05	0.72 ± 0.01

^a α , the molar fraction of **4** in the triplet state, $(1 - \alpha)$ corresponds to the molar fraction of the singlet and was calculated from the relative spectral absorption areas of the two Mössbauer doublets. ^b α was calculated from $|\Delta E_{\text{ST}}| = 39.1$ K using the Boltzmann thermal population law.

**Figure 2.** Variable-temperature ^{57}Fe Mössbauer spectrum for **4** (velocity scale referenced to iron metal, source ^{57}Co).**Scheme 4**

carried out for various iron(II) and iron(III) mononuclear complexes of the $\text{Cp}^*\text{Fe}(\text{dppe})$ series, these small QS parameters are typical of $\text{Cp}^*(\text{dppe})\text{Fe}(\text{III})$ centers¹⁹ and strongly support the structure expected for the triplet state. The isomeric shift seems to be large for an iron(III) derivative of this series, which more usually range between 0.2 and 0.4 mm s⁻¹ vs Fe.⁸ However,

Scheme 5

considering that the larger δ value reported for the iron(II) complexes of this series was obtained for the vinyl iron(II) compound $\text{Cp}^*(\text{dppe})\text{Fe}-\text{C}(\text{=CH}_2)\text{OCH}_3$ (**7**, $\delta = 0.323$ mm s⁻¹ vs Fe, QS = 1.904 mm s⁻¹ at 80 K)¹⁹ and the fact that the isomeric shifts are often larger for the low-spin iron(III) compounds than for the corresponding iron(II) derivatives,⁸ the large δ value obtained for **4** in the high-spin state can be regarded as consistent with the proposed structure **4b**.

The relative spectral absorption areas corresponding to the two different iron centers depend on the temperature. As the temperature increases from 4 to 293 K, the molar fraction α of high-spin molecules ($S = 1$) increases. This result was deduced from the relative areas found for the doublets of the high-spin and low-spin molecules (Table 1). At 15 K, the high-spin signal area is roughly 15% of the total spectral area, while the relative amount of high-spin molecules was calculated to be close to 77% at 293 K. The values of α were also independently calculated at all temperatures using the Boltzmann thermal population law [$\alpha = 3/(3 + \exp(-\Delta E_{\text{ST}}/kT))$] for a singlet–triplet energy gap $|\Delta E_{\text{ST}}| = 39.1$ K as determined from the magnetic susceptibility measurements. Assuming 5–8% of experimental error in the determination of the relative surface areas of the Mössbauer doublets (see Table 1), the values of α determined by both methods are in good agreement (Figure 3). We have checked by ^1H NMR that **4** still exhibits a diamagnetic behavior in solution, and further addition of diethyl ether gives back a paramagnetic solid sample. However, at this stage it must be emphasized that the singlet–triplet ratio varies from one microcrystalline sample to another by ca. ± 5 –10%, as derived

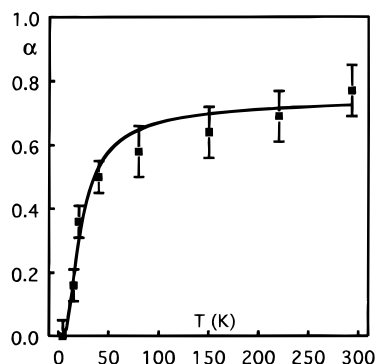


Figure 3. Temperature dependence of the molar fraction α of the high-spin isomer of **4**. Solid line is the curve calculated for $|\Delta E_{ST}| = -27.4 \text{ cm}^{-1}$, and the squares represent the experimental values determined from the relative spectral absorption areas of the Mössbauer quadrupole doublets.

by Mössbauer spectroscopy. This was also noted for spin transitions in various inorganic compounds.^{2,20,21}

The fact that two distinct signals are seen in the Mössbauer spectra of **4** means that the rate at which individual molecules interchange from singlet to triplet (or vice versa) is less than the inverse of the ^{57}Fe Mössbauer time scale (10^{-6} s). The separation between the low-spin and high-spin doublets ($\Delta\delta$) remains constant in the range 10–293 K, and there is very little line broadening as the temperature increases. Therefore, coalescence effects cannot be detected and the rate of spin flipping is expected to be less than 10^6 s^{-1} , suggesting the existence of a thermal barrier between the two spin states. At present, compound **4** constitutes the first example of an organometallic symmetric dimer stable enough in two different spin states to allow the spectroscopic observation of both the triplet and the singlet. However, the discrepancy between the magnetic properties of **4** in solution and in the solid state remains an open question. The interaction of the dication with the solvent, the more polar nature of the ionic solid, or changes in the geometry of the bridge could constitute possible explanations for this effect.

On the other hand, as most of the organometallic compounds were spectroscopically characterized in solution, it cannot be excluded that for some of them having a structure close to **4** a spin transition has not yet been identified. Comparison of the singlet–triplet separation in the complexes **1** and **4** is also interesting. As both

compounds have the same terminal ends, it can be stated that a two-dimensional spacerlike $-\text{C}(\text{OCH}_3)-\text{CHCHC}(\text{OCH}_3)-$ seems to give a larger low-spin, high-spin energy gap than the rodlike all-carbon $-\text{C}_4-$ structure, at least in the solid state. Current work is underway in order to explore further the evolution of the singlet–triplet gap upon bridge extension²² and in nonsymmetrical organometallics.²³

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were dried and distilled from sodium benzophenone ketyl prior to use. Pentamethylcyclopentadiene was prepared according to the published procedure,²⁴ and other chemicals were used as received. All the manipulations were carried out under an argon atmosphere using Schlenk techniques or in a Jacomex 532 drybox filled with nitrogen. Routine NMR spectra were recorded using a Bruker DPX 200 spectrometer. High-field NMR spectra experiments were performed on a multinuclear Bruker WB 300 instrument. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra, and H_3PO_4 for ^{31}P NMR spectra. X-band ESR spectra were recorded on a Bruker ESP-300E spectrometer. An Air Products LTD-3-110 liquid helium transfer system was attached for the low-temperature measurements. Magnetic susceptibility measurements were performed with a SQUID (susceptometer quantum interface device) instrument. Data were corrected for magnetization of the sample holder and capsule used, and diamagnetic contributions were estimated from Pascal's constants. The ^{57}Fe Mössbauer spectra were obtained by using a constant acceleration spectrometer previously described with a 50 mCi ^{57}Co source in a Rh matrix.²⁵ The sample temperature was controlled by an Oxford MD306 cryostat and a Oxford ITC4 temperature controller. Computer fitting of the Mössbauer data to Lorentzian line shapes was carried out with a previously reported computer program.^{26,27} The isomer shift values are reported relative to iron foil at 298 K and are not corrected for the temperature-dependent second-order Doppler shift. The Mössbauer sample cell consists of a 2 cm diameter cylindrical Plexiglas holder. Elemental analyses were performed at the Centre for Microanalyses of the CNRS at Lyon-Solaise, France.

[Cp*(dppe)Fe=C(OMe)CH=CHC(OMe)=Fe(dppe)Cp*]·[PF₆]₂ (4**).** To 0.680 g (0.43 mmol) of $[\text{Cp}^*(\text{dppe})\text{Fe}=\text{C}(\text{OMe})-\text{CH}_2\text{CH}_2\text{C}(\text{OMe})=\text{Fe}(\text{dppe})\text{Cp}^*][\text{PF}_6]_2$ in 30 mL of THF was added 2.4 equiv of KOBut (0.116 g). The mixture was stirred for 5 h at 20 °C. The solution was filtered and the solvent removed under vacuum. The salmon pink solid was washed with cold pentane ($2 \times 10 \text{ mL}$). The solid was dried under vacuum and dissolved in CH_2Cl_2 (30 mL), and 1.9 equiv (0.270 g, 0.8 mmol) of ferricinium salt was added. The solution turned blue and was stirred for an additional 8 h. The solvent was removed under vacuum to 2–3 mL, and a large excess of pentane (75 mL) was added to precipitate a dark blue powder. The solid was washed with pentane, dried, and identified as **4** (yield 0.516 g, 80%). Anal. Calcd for $\text{C}_{87}\text{H}_{86}\text{F}_{12}\text{Fe}_2\text{O}_2\text{P}_6$: C, 56.29; H, 5.42. Found: C, 56.76; H, 5.40. ^1H NMR (20 °C, CD_2Cl_2): δ_{H} 7.40 (m, 40 H, Ph); 5.48 (s, 2 H, CH); 3.26 (m, 4 H, CH_2P); 2.88 (m, 4 H, CH_2P); 2.69 (s, 6 H, OCH_3); 1.22 (s, 30 H, C_5Me_5). ^{13}C NMR (20 °C, CD_2Cl_2): δ_{C} 293.2 (t, $^2J_{\text{CP}} = 27 \text{ Hz}$, $\text{C}=\text{Fe}$); 133.0 (m, Ph); 99.8 (s, C_5Me_5); 64.8 (q, $^1J_{\text{CH}} = 147 \text{ Hz}$, OCH_3); 32.3 (t, $^1J_{\text{CP}} = 21.1 \text{ Hz}$, CH_2P); 10.86 (q, $^1J_{\text{CH}} = 127.4 \text{ Hz}$, C_5Me_5). ^{31}P NMR (20 °C, CD_2Cl_2): δ_{P} 105.4, s.

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