

Cationic diphosphaferrocene gallium dichloride complexes†

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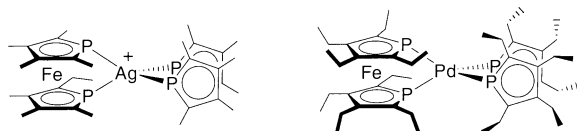
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The octaethyldiphosphaferrocene ligand **1** reacts with gallium trichloride at room temperature to afford the cationic complex $[(1)GaCl_2]^+[GaCl_4]^-$. To definitely establish the formula of **2**, which could not be crystallized, the synthesis of the corresponding complex incorporating the octa(*n*-propyl)diphosphaferrocene ligand **6** was carried out. Preparation of ligand **6** was achieved *via* a three-step sequence. In a first step the tetra(*n*-propyl)zirconacyclopentadiene **3** was synthesized from dichlorozirconocene, 4-octyne and butyllithium. Reaction of **3** with 1 equiv. of PCl_3 affords the 1-*P*-chloro-2,3,4,5-tetra(*n*-propyl)phosphole **4**, which is subsequently converted to the corresponding tetra(*n*-propyl)phospholide anion **5** through reaction with lithium metal. Reaction of **5** with half an equivalent of $FeCl_2$ yields ligand **6**. The formulation of **6** was ascertained by an X-ray crystal structure, which reveals that the ligand adopts a C_i conformation. Reaction of an equimolar amount of **6** with $GaCl_3$ affords the $[(6)GaCl_2]^+[GaCl_4]^-$ complex **7**, which was successfully characterized by X-ray crystallography. In **7**, the diphosphaferrocene ligand acts as a chelate and the overall geometry around gallium is tetrahedral. Theoretical calculations carried out using the BP86 functional indicate that the bonding of the diphosphaferrocene ligand to the $[GaCl_2]^+$ fragment involves the lone pairs on the phosphorus atoms and a contribution of the P–Fe bond.

Though they were discovered more than twenty years ago,¹ the coordination chemistry of phosphaferrrocenes has only become the focus of great deal of research over the last few years.² This interest mainly results from their potential use as ligands in some catalytic processes of importance.³ In contrast, less attention has been paid to diphosphaferrocenes, essentially because the presence of the two phosphorus atom lone pairs seriously complicates the outcome of their reaction with metals. Indeed, η^1 -coordination appears to be the most widespread bonding mode with complexes having potentially one vacant site. However, dimers or polymeric materials often result from their reaction with precursors having at least two vacant sites. The substitution scheme of the ring was found to play a decisive role in the outcome of these reactions, and earlier studies by Cowley *et al.* have showed that α,α' -disubstituted diphosphaferrocenes, such as the octamethyl derivative, can bind one metal center in a chelate fashion (Scheme 1).⁴ Interestingly, this binding mode involves an unusual side-on coordination of the two phosphorus atom lone pairs. Assuming that the high sphericity of the P lone pair may be responsible for this very specific reactivity, we launched a

program aimed at exploring the coordinative behavior of such sterically encumbered ligands. Recently, we synthesized the first homoleptic group 10 metal complexes with Pd(0) and Ni(0) (Scheme 1).^{3d} During the course of this study, we observed that this side-on coordination significantly reduces the strength of the phosphorus–metal bond and that diphosphaferrocenes can behave as hemilabile ligands when they are coordinated in such a way. We then postulated that this weakly coordinating behavior could be exploited to devise highly active catalysts. Thus, the $[Pd(1)_2]$ complex efficiently catalyzes the Suzuki cross-coupling reaction of boronic acid with aryl bromides and the coupling between dialkoxyboranes and aryl iodides (Myaura reaction) at very low catalyst loads.^{3e}

With these promising results at hand we next focused our attention on the chemistry of group 13 complexes. Indeed, though some studies have been carried out in the past,⁵ no stable diphosphaferrocene complexes of group 13 elements have been synthesized so far and we thought to exploit the isolobal analogy between the 14 valence electron fragments $[MX_2]^+$ (M = group 13 element) and $[M'L_2]$ (M' = group 10 metal) to isolate stable species. We report herein the preparation, characterization and theoretical investigations on cationic gallium chloride derivatives.



Scheme 1 Chelate diphosphaferrocene complexes.

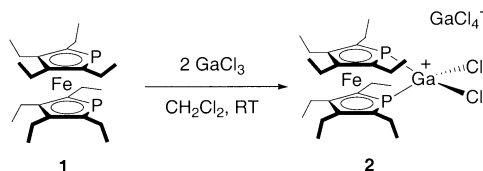
† Electronic supplementary information (ESI) available: optimized geometries of the ligand and gallium complexes and some MOs. See <http://www.rsc.org/suppdata/nj/b2/b204075c/>

Results and discussion

Syntheses of ligands and complexes

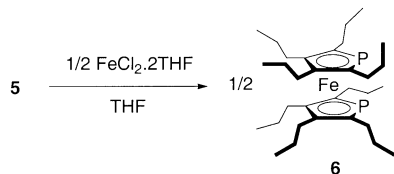
Preliminary experiments were carried out with the readily available tetra(*n*-ethyl)-1,1'-diphosphaferrocene **1**. Reaction of 1 equiv. of ligand with 2 equiv. of $GaCl_3$ in dichloromethane proceeds cleanly to yield a single species, which is characterized by a strong upfield ^{31}P NMR chemical shift:

$\delta(\text{CH}_2\text{Cl}_2) -265.1$ ppm ($\Delta\delta$ compared to the free ligand **1** = -199.1 ppm).

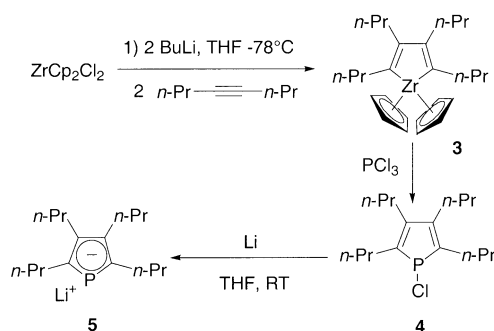


The formulation of this compound could not be unambiguously established on the basis of ^1H , ^{13}C , ^{31}P NMR data and elemental analyses. Though analyses indicated the presence of one ligand molecule, two gallium and six chloride atoms, two different formulations can be proposed. A cationic chelate complex **2a**, shown in eqn. (1), in which the ligand binds a $[\text{GaCl}_2]^+$ fragment or a classical bis η^1 -complex **2b**. Unfortunately, despite many attempts, no suitable single crystals could be obtained, thus precluding a X-ray crystallographic study.

As in many cases, a subtle change in the substitution scheme of the ligand can induce significant improvements in the growing of suitable crystals. Therefore, we focused our study on the unknown octa(*n*-propyl) derivative **6**. Its synthesis was achieved using a similar procedure as that used for ligand **1**. The strategy (Scheme 2) relies on a metallacycle transfer reaction from the tetra(*n*-propyl) zirconacyclopentadiene **3**, which is obtained by reacting zirconocene with 2 equiv. of 4-octyne according to a previously reported procedure.^{3d} The 1-chloro-phosphole **4**, which results from the reaction of **3** with PCl_3 , was then subsequently reduced with 2 equiv. of lithium to yield the phospholide anion **5**, which was characterized by ^{31}P NMR spectroscopy exclusively. All NMR data of **4** and **5** compare with those of their *n*-tetraethyl counterparts and thus deserve no particular comments. Diphosphaferrocene **6** was prepared in a manner similar to **1** by reacting 2 equiv. of anion **5** with 1 equiv. of FeCl_2 in THF.



The formulation of **6** was unambiguously established on the basis of NMR data and elemental analyses. A definitive evidence was given by a X-ray crystallographic study. An ORTEP view of one molecule of **6** is presented in Fig. 1, experimental data are given in Table 1 and the most important bond distances and angles are listed in Table 2. As can be seen, the ligand adopts a C_i conformation, the two phosphorus atoms pointing in opposite directions ($\theta = 180^\circ$), and all the *n*-propyl groups point out of the planes of the rings to relieve



Scheme 2 Synthesis of phospholide anion **5**.

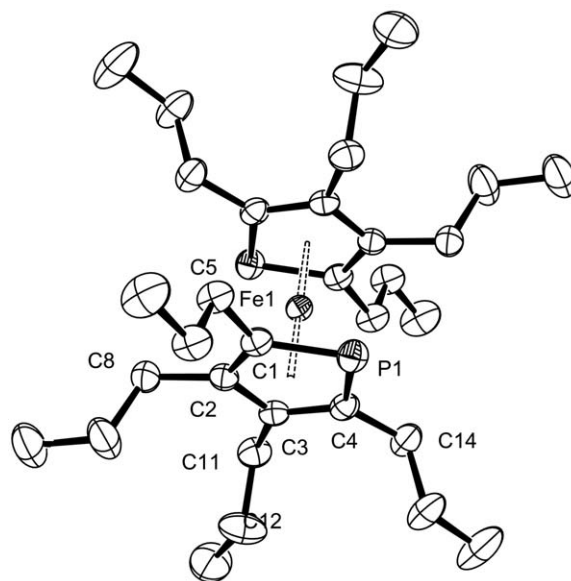
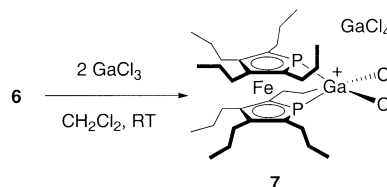


Fig. 1 The molecular structure of compound **6**.

steric congestion.⁶ Bond distances and angles are very similar to those reported for **1**.

As described for the synthesis of complex **2**, ligand **6** cleanly reacts with GaCl_3 to yield complex **7**, which was fully characterized by NMR spectroscopy.



All NMR data are very similar to those recorded for **2** and the presence of eight additional methylene groups does not induce any important changes. On the basis of these data we assumed that both complexes adopt the same overall geometry. However, the change in the substitution scheme of the ligand turned out to be fruitful and we succeeded in growing large crystals of

Table 1 Crystal data and structural refinement details for structures of compounds **6** and **7**

	6	7
Empirical formula	$\text{C}_{32}\text{H}_{56}\text{FeP}_2$	$\text{C}_{32}\text{H}_{56}\text{Cl}_6\text{FeGa}_2\text{P}_2$
FW	558.56	910.70
T/K	223.0(1)	150.0(1)
$\lambda/\text{\AA}$	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
$a/\text{\AA}$	18.759(5)	11.558(5)
$b/\text{\AA}$	17.551(5)	14.425(5)
$c/\text{\AA}$	9.964(5)	25.091(5)
β/deg	91.310(5)	
$U/\text{\AA}^3$	3280(2)	4183(2)
Z	4	4
$\mu(\text{Mo K}\alpha)/\text{cm}^{-1}$	0.575	2.102
Reflect measured	12676	12107
Ind. reflect.	7512	12107
reflect. used	5770	10601
R_{int}	0.0221	0.0000
$R_1^a [I > 2\sigma(I)]$	0.0374	0.0310
$wR_2^b [I > 2\sigma(I)]$	0.0986	0.0716

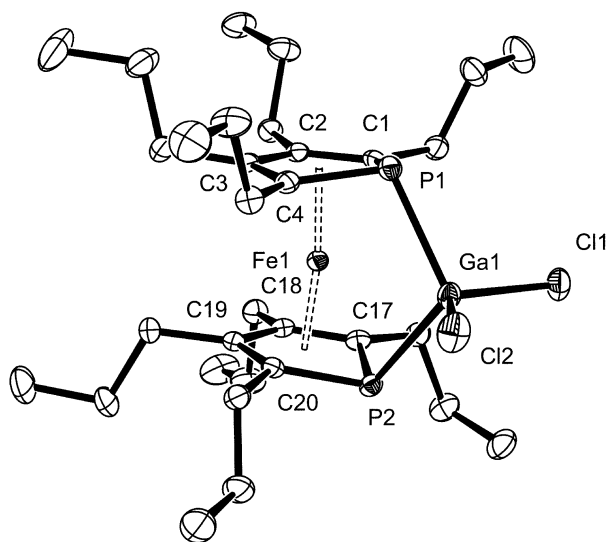
^a $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$, ^b $wR_2 = (\Sigma w|F_o| - |F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (deg) for compound **6**

P(1)–C(1)	1.776(2)	C(4)–P(1)–C(1)	89.82(8)
C(1)–C(2)	1.423(2)	P(1)–C(1)–C(2)	112.9(1)
C(2)–C(3)	1.434(2)	C(1)–C(2)–C(3)	112.3(2)
P–Fe	2.299(1)	C(2)–C(3)–C(4)	112.0(2)
C(3)–C(4)	1.425(2)	C(3)–C(4)–P(1)	113.0(1)
C(4)–P(1)	1.777(2)		
Ct–Fe(1)	1.659		

7 by slow diffusion of hexanes in a dichloromethane solution of the complex. An ORTEP view of one molecule of **7** is presented in Fig. 2, experimental data are given in Table 1 and the most important bond distances and angles are listed in Table 3.

As can be seen, the complex is cationic and coordination of a $[\text{GaCl}_2]^+$ fragment occurs through the two phosphorus atom lone pairs in a chelate fashion. The overall geometry around gallium is tetrahedral as expected for a Ga(III) center. As previously observed in the X-ray structure of the bis chelate $[\text{Pd}(\text{I})_2]$ complex, there is an important deviation from the ideal in-plane coordination of the phosphorus atom lone pairs (θ about 35°). This very particular bonding renders difficult any comparisons between P–Ga bond lengths in **7** and classical η^1 -phosphine and μ^2 -phosphido-based complexes.⁷ Nevertheless, at 2.3831(7) and 2.390(1) Å, these bond distances compare with those of the $[\text{Ga}(1,2\text{-bis}(\text{diphenylphosphanyl})\text{benzene})\text{I}_2]\text{-}[\text{GaI}_4]$ complex [2.3976(13) and 2.4085(12) Å].^{7c} Ga–Cl [2.1536(7), 2.1627(8)] bond distances also fall in the usual range. An important structural feature is given by the out-of-plane distortion of the two phosphorus atoms (average $\theta = 8.9^\circ$ vs. 1.2° in the free ligand **6**), which reveals that the P–Fe bond probably participates in the bonding to gallium. Apart from this distortion, the other metric parameters in the ligands are not significantly modified relative to the free ligand. A second interesting point concerns the presence of an interaction between the central iron atom and gallium. Indeed, like in ferrocenes, diphosphaferrocenes possess a set of two non-bonding orbitals at iron (degenerated e_{2g} in ferrocenes, $d_{x^2-y^2}$ and d_{xy} in diphosphaferrocenes).⁸ Apparently, no strong bonding occurs here, and at 2.740(1) Å the Fe–Ga distance is quite long relative to complexes that feature genuine dative bonding (between 2.22 and 2.45 Å).⁹ Besides, like in Pd(0) complexes, such bonding would not be expected here because no orbitals (d^{10} electronic configuration) are available at gallium.

**Fig. 2** The molecular structure of one molecule of **7**.**Table 3** Selected bond lengths (Å) and angles (deg) for compound **7**

P(1)–C(1)	1.791(2)	C(4)–P(1)–C(1)	91.8(1)
C(1)–C(2)	1.412(3)	P(1)–C(1)–C(2)	109.4(2)
C(2)–C(3)	1.441(3)	C(1)–C(2)–C(3)	113.9(2)
C(3)–C(4)	1.416(3)	C(2)–C(3)–C(4)	113.1(2)
C(4)–P(1)	1.782(2)	C(3)–C(4)–P(1)	109.8(2)
Ct1–Fe(1)	1.707	P(1)–Ga(1)–P(2)	109.15(2)
P(1)–Ga(1)	2.390(1)	Cl(2)–Ga(1)–P(2)	107.86(4)
Ga(1)–Cl(1)	2.1536(7)	Cl(2)–Ga(1)–P(1)	107.86(4)
Fe(1)–Ga(1)	2.740(1)	Cl(1)–Ga(1)–Fe(1)	118.73(2)
P(2)–C(17)	1.784(2)	C(20)–P(2)–C(17)	92.1(1)
C(17)–C(18)	1.416(3)	P(2)–C(17)–C(18)	109.8(1)
C(18)–C(19)	1.449(3)	C(17)–C(18)–C(19)	113.2(2)
C(19)–C(20)	1.413(3)	C(18)–C(19)–C(20)	113.4(2)
C(20)–P(2)	1.784(2)	C(19)–C(20)–P(2)	109.9(2)
Ct1–Fe(2)	1.714	Cl(1)–Ga(1)–Cl(2)	116.91(3)
P(2)–Ga(1)	2.3831(7)	Cl(1)–Ga(1)–P(2)	109.06(3)
Ga(1)–Cl(2)	2.1627(8)	Cl(1)–Ga(1)–P(1)	105.12(2)
P–Fe(1)	2.3707(7)	Cl(2)–Ga(1)–Fe(1)	124.29(2)
Ga(2)–Cl(3)	2.16975(7)		
Ga(2)–Cl(4)	2.173(1)		
Ga(2)–Cl(5)	2.174(1)		
Ga(2)–Cl(6)	2.1662(7)		

Theoretical study

To gain further insights into the electronic nature of the bonding in **2** and **7**, a theoretical investigation was carried out using DFT. A first series of calculation was attempted using the parent diphosphaferrocene $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}$ as the ligand of the $[\text{GaCl}_2]^+$ fragment but the metric parameters of the structure obtained were found to be very different from those of the experimental structure. Better results were obtained by using the 2,2',5,5'-tetramethyldiphosphaferrocene (tmdpf) ligand. In all cases several functionals (B3LYP, B3PW91 and BP86) were tested with different basis sets. In all cases, BP86 yielded a structure closest to the experimental one but the nature of the basis sets were also found to be crucial for Ga and Fe. Thus, the use of basis sets incorporating a relativistic effective core potential (ECP) at iron and neglecting the 3d core at gallium always yielded structures featuring a relatively long Fe–Ga bond. The best result was obtained using the combination of BP86 with the DZVP2 (on C, H, P, Fe and Cl) and DZVP (on Ga) basis sets. As can be seen in Table 4, there are still some minor discrepancies between the calculated and the experimental structures, which probably arise from the difference between the substitution scheme of the rings (eight *n*-propyl groups in **7** vs. four methyl groups in the theoretical structure). Thus, the P–Ga bond lengths [2.466 Å vs. 2.390(1) Å in **7**] and the Cl–Ga–Cl bond angle [121.281° vs. $116.91(3)^\circ$ in **7**] were found to be slightly larger than the experimental values. The Fe–Ga bond length is also slightly longer [2.799 Å vs. 2.740(1) Å in **7**] but the distortion was found to be acceptable. Interestingly, the out-of-plane distortion of the two phosphorus atoms is reproduced ($\theta = 6.85^\circ$) in this theoretical structure.

Inspection of the molecular orbitals reveals that nine orbitals mainly account for the bonding of the ligand to the $[\text{GaCl}_2]^+$ fragment (H-3, H-5, H-9, H-10, H-11, H-14, H-15, H-16 and H-17 with H meaning HOMO). Three of these,

Table 4 Theoretical bond lengths (Å) and bond angles ($^\circ$) of $[\text{GaCl}_2(\text{bmdpf})]$

P1–C α	1.815	C α –P–C α'	91.918
C α –C β	1.428	P–C α –C β	109.348
C β –C β'	1.441	C α –C β –C β'	114.182
P–Ga	2.466	P–Ga–P	107.521
Ga–Cl	2.170	Cl–Ga–Cl	121.281
Fe–Ga	2.799	P–Ga–Cl	106.862

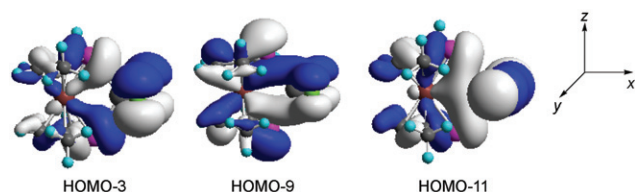


Fig. 3 Selected orbitals describing the bonding in 7.

which were found to be the most representative for the bonding, are presented in Fig. 3. The atomic orbitals (AO) concerned on each phosphorus atom mainly describe the lone pair at phosphorus ($3p_x$, $3p_z$, $3s$).¹⁰ Interestingly, in two of these MOs (H-3 and H-9), the $3d_{xz}$ at iron is also involved in the bonding. This allows one to rationalize the small out-of-plane position of the phosphorus atom since the P–Fe bond is slightly weakened. Note that a similar distortion had already been observed in the structure of the homoleptic complex $[\text{Pd}(\text{I})_2]$ in which the metal possesses the same electronic configuration. See, for example, the H-9, which involves the combination of the $3p_z$ and $3s$ AOs at phosphorus and the $3d_{xz}$ at iron with the $3p_z$ at gallium. On the other hand, two of these MOs feature some electronic density in the Fe–Ga axis (H-10 and H-11), meaning that a weak interaction probably occurs between the two elements. For example, in H-11, the combination of the $3p_x$ at phosphorus and the $d_{x^2-y^2}$ at iron interacts with the $3p_x$ at gallium.

Other important information is given by the natural bond orbital (NBO) population analysis, which reveals the electron deficiency of the ligand ($\Sigma q = +0.919$).¹¹ The net effect of this electronic transfer to gallium is to slightly reinforce the positive charge at phosphorus ($q_p = +0.639$ in the complex *vs.* $+0.540$ in the free ligand, calculated at the same level of theory) and at the α and β carbon atoms of the ring, though to a smaller extent. The iron atom also experiences this electronic transfer and the charge changes from 0.156 in the ligand to 0.199 in the complex (see Table 5). As expected from the electronic configuration of the two fragments and from the examination of the MOs, there is no real bonding between Fe and Ga and the calculated Wyberg bond index, which is very small [$P(\text{Fe}–\text{Ga}) = 0.12$], supports the idea of a weak electrostatic interaction between these two atoms.

In order to draw a comparison between diphosphaferrocenes and a classical tertiary phosphine, the theoretical structure of the cationic $[\text{Ga}(\text{dpe})\text{Cl}_2]^+$ ($\text{dpe} = 1,2\text{-bis}(\text{diphosphino})\text{ethane}$) complex was calculated at the same level of theory. Interestingly, the bond dissociation energies of both ligands were found to be quite similar. Further information on the nature of the interaction between phosphorus and gallium was obtained by performing a charge decomposition analysis (CDA). This method, developed by Frenking and colleagues, already proved to be a powerful tool in decomposing donor-acceptor interactions in terms of common

Table 5 NBO charges (e) of the $[(\text{C}_{12}\text{H}_{16}\text{P}_2\text{Fe})\text{GaCl}_2]^+$ complex given by calculations. Numbers in parentheses refer to NBO charges in the free ligand calculated at the same level of theory

Atom	Charge
P	0.639 (0.540)
C α	−0.240 (−0.284)
C β	−0.219 (−0.252)
Fe	0.199 (0.156)
Ga	0.858
Cl	−0.391
$\Sigma(q)$ ligand	0.919
$\Sigma(q)$ GaCl_2	0.081

Table 6 Results of the charge decomposition analysis for $[\text{Ga}(\text{tmdpf})\text{Cl}_2]^+$ and $[\text{Ga}(\text{dpe})\text{Cl}_2]^+$ complexes. Donation and back-donation values are expressed in e and energies in kcal mol^{-1}

	$[\text{Ga}(\text{tmdpf})\text{GaCl}_2]^+$	$[\text{Ga}(\text{dpe})\text{Cl}_2]^+$
d^a	1.148	1.113
b^b	0.089	0.025
d/b	12.90	44.52
$b/(d+b)$	0.089	0.0220
r^c	−0.194	−0.195
Δ^d	−0.062	−0.049
D_e	112.98	115.19

^a d = donation. ^b b = back donation. ^c r = repulsion. ^d Δ = residual.

Dewar–Chatt–Duncanson (DCD) model concepts.¹² The results given by the CDA analysis are summarized in Table 6 as well as the dissociation energies of the ligand–Ga bonds. Further explanations about the method, the terms used and their relevance are given in the experimental. A first important value is the residual term (Δ), which allows one to consider the interaction in terms of donor-acceptor behavior. In both cases, the values calculated are relatively small and compare with those already reported in the literature for various ligands that were described following the DCD model. Analyses of the CDA data in terms of orbitals confirmed that the nine MOs quoted above effectively contribute to the bonding. The most significant information was provided by the analysis of the ratio between donation (term d) and back-bonding (term b). It is clearly evident that in both complexes the tmdpf and the dpe ligands essentially behave as donors and only exhibit a poor π -accepting capability.

In this study, we have showed that the side-on coordination mode of diphosphaferrocenes can be used to stabilize the GaCl_2^+ fragment. Furthermore, complexes such as 2 and 7 are the first examples of structurally characterized diphosphaferrocene group 13 complexes. Further studies aimed at extending the synthesis of such chelate complexes to metallic centers having a different electronic configuration than d^{10} are currently under investigation in our laboratories.

Experimental

General

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 and CDCl_3 from P_2O_5 . CD_2Cl_2 was dried and stored, like CDCl_3 , over 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H , 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P . Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. The following abbreviations are used: b, broad, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; sext, sextuplet; sept, septuplet; v, virtual. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the Service d'Analyse du CNRS at Gif sur Yvette, France.

Syntheses

$[\text{Ga}(\text{octaethyl-1,1'-diphosphaferrocene})\text{Cl}_2]^+[\text{GaCl}_4]^-$ (2). In a glovebox, 2 equiv. of GaCl_3 (35 mg, 0.2 mmol) were added to a solution of diphosphaferrocene 1 (45 mg, 0.1 mmol) in

dichloromethane (3 mL). After controlling the formation of complex **2** by ^{31}P NMR, the solvent was evaporated. After two washings with hexanes (5 mL), complex **2** was recovered as a dark pink powder (76 mg, 95%). ^{31}P NMR (CD_2Cl_2): δ -265.1. ^1H NMR (CD_2Cl_2): δ 1.14 (t, $^3J_{\text{HH}} = 7.30$, 12H, $4 \times \text{CH}_3$), 1.28 (t, $^3J_{\text{HH}} = 7.40$, 12H, $4 \times \text{CH}_3$), 1.77 (m, 4H, CH_2), 1.98 (m, 4H, CH_2), 2.39 (m, 4H, CH_2), 2.71 (m, 4H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 15.5 (s, Me), 20.3 (br s, Me), 21.2 (m, $\sum J_{\text{PC}} = 13.0$, $^2J_{\text{PP}} = 13.9$, CH_2), 21.7 (s, CH_2), 112.3 (m, $\sum J_{\text{PC}} = 35.6$, $\text{C}_{2,5}$), 115.8 (s, $\text{C}_{3,4}$). Anal. calcd. for $\text{C}_{24}\text{H}_{40}\text{Cl}_6\text{FeGa}_2\text{P}_2$: C, 36.10; H, 5.05. Found: C, 35.89; H, 5.12.

2,3,4,5-Tetra-*n*-propyl-1,1'-bis(cyclopentadienyl)zirconacyclopentadiene (3). A solution of *n*-BuLi (25 mL, 1.6 M in hexanes, 40 mmol, 2 equiv.) was added at -78°C to a solution of zirconocene dichloride (5.84 g, 20 mmol) in THF (200 mL). The resulting solution was then stirred for 1 h at -80°C and 4-octyne (4.41 g, 40 mmol) was added. The resulting mixture was then allowed to warm up to room temperature and stirred for an additional 2 h. After evaporation of the THF, dichloromethane was added (2×75 mL) and the resulting orange solution was filtered. After evaporation of the solvent, zirconacyclopentadiene **3** was obtained as a red powder. Yield: 7.5 g (85%). ^1H NMR (CDCl_3): δ 0.91 (m, 12 H, $4 \times \text{CH}_3$), 1.21 (m, 8 H, $4 \times \text{CH}_2$), 1.98 (m, 4H, CH_2), 1.94 (m, 8H, CH_2), 2.21 (m, 4H, CH_2), 6.10 (s, 10 H, Cp). ^{13}C NMR (CDCl_3): δ 14.9 (s, Me), 15.2 (s, Me), 23.4 (s, CH_2), 25.4 (s, CH_2), 31.4 (s, CH_2), 40.6 (s, CH_2), 110.1 (s, Cp), 132.8 (s, $\text{C}_{3,4}$), 193.7 (s, $\text{C}_{2,5}$). Anal. calcd. for $\text{C}_{26}\text{H}_{38}\text{Zr}$: C, 70.68; H, 8.67. Found: C, 70.35; H, 8.55.

2,3,4,5-Tetra-*n*-propyl-1-chlorophosphole (4). A solution of freshly prepared zirconacyclopentadiene **3** in dichloromethane (100 mL) was reacted with PCl_3 (7.5 g, 17 mmol) at 40°C for 1 h. After cooling the resulting solution to room temperature, the solvent was evaporated and freshly distilled hexane was added (2×50 mL). After filtration and evaporation of hexane, chlorophosphole **4** was obtained as a moisture sensitive yellow oil. Yield: 4.48 g (92%). ^{31}P NMR (CDCl_3): δ 75.4. ^1H NMR (CDCl_3): δ 0.97 (t, $^3J_{\text{HH}} = 7.33$ Hz, 12 H, $4 \times \text{CH}_3$), 1.41 (q, $^3J_{\text{HH}} = 7.79$ Hz, 4H, $4 \times \text{CH}_2$), 1.60 (q, $^3J_{\text{HH}} = 7.79$ Hz, 4 H, CH_2), 2.23 (m, 4 H, CH_2), 2.41 (m, $^3J_{\text{HH}} = 7.32$ Hz, 4 H, CH_2). ^{13}C NMR (CDCl_3): δ 15.0 (s, Me), 23.9 (d, $^4J_{\text{CP}} = 4.5$ Hz, CH_2), 25.2 (d, $^3J_{\text{CP}} = 6.3$ Hz, CH_2), 30.2 (d, $^3J_{\text{CP}} = 19.5$ Hz, CH_2), 30.4 (s, CH_2), 143.4 (d, $^1J_{\text{CP}} = 21.5$ Hz, $\text{C}_{3,4}$), 149.4 (d, $^2J_{\text{CP}} = 11.2$ Hz, $\text{C}_{2,5}$). Phosphole **4** proved to be too moisture sensitive for elemental analysis.

Octa-*n*-propyldiphosphaferrocene (6). A solution of freshly prepared chlorophosphole **4** (4.48 g, 15.6 mmol) in THF (100 mL) was reacted with excess lithium (3.28 g, 47 mmol) at room temperature. The reaction was followed by ^{31}P NMR. After 45 min, all the starting material was converted into the 1,1'-biphosphole P-P dimer. After an additional hour, a ^{31}P NMR control indicated the complete formation of anion **5**. The excess lithium was then filtered and 0.5 equiv. of anhydrous FeCl_2 (1.0 g, 7.8 mmol) was added at room temperature. The solution was stirred for 40 min at room temperature, while the color evolved from orange to dark red. After evaporation of the solvent, hexane (150 mL) was added and the resulting mixture was filtered. After evaporation, the oily residue obtained was quickly purified by flash chromatography using hexane as eluant. Diphosphaferrocene **6** was obtained as an orange powder and was recrystallized in methanol. Yield: 3.80 g (87%). ^{31}P NMR (CDCl_3): δ -58.0. ^1H NMR (CDCl_3): δ 0.93 (t, $^3J_{\text{HH}} = 7.30$, 12H, $4 \times \text{CH}_3$), 1.02 (t, $^3J_{\text{HH}} = 7.16$, 12H, $4 \times \text{CH}_3$), 1.41 (m, 16H, CH_2), 1.94 (m, 8H, CH_2), 2.24 (m, 4H, CH_2), 2.49 (m, 4H, CH_2). ^{13}C NMR (CDCl_3): δ 16.0

(s, Me), 16.5 (s, Me), 26.4 (s, Me), 28.4 (d, $^2J_{\text{PC}} = 4$ Hz, CH_2), 31.9 (s, CH_2), 32.7 (d, $^3J_{\text{PC}} = 9.8$ Hz, CH_2), 99.9 (d, $^3J_{\text{PC}} = 4.6$ Hz, $\text{C}_{3,4}$), 101.0 (d, $^2J_{\text{PC}} = 55.7$ Hz, $\text{C}_{2,5}$). Anal. calcd. for $\text{C}_{32}\text{H}_{56}\text{FeP}_2$: C, 68.81; H, 10.11. Found: C, 68.70; H, 9.85.

[Ga(octa-*n*-propyl-1,1'-diphosphaferrocene)GaCl $_2$] $^+[\text{GaCl}_4]^-$ (7). In a glovebox, 2 equiv. of GaCl_3 (35 mg, 0.2 mmol) were added to a solution of diphosphaferrocene **6** (56 mg, 0.1 mmol) in dichloromethane (3 mL). After verifying the formation of complex **7** by ^{31}P NMR, the solvent was evaporated and **7** was obtained as a light pink powder. Yield: 55 mg (96%). ^{31}P NMR (CD_2Cl_2): δ -264.5. ^1H NMR (CD_2Cl_2): δ 0.96 (t, $^3J_{\text{HH}} = 6.55$, 12H, $4 \times \text{CH}_3$), 1.16 (t, $^3J_{\text{HH}} = 7.27$, 12H, $4 \times \text{CH}_3$), 1.52 (m, 16H, CH_2), 1.98 (m, 4H, CH_2), 2.29 (m, 8H, CH_2), 2.58 (m, 8H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 14.7 (s, Me), 15.6 (s, Me), 25.6 (s, CH_2), 29.9 (br s, $2 \times \text{CH}_2$), 30.95 (s, CH_2), 110.3 (d, $^1J_{\text{PC}} = 37.3$ Hz, $\text{C}_{2,5}$), 114.7 (s, $\text{C}_{3,4}$). Anal. calcd. for $\text{C}_{32}\text{H}_{56}\text{Cl}_6\text{FeP}_2\text{Ga}_2$: C, 42.20; H, 6.20. Found: C, 42.55; H, 6.19.

Theoretical methods

The calculations were carried out using the Gaussian 98¹³ set of programs within the framework of DFT at the BP86¹⁴ level of theory. The DZVP2 basis set was used for H, C, P, Cl and Fe atoms.¹⁵ As this basis set is not available for Ga, the DZVP one was chosen.¹⁵ Vibrational frequencies of the stationary points were calculated at BP86 from numerical second derivatives of the energy with respect to the coordinates. The structures calculated were located at minima on the potential energy surface. The bonding characteristics of the experimental structure were analyzed using the natural bond orbital (NBO) method developed by Weinhold *et al.*¹⁶ Inspection of the ligand and GaCl_2 fragments was performed using the charge decomposition analysis (CDA) developed by Frenking *et al.*¹² In the CDA method the (canonical, natural, or Kohn-Sham) molecular orbitals of the complex are expressed in terms of MOs of the appropriately chosen fragments. In the cases studied, the Kohn-Sham orbitals of the calculations are formed in the CDA procedure as a linear combination of the MOs of the ligand and those of the remaining fragment, $[\text{GaCl}_2]^+$. The ligands and the $[\text{GaCl}_2]^+$ fragments were computed in the geometry of the corresponding complexes. The orbital contributions are divided into four parts: (i) the mixing of the occupied MOs of the ligand and the unoccupied MOs of the metal fragment. This value (noted *d*) represents the donation ligand \rightarrow [metal fragment]; (ii) the mixing of the unoccupied MOs of the ligand and the occupied MOs of the metal fragment. This value (noted *b*) accounts for the back donation [metal fragment] \rightarrow ligand; (iii) the mixing of the occupied MOs of the ligand and the occupied MOs of the metal fragment. This term (noted *r*), which describes the repulsive polarization ligand \leftrightarrow [metal fragment], is negative because electronic charge is removed from the overlapping area of the occupied orbitals; (iv) the residual term (Δ), which results from the mixing of the unoccupied MOs of the two respective fragments. Usually this term is very close to zero for closed-shell interactions. This value constitutes an important probe to determine whether the bonding studied can really be classified as a donor-acceptor interaction following the Dewar-Chatt-Duncanson model. Important deviations from $\Delta = 0$ imply that the bond studied is more conventionally described as a normal covalent bond between two open-shell fragments. A more detailed presentation of the CDA method and the interpretation of the results can be found in the literature.^{12b} CDA calculations were performed with the CDA program, version 2.1.^{12a}

X-ray structural determination

Single crystals of compound **6** suitable for X-ray crystallography were obtained by diffusing methanol into a dichloromethane solution of the compound. Single crystals of complex **7** were obtained by diffusing hexane into a dichloromethane solution of the complex in a sealed tube. Due to the moisture and oxygen-sensitivity of complex **7**, the tube was broken in the glovebox, crystals were protected with paratone oil for handling and then submitted to X-ray diffraction analysis. Data were collected on a Nonius Kappa CCD diffractometer using a Mo K α ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. Experimental details are given in Table 1. The crystal structures were solved using SIR 97¹⁷ and SHELXL-97.¹⁸ ORTEP drawings were made using ORTEP-3 for Windows.¹⁹

CCDC reference numbers 191647 and 191648/. See <http://www.rsc.org/suppdata/nj/b2/b204075c/> for crystallographic data in CIF or other electronic format.

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References

- 1 F. Mathey, *New. J. Chem.*, 1987, **11**, 585–605.
- 2 (a) K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998; (b) L. D. Quin, in *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*, ed. F. Mathey, Pergamon, Amsterdam, 2001, p. 219–305.
- 3 See, for example: (a) C. Ganter, L. Brassat, C. Glinsböckel and B. Ganter, *Organometallics*, 1997, **16**, 2862–2867; (b) K. Tanaka, S. Qiao, M. Tobisu, M. M.-C. Lo and G. C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 9870–9871; (c) R. Shintani, M. M.-C. Lo and G. C. Fu, *Org. Lett.*, 2000, **2**, 3695–3697; (d) X. Sava, L. Ricard, F. Mathey and P. Le Floch, *Organometallics*, 2000, **19**, 4899–4903; (e) M. Melaimi, F. Mathey and P. Le Floch, *J. Organomet. Chem.*, 2001, **640**, 197–199.
- 4 D. A. Atwood, A. H. Cowley and S. M. Dennis, *Inorg. Chem.*, 1993, **32**, 1527–1528.
- 5 R. G. M. Roberts, J. Silver and A. S. Wells, *Inorg. Chim. Acta*, 1986, **119**, 165–171.
- 6 For discussions regarding conformational problems in phosphaferrrocenes and diphosphaferrrocenes, see: (a) G. Guimon, D. Gonbeau, G. Pfister-Guillouzo, G. De Lauzon and F. Mathey, *Chem. Phys. Lett.*, 1984, **105**, 560–567; (b) X. Sava, N. Mézailles, N. Maigrot, F. Nief, L. Ricard, F. Mathey and P. Le Floch, *Organometallics*, 1999, **18**, 4205–4215; (c) M.-D. Su and S.-Y. Chu, *J. Phys. Chem.*, 1989, **93**, 6043–6051.
- 7 For general references concerning phosphide and phosphine gallium complexes, see: (a) J. C. Carter, G. Jugie, R. Enjalbert and J. Galy, *Inorg. Chem.*, 1978, **17**, 1248–1254; (b) J. L. Atwood, K. D. Robinson, F. R. Bennett, F. M. Elms, G. A. Koutsantonis, C. L. Raston and D. Young, *Inorg. Chem.*, 1992, **31**, 2673–2674; (c) M. Sigl, A. Schier and H. Schmidbaur, *Eur. J. Inorg. Chem.*, 1998, 203–210.
- 8 N. M. Kostic and R. F. Fenske, *Organometallics*, 1983, **2**, 1008–1015.
- 9 For recent discussions on the nature of the Fe-Ga interaction, see, for example: (a) J. Su, X.-W. Li, R. C. Crittendon, C. F. Campana and G. H. Robinson, *Organometallics*, 1997, **16**, 4511–4513; (b) F. A. Cotton and X. Feng, *Organometallics*, 1998, **17**, 128–130; (c) C. Boehme and G. Frenking, *Chem. Eur. J.*, 1999, **5**, 2184–2190; (d) R. A. Fischer and J. Weiss, *Angew. Chem., Int. Ed.*, 1999, **38**, 2830–2850.
- 10 In diphosphaferrrocenes, three orbitals describe the lone pair at the phosphorus atom: the HOMO-3, which involves a combination of the 3d_{xz} orbital at iron with the π_p and the σ_p (lone pair) orbitals of the phospholide ligand; the HOMO-7, which is the symmetrical combination of the σ_p orbitals of the phospholide ligands with a small contribution of the d_{z²} orbital at iron and the HOMO-8, which is the antisymmetrical combination of the σ_p orbitals of the phospholide ligands with a small contribution of the d_{xz} orbital at iron.
- 11 For this calculation, the molecule was divided in two fragments, the ligand and the [GaCl₂] complexing group. Σq means that the charges on the C, H, P and Fe atoms were summed.
- 12 (a) S. Dapprich and G. Frenking, CDA 2.1, Marburg, 1995. The program is available on-line: <ftp://chemie.uni-marburg.de/pub/cda/>; (b) G. Frenking and N. Fröhlich, *Chem. Rev.*, 2000, **100**, 717.
- 13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 98, rev. A.11, Gaussian, Inc., Pittsburgh, PA, 2001.
- 14 (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3108; (b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8832.
- 15 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.
- 16 A. E. Reed, L. A. Curtis and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
- 17 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, SIR97, an Integrated Package of Computer Programs for the Solution and Refinement of Crystal Structures using Single Crystal Data, 1999.
- 18 G. M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1998.
- 19 L. J. Farrugia, ORTEP-3, Department of Chemistry, University of Glasgow, UK, 2000.