

A Ferrocenophane-based diaminophosphenium ion

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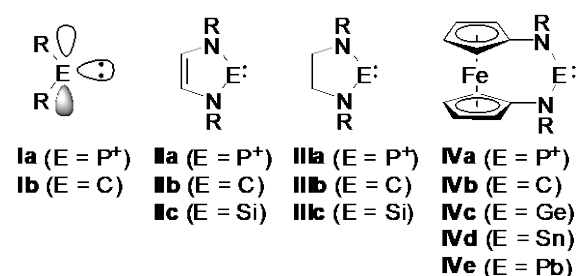
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ABSTRACT: Reactions of P-chloro-1,3,2-diazaphospha-[3]ferrocenophanes with ECl_3 ($\text{E} = \text{Al}, \text{Ga}$) under solvent-free conditions and with $\text{Na}[\text{Mn}(\text{CO})_5]$ furnished salts featuring a ferrocenophane-based phosphonium cation or neutral phosphonium complexes, respectively. All products were characterized by spectroscopic studies. Single-crystal X-ray diffraction studies confirmed the ionic nature of the phosphonium tetrachloroaluminate and the structural analogy between the phosphonium complexes and Fischer-type carbene complexes. Distinct deviations in the conformation of the *ansa*-bridge suggest electronic stabilization of the electrophilic phosphorus atom by phosphorus-nitrogen π -interactions in the free cation and by phosphorus-metal π -bonding in the complexes. The observation of short intermolecular contacts in the crystalline phosphonium salt and its chemical behavior towards donor solvents attest the cation an unusually high degree of Lewis-acidity, which was confirmed by DFT studies and related to the presence of a rather large N–P–N angle. Computational studies indicate further that the free phosphonium cation exhibits a closed-shell electronic structure with a formal Fe(II) oxidation state and is thus a true analogue to ferrocenophane-based diaminotetrylenes.

INTRODUCTION

Even if the discovery of isolable salts of phosphonium cations **1a** ($\text{E} = \text{P}^+$, Chart 1)¹ preceded that of stable carbenes **1b** ($\text{E} = \text{C}$),² the realization of the isovalent relationship between both species has greatly fostered the development of phosphonium ion chemistry.³ This is in particular true for N-heterocyclic phosphonium (NHP) cations **IIa**, **IIIa** ($\text{E} = \text{P}^+$), which are formally isovalent to the well-known N-heterocyclic carbenes **IIb**, **IIIb**, but exhibit complementary chemical properties in behaving predominantly as electrophiles rather than nucleophiles.^{3b-d} This dichotomy decreases, however, when comparing NHPs with the corresponding, truly isoelectronic silylenes **IIc**, **IIIc** ($\text{E} = \text{Si}$) or higher homologues thereof, all of which exhibit increasingly electrophilic properties.⁴

Chart 1. Generic molecular structures of carbenes and carbene analogues.



A class of cyclic diaminocarbenes and diaminocarbene homologues that has recently gathered attention are ferrocenophane-based tetrylenes **IVb-e**,⁵⁻⁷ in which the five-

membered heterocyclic ring is formally replaced by a [3]ferrocenophane backbone.⁸ The combination of the subvalent main-group element with a redox-active ferrocene unit provides for an interesting chemistry that enabled, among others, the generation of unprecedented persistent tetrylene radical cations.^{5c,6b} The cationic carbene derivatives feature a peculiar delocalization of the spin density between the ferrocene unit and the subvalent carbon atom,^{5c} while their heavier homologues exhibit a localized ferrocenium-type nature which does not compromise the tetrylene character.^{6b} The redox non-innocence of the ferrocene-based carbenes is also conserved in transition metal complexes and enabled their use as redox-switchable catalysts.^{5a}

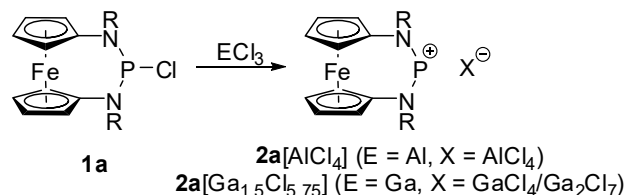
The intriguing properties of the ferrocenophane-based tetrylenes **IVb-e** and their metal complexes raised our interest to explore the chemistry of the isoelectronic, but yet unknown, phosphonium ions **IVa**. Considering that reactions of diamino-halogenophosphines under halide abstraction or metathesis with suitable transition metal nucleophiles provide well established access routes to phosphonium ions and their complexes,³ we anticipated that the recently described P-halogeno-1,3-diaza-2-phospha-[3]ferrocenophanes **1**⁹ might provide an entry point for our studies. We report here on validation of this hypothesis by conveying the syntheses of [3]ferrocenophane-based phosphonium ions and phosphonium complexes which constitute, to the best of our knowledge, the first examples of molecules with this specific architecture.

RESULTS AND DISCUSSION

Stable and persistent diaminophosphonium ions are usually accessed via cleavage of an anionic substituent from a neutral

phosphine precursor.^{1,3} Halide ions are privileged leaving groups, and their abstraction can be accomplished by action of a strongly electrophilic halide scavenger (e. g. aluminum or gallium trihalide), or through condensation or metathesis with trimethylsilyl triflate (Me_3SiOTf) or metal triflates (AgOTf , TfOTf), respectively.^{3,10} Monitoring the appropriate reactions of P-chloro-diazaphospha-[3]ferrocenophane **1a** in various solvents (pure CH_2Cl_2 or its mixtures with pentane or Et_2O) by ^{31}P NMR spectroscopy, we found that condensation with Me_3SiOTf did not yield any products qualifying as phosphonium ions, whereas metathesis with AgOTf and TfOTf suffered from low selectivity and reproducibility. Reactions with AlCl_3 and GaCl_3 seemed more promising, but the formation of side products arising from hydrolysis could not be avoided, and no isolable products were obtained. Attributing the synthetic problems to the presence of trace amounts of water even in rigorously dried solvents, we attempted accessing the target cations using a solvent-free protocol. Gratifyingly, we found that mechanical agitation of mixtures of solid **1a** and stoichiometric quantities of AlCl_3 or GaCl_3 produced deep red oils or solids identified as the expected phosphonium salts **2a** $[\text{AlCl}_4]$ and **2a** $[\text{Ga}_{1.5}\text{Cl}_{5.75}]$ (Scheme 1).¹¹ Both species are highly sensitive towards air and moisture, but dissolved without decomposition in anhydrous CH_2Cl_2 . Layering with pentane and allowing for mixing of the solvents by diffusion afforded **2a** $[\text{AlCl}_4]$ as deep red, crystalline product which could be fully characterized, while the gallium salt remained oily and was only identified spectroscopically.

Scheme 1. Formation of [3]ferrocenophane-based dia-minophosphonium salts ($\text{R} = \text{CH}_2^t\text{Bu}$).



Solvent-free reactions of P-bromo-[3]ferrocenophane **1b** (with $\text{R} = \text{SiMe}_3$) with AlCl_3 or GaCl_3 proceeded in a similar manner as those of **1a**. Analysis of the resulting red oils by ^{31}P NMR spectroscopy revealed, however, that in this case a mixture of two phosphorus-containing species with chemical shifts of 300 and 312 ppm had formed. Even if attempts to separation and unambiguous identification of any component remained unsuccessful, the observed chemical shifts support tentative assignment of one of the components as a phosphonium cation **2b**⁺ (Chart 2). We explain the formation of a second species as resulting from a side reaction involving dechlorosilylation of **1b** and stabilization of the formed transient amino-iminophosphine as a complex **3b**.¹²

Chart 2. Proposed molecular structures of **2b⁺ and **3b**.**



In accord with their postulated constitution as salts with the same cation, CD_2Cl_2 solutions of **2a** $[\text{AlCl}_4]$ and **2a** $[\text{Ga}_{1.5}\text{Cl}_{5.75}]$

exhibit essentially identical ^1H , ^{13}C and ^{31}P NMR spectra and display the characteristic NMR signals of $[\text{AlCl}_4]^-$ ($\delta^{27}\text{Al}$ 103.7 ppm) or $[\text{GaCl}_4/\text{Ga}_2\text{Cl}_7]^-$ ($\delta^{71}\text{Ga}$ 248.3 ppm) anions, respectively. The phosphonium nature of the cation is alluded by a ^{31}P NMR chemical shift ($\delta^{31}\text{P}$ 296 ppm) that matches values reported for acyclic bis(dialkylamino)phosphoniums ($\delta^{31}\text{P}$ 264 – 313 ppm^{3a}) while exceeding those of cyclic diazaphospholidinium (**IIIa**, $\delta^{31}\text{P}$ 254 – 264 ppm^{3a}) and diazaphospholenium ions (**IIa**, $\delta^{31}\text{P}$ 210 – 200 ppm¹³), respectively. Moreover, the signal patterns in the ^1H and ^{13}C NMR spectra of **2a** $[\text{Ga}_{1.5}\text{Cl}_{5.75}]$ reflect the effective C_{2v} -symmetry expected for a phosphonium cation with a planar ferrocenophane ring. We interpret minor deviations between the ^{31}P chemical shifts of the aluminum and gallium salts ($\Delta\delta^{31}\text{P} = 0.2$ ppm) and the appreciable linewidth of the ^{27}Al NMR signal ($\Delta w_{1/2} = 16$ Hz) as hints to the occurrence of ion pairing in solution. The large linewidth of the ^{71}Ga NMR signal ($\Delta w_{1/2} = 2.3$ kHz) reflects dynamic exchange between $[\text{GaCl}_4]^-$ and $[\text{Ga}_2\text{Cl}_7]^-$.

Attempted dissolution of **2a** $[\text{AlCl}_4]$ in other polar solvents than dichloromethane (e.g. THF or MeCN) resulted inevitably in recovery of **1a** via recapture of a chloride from the anion. We explain this behavior by assuming that, as in case of other highly electrophilic phosphonium ions,¹⁴ sequestering of AlCl_3 through formation of an adduct with a donor solvent reverses the chloride transfer reaction shown in Scheme 1. It should be noted that the obvious stability of **2a** $[\text{AlCl}_4]$ in CD_2Cl_2 seems at first glance in contrast to the difficulties encountered during the attempted preparation of this species by halide abstraction from **1a** in the same solvent. However, in the light of previous reports, which had established that ion pairing increases the chemical stability of phosphonium ions in solution,¹⁵ the apparent paradox can be resolved if one assumes that such 'anionic protection' is weakened or even absent during the early stages of the ion formation process, and becomes only fully effective once the salt is formed.

The constitution of **2a** $[\text{AlCl}_4]$ was confirmed by a single-crystal X-ray diffraction study (see Table 1 for selected distances and angles). The crystal is composed of separated phosphonium cations and tetrachloroaluminate anions. Two chlorine atoms in each anion exhibit intermolecular contacts to the phosphorus atoms in adjacent cations (P–Cl 3.2188(3) and 3.2408(3) Å) that are distinctly shorter than the sum of van der Waals radii (3.72 Å¹⁶) and cause the formation of one-dimensional stacks of alternating anions and cations parallel to the crystallographic b-axis (Figure 1).

Figure 1. Representation of the molecular structure of a cation and two adjacent anions (the extra anion belongs to an adjacent ion pair was included to illustrate the intermolecular association) in crystalline **2a** $[\text{AlCl}_4]$. Thermal ellipsoids were drawn at the 50% probability level and hydrogen atoms were omitted for clarity. Selected metric parameters are listed in Table 3.

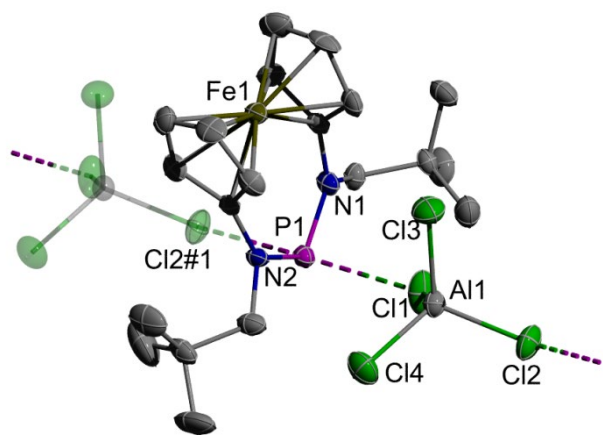


Table 1. Selected intramolecular distances (in Å) and angles (in °) for **2a**[AlCl₄] and complexes **8a**,**b**.

	2a [AlCl ₄]	8a	8b
P–N	1.619(3) 1.628(3)	1.713(2) 1.714(2)	1.686(6) 1.698(5)
N–C(Cp)	1.437(5) 1.442(5)	1.420(4) 1.427(4)	1.429(9) 1.456(9)
Fe–Cp _{cent} ^a	1.625(3) 1.629(3)	1.648(3) 1.653(3)	1.640(6) 1.649(6)
Mn–P		2.1198(9)	2.109(2)
Mn–C(CO)		1.787(4) 1.816(4) 1.831(4) 1.851(3)	1.774(10) 1.809(9) 1.819(9) 1.825(10)
Al–Cl	2.1233(16) 2.1300(16) 2.131(2) 2.134(2)		
N–P–N	111.3(2)°	108.54(12)	107.4(3)
Mn–P–N		122.66(9) 127.93(8)	125.7(2) 126.6(2)
Σ(X–P–Y) ^b		359.2(3)	359.7(7)
Σ(X–N–Y) ^b	358.9(9) 359.3(9)	348.8(6) 347.0(6)	360.0(13) 359.6(11)
α ^c	11.6(1)	7.6(1)	9.1(3)
δ ^d	9.1(1)	-0.1(2)	0.6(4)

a) Cp_{cent} = Cp-ring centroid; b) sum of bond angles at the phosphorus and nitrogen atoms, respectively; c) dihedral angle between the C–N vectors in the ferrocene unit; d) tilt angle between the least-squares planes through the Cp-rings in the ferrocene unit.

The *ansa*-bridge is characterized by short P–N distances (P–N 1.619(3), 1.628(3) Å vs. values of 1.664(2) to 1.730(1) Å in the previously reported neutral NPN-[3]ferrocenophanes^{9,17} reflects) and planar coordination at the nitrogen atoms (sum of bond angles 358.9(9) and 359.3(9)°). The staggering of the Cp-rings (dihedral angle δ = 9.1 (1)°) results in a skewed, C₂-symmetric conformation of the ferrocenophane unit in which the nitrogen coordination planes deviate (torsional angle 17°) from the parallel alignment granting optimum NPN-π-conjugation. The inclination of the diaminophosphonium unit to retain such a planar conformation³ results further in an opening of the NPN valence angle (111.3(2)° vs. ≈ 90° in N-

heterocyclic phosphonium ions)^{3d,13} and a distinct spatial separation of the phosphorus and iron atoms (Fe⋯P 3.625(3) Å).

The structural features of the cation in **2a**[AlCl₄] epitomize typical characteristics of diaminophosphonium ions.^{3,13} The P–N bond shortening with respect to neutral NPN-[3]ferrocenophanes reflects the increased P–N π-bonding in the cation, the close match of the observed distance with a mean value of 1.615 Å^{3d} suggesting that the diaminophosphonium moiety is unperturbed by any conjugation interaction with the ferrocene unit. Moreover, the conformation of the NPN-bridge and the large Fe⋯P distance imply that direct back-bonding from the π-basic metal atom does not contribute to the stabilization of the remote electrophilic center in the bridging unit, which had been suggested for a [3]ferrocenophane-based plumblyene.⁷

The observation of intermolecular contacts at directions that are often close to perpendicular to the local NPN-plane is a common phenomenon in crystal structures of phosphonium ions and attributable to electrostatic stabilization of the highly electrophilic cations.^{3b,3d,13} However, intermolecular P⋯Cl interactions in diaminophosphonium tetrachloroaluminates and -gallates remain close to the sum of van-der-Waals radii (P–Cl > 3.4 Å),^{3b} whereas short contacts with similar distances as in **2a**[AlCl₄] are only known for strongly electrophilic cations obtained by formal exchange of one amino group by a substituent of weaker π-donating power.^{3b,3d,18} In this context, we regard both the short inter-ion contacts in crystalline **2a**[AlCl₄] and the observation of a relatively short P–Cl distance in the chlorophosphine precursor **1a**⁹ as structural indicators of an unusually high (for a cyclic diaminophosphonium ion) Lewis acidity of **2a**⁺. Enhanced electrophilicity with respect to conventional N-heterocyclic derivatives was also observed for ferrocenophane-based carbenes and is presumably attributable to the increased bond angle enforced by the geometrical constraints of the ferrocenophane skeleton.^{5c,d} It should be noted, however, that the electron withdrawing power of the cation causes hardly any imbalance between the distances of 'coordinating' (2.123(2), 2.130(2) Å) and 'free' (2.131(2), 2.134(2) Å) Al–Cl bonds, all of which remain essentially indistinguishable within experimental error.¹⁹

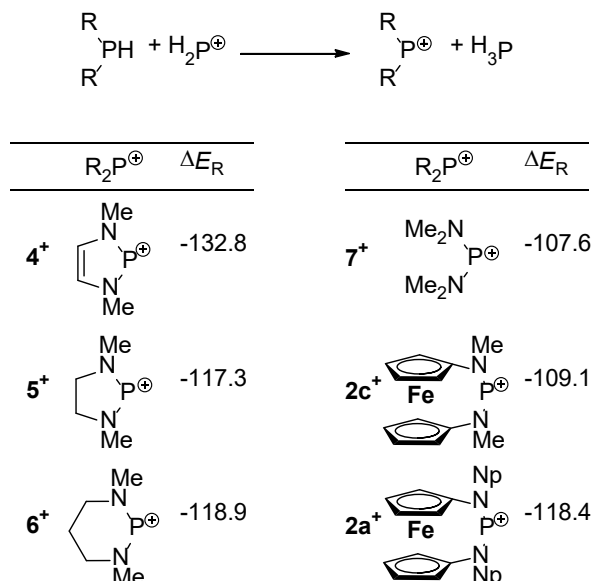
In order to delve further into the electronic interaction between the ferrocene and diaminophosphonium moieties in cation **2a**⁺ and assess its Lewis-acidity relative to other phosphonium cations, we performed a computational study. An initial evaluation of the performance of different computational approaches disclosed that the calculated distance between the centroids of the Cp rings in ferrocene is highly sensitive to the applied functional and basis set (Table S2, Supporting Information). The best match between computed and experimental structures was obtained at the ωB97X-D/6-311+G** level, which was then employed for optimizing the molecular structures of the isolated cations **2a**⁺ and **2c**⁺ (with *N*-Me instead of *N*-neo-pentyl substituents) and the ion pairs **2a**[AlCl₄] and **2c**[AlCl₄], respectively. The calculated structural parameters of isolated **2a**⁺ and the ion pair **2a**[AlCl₄] obtained at this level displayed only minor differences and are in good agreement with the X-ray diffraction data. Moreover, Bader analysis of the electron density of the ion pair **2a**[AlCl₄] disclosed negligible electron densities at all bond critical points between cation and anion (see Figure S19³⁷), and we conclude that both ions are electronically sufficiently separated to allow further analysis of the electronic situation in the ferrocenyl-phosphonium unit under neglect of the anion.

Our approach started with an analysis of electron densities resulting from restricted DFT calculations on $2a^+$ and model cation $2c^+$ at the ω B97X-D/6-311+G** level of theory. Inspection of the frontier Kohn-Sham (KS) orbitals allowed us to identify the KS-HOMO of $2a^+$ as a metal-centered MO with predominant 3d character, and the KS-LUMO as the P,N-centered π_3^* -MO of the heteroallylic NPN-unit. While the KS-LUMO has thus the same characteristics as in all diamino-phospheniums,³ KS-orbitals with predominant n(N) and n(P) character, which commonly make the KS-HOMO and KS-HOMO-1 in these species,³ are in case of $2a^+$ located by 2.85 eV (n(N), KS-HOMO-9) and 3.65 eV (n(P), KS-HOMO-14) below the KS-HOMO (Table S4). The remaining closely spaced KS-Orbitals between HOMO and the n(N) orbitals are mixtures of Fe d-orbitals and cyclopentadienyl π -orbitals, and their ordering depends strongly on the level of theory applied. The results obtained on $2c^+$ are similar and are given in Table S4.

The existence of energetically high-lying ferrocene-centered MOs in $2a^+$ cuts down the energy gap between the electronic ground state and excited states and is expected to render both excited singlet and triplet states more easily accessible. In accord with this assumption, we found that $2a^+$ and $2c^+$ exhibit both distinctly lower singlet-triplet excitation energies ($\Delta E_{S\rightarrow T} = 25.4$ ($2a^+$), 38.3 ($2c^+$) kcal/mol) and optical transition energies (see further below) than conventional N-heterocyclic phosphonium ions (e.g. $\Delta E_{S\rightarrow T} = 53.5$ kcal/mol for 1,3-dimethyl-1,3,2-diazaphosphenium 5^+ shown in Scheme 2). On the other hand, broken-symmetry approaches to the calculation of the DFT density of model cation $2c^+$ converged to the restricted KS-solution, suggesting a closed-shell ground state. This was also confirmed by CASSCF(2,2)/6-31G* calculations on $2c^+$ using the b_1 -symmetrical ferrocenium-based HOMO-2 and the phosphorus based LUMO from the HF/6-31G* wavefunction (see Table S4) in the active space, which showed the predominant ($c = 0.999$) involvement of the HF determinant in the wavefunction. Further CASSCF calculations with more b_1 and even a pair of a_2 orbitals gave no indication that alternative electron configurations, like a 'ferrocenium-phosphinyl radical' resonance structure resulting from promotion of one electron from the Fe-centered HOMO into the phosphonium-centered LUMO, contribute significantly to the electronic ground state (see Table S5). We conclude therefore that the ferrocenophane-based phosphonium cations in their electronic ground state can be represented as closed-shell species with 'ferrocene-phosphonium ion' character and a formal Fe(II) oxidation state. This description is also in accord with the outcome of natural population analyses, which imply that the positive charge is centred on the NPN unit and not, as in a species like $fc'(P^tBu)_2BMes^{++}$,²⁰ delocalized between the iron and an adjacent phosphorus atom.

To assess the stabilization of $2a^+$ and model cation $2c^+$ with respect to other types of diamino-phosphenium ions (4^+ to 7^+) and parent PH_2^+ as a common standard, we evaluated the energies of isodesmic hydride transfer reactions (Scheme 2, all calculations at the ω B97X-D/6-311+G** level, gas phase).²¹

Scheme 2. Energies (in kcal mol⁻¹) of isodesmic hydride transfer reactions between diamino-phosphines and PH_2^+ calculated at the ω B97X-D/6-311+G level of theory.**



The results indicate that formal exchange of the bridging ethylene unit in 5^+ by a ferrocene moiety destabilizes cation $2c^+$ by 8.2 kcal mol⁻¹, which is close to the 9.7 kcal mol⁻¹ relative destabilization of the acyclic cation 7^+ . Since the N-substituents in all three species exhibit similar electronic characteristics, we relate the lower cation stabilization in 2^+ and 7^+ at least in part to the opening of the NPN angle (from 94.9° in 5^+ to 111.2° and 109.8° in $2c^+$ and 7^+), which is known to have an adverse effect on the ground state stability of phosphonium ions.²² The impact of these changes trails behind that of cyclic π -delocalization, which renders cation 4^+ more stabilized than 5^+ by 15.5 kcal mol⁻¹, but matches that of the inductive effects reflected in the 9.3 kcal mol⁻¹ extra stabilization upon formal replacement of the N-Me substituents of $2c^+$ by more electron releasing *neo*-pentyl groups in $2a^+$. In total, the trends in calculated hydride transfer energies endorse that ferrocenophane-based diamino-phosphenium cations exhibit similar or even slightly lower stabilization than acyclic phosphonium ions with comparable peripheral substituents.

The deep red color of $2a[ExCl_{3x+1}]$ ($E = Al, Ga$), which contrasts the yellow appearance of known diaminoferrocenes (including precursor [3]ferrocenophane $1a$), can be traced to a broad absorption in the visible region ($\lambda_{max} = 518$ nm). The marked red-shift of this band compared to the absorptions of other diamino-phosphenium ions (which generally lie outside the visible region²³) gives a first hint that electronic communication between the ferrocene and phosphonium fragments of $2a^+$, even if it is absent in the electronic ground state, may play a role in the electron excitation process. Confirmation of this hypothesis comes from a TD-DFT calculation, which predicts that the first transition in the electronic spectrum of $2a^+$ (496 nm) occurs at much larger wavelength (lower energy) than in case of 5^+ (259 nm) and is not attributable to an n- π^* transition as usual, but rather to an excitation from the metal-centered KS-HOMO into the NPN-centered KS-LUMO. Although this transition exhibits MLCT character, the oscillator strength is small. Further transitions involving KS-orbitals close to the frontier orbitals give rise to absorptions at slightly shorter wavelengths with even lower intensities. A transition exhibiting n- π^* character does not appear among the ten lowest energy excitations, which is not surprising since the n- π^* orbital is KS-HOMO-14. Calculations on a contact ion pair $2a[GaCl_4]$

(using the PCM solvation model with solvent acetonitrile) reveal minor interactions between ions, which reshuffle the closely spaced excited states and induce a slight blue shift and an overall broadening of the observable absorption band.

Besides the free phosphonium ions, also their transition metal complexes raised considerable interest because of the analogy of these species to Fischer-type carbene complexes.³ While our attempts to prepare cationic complexes of **2a**⁺ remained as yet unsuccessful, we succeeded in obtaining neutral species **8a,b** through metathesis of ferrocenophanes **1a,b** with Na[Mn(CO)₅] in ethereal solution (Scheme 3). Work-up afforded both species as deep red, crystalline, air and moisture sensitive products that were characterized by analytical and spectral data as well as single-crystal X-ray diffraction studies. The isolated solid samples are thermally stable at ambient temperature, but decompose eventually in solution. The ³¹P NMR spectra of both compounds reveal broadened resonances at chemical shifts ($\delta^{31}\text{P}$ 320 (**8a**), 290 (**8b**)) exceeding that of free cation **2a**⁺. A similar line broadening, which is attributable to unresolved spin coupling of the ³¹P nuclear spin with the quadrupolar ⁵⁵Mn nucleus (100% nat. abundance, $I = 5/2$), and a positive coordination shift were previously observed for complexes **9**²⁴ and **10**²⁵ (Chart 3) and may be considered typical features of phosphonium complexes of manganese. A species featuring a broad ³¹P NMR signal at 350 ppm was also formed in the reaction of **1a** with Na[Co(CO)₄] and assigned as a neutral phosphonium-Co(CO)₃ complex,²⁶ but evaded all attempts toward isolation and further characterization by undergoing slow decomposition in solution.

Scheme 3. Formation of [3]ferrocenophane-based neutral diaminophosphonium complexes (R = *neo*-C₅H₁₁ (1a**, **8a**), Me₃Si (**1b**, **8b**), X = Cl (**1a**), Br (**1b**)).**

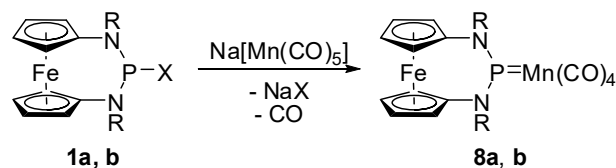
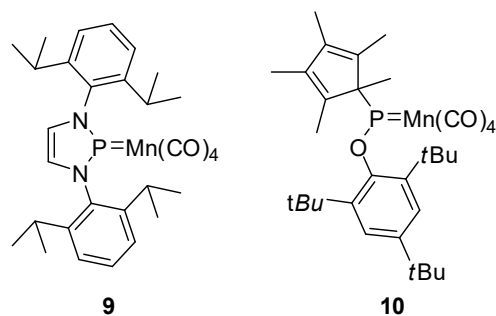


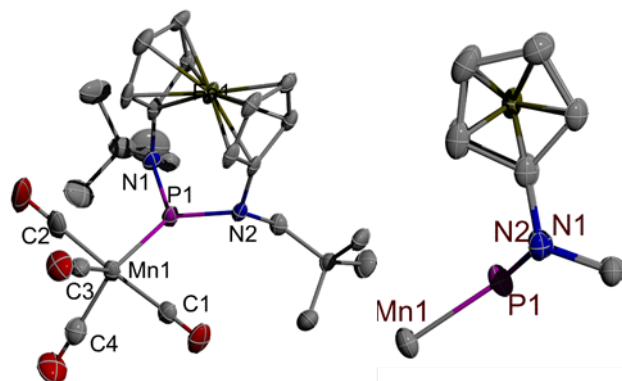
Chart 3. Molecular structures of **9, **10**.**



The molecular structures of **8a,b** in the crystal (Figure 2 and Figure S1) are, apart from the presence of different *N*-substituents, closely similar and exhibit eclipsed ferrocene units with slightly tilted Cp-rings (see Table 1). The atoms in the NPN-bridge and the Cp-centroids form an 'envelope'-shaped array in which the phosphorus atom is dislocated out of the plane defined by the four remaining centers. This conformation contrasts the flat arrangement of the NPN-bridge in **2a**[AlCl₄], but compares well to the alignment of the ferrocenophane moiety in the neutral phosphines **1a,b**,⁹ even if the

phosphonium complexes and phosphines are clearly distinguished by their pyramidal (**1a,b**) or planar (**8a,b**) coordination environment at the central phosphorus atom. The nitrogen atoms in the phosphonium complexes exhibit planar (**8b**, sum of bond angles 360°) or quasi-planar (**8a**, sum of bond angles around 348°) coordination, and the folded conformation of the ferrocenophane framework enforces a twisted orientation of the amino fragments relative to the NPN-plane with torsional angles between 70° and 90°. The P–N distances in **8a,b** exceed those in **2a**[AlCl₄] and fall into the range observed for **1a,b**⁹ and related NPN-[3]ferrocenophanes¹⁷ (1.664(2) to 1.730(1) Å). The short P–Mn distances (2.109(2) and 2.110(1) Å) and the attachment of the phosphonium unit to an equatorial site of the *tbp*-coordination sphere around the metal center match appropriate features of **9** and **10**.

Figure 2. Molecular structure of **8a in the crystal (left) and reduced plot (right, with carbonyl ligands and peripheral *t*Bu-moieties omitted for clarity) showing a side view of the molecule. Thermal ellipsoids were drawn at the 50% probability level and hydrogen atoms were omitted for clarity. Selected geometric parameters are listed in Table 1.**



The observed structural features suggest depicting **8a,b** as Fischer carbene-analogue phosphonium complexes^{3c} in which the electron deficiency at phosphorus is alleviated by formation of a P=M double bonding interaction, while P,N- π -bonding remains negligible. A bonding situation of this type prevails frequently in metal complexes of acyclic phosphonium ions³ and further underlines the nature of cation **2a**⁺ as a strongly Lewis-acidic ligand. It has already been noted that the ordering of P–Mn distances in these complexes (the shortest and longest bonds being found for **9** and **8a,b**, respectively) does not necessarily correlate with the trend in π -acceptor capabilities of the phosphonium ligand, but may reflect other influences like the effects of rehybridization at the phosphorus atom.²⁴ Specifically, the observed correlation between the increase in Mn–P distances and the opening of the NPN bond angles (**9**: N–P–N 89.0(2)°, **10**: O–P–C 99.2(3)°, **8a,b**: N–P–N 107.4(3) and 108.54(12)°) suggests that the bond lengthening may reflect the admixture of increasing *p*-character to the phosphorus-metal bond.

Bearing in mind that many ferrocene derivatives exhibit rich redox chemistry and are attractive targets for electrochemical studies, we also explored the electron transfer behavior of the newly synthesized ferrocenophane-phosphonium species using cyclic voltammetry. The cyclic voltammogram of **2a**[AlCl₄] displayed an irreversible reduction event ($E_p = -0.92(1)$ V vs. Fc/Fc⁺), whereas electrochemical oxidation was not observable. The reduction of cation **2a**⁺ yields presumably a phos-

phenyl radical, the instability of which was inferred in a previous study¹⁷ and would perfectly explain the irreversible behavior. Investigation of the phosphonium complexes **8a,b** gave only inconclusive and poorly reproducible results, presumably as a consequence of the decomposition of these species or their reaction products in solution.

CONCLUSIONS

A ferrocenophane-based diamino-phosphonium ion and neutral metal complexes with such ligands were prepared from *P*-halogeno-substituted precursors via halide abstraction or metathesis with Na[Mn(CO)₅], respectively. Experimental and computational evidence suggests that the free cation is best described as being composed of formally cationic diamino-phosphonium and neutral ferrocene units, and behaves as a stronger Lewis-acid than other N-heterocyclic phosphonium ions, presumably because of its widened N–P–N-angle. While these features highlight the similarity in electronic structure and bonding with isoelectronic and isosteric ferrocenophane-based tetrylenes,^{5–7} the phosphonium ion lacks the ability of its neutral analogues to undergo iron-centered oxidation, which we attribute to the increased positive charge. Electrochemical reduction was found to be irreversible and the postulated product – an elusive ferrocene-based phosphinyl radical – evaded characterization. Binding to a Mn(CO)₄-unit induces a trade-off of the P–N π -bonding for the formation of a metal-phosphorus double bond. While this phenomenon is well-known for phosphonium complexes with strongly electrophilic ligands,³ it is in the present case accompanied by a rather unprecedented structural change from a planar to a strongly folded conformation of the ferrocenophane bridge.

EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of inert argon and in flame-dried glassware. Solvents were dried as described²⁷ and distilled prior to use. NMR spectra were recorded on Bruker AV250 or AV400 spectrometers, respectively. Chemical shifts in ¹H NMR spectra were referenced to TMS using the signals of the residual protons of the deuterated solvent (¹H, δ (CD₂Cl₂) = 5.34; δ (C₆D₆) = 7.15) as secondary reference. NMR Spectra of heteronuclei were referenced using the Ξ -scale²⁸ with TMS (Ξ = 25.145020 MHz, ¹³C; Ξ = 19.867187 MHz, ²⁹Si), MeNO₂ (Ξ = 10.136767 MHz, ¹⁵N), 1.1 M Al(NO₃)₃ (Ξ = 26.056859 MHz, ²⁷Al), and 85 % H₃PO₄ (Ξ = 40.480747 MHz, ³¹P) as secondary references. FTIR spectra were recorded with a Thermo Scientific iS5 instrument equipped with an iD5 attenuated total reflectance (ATR) accessory. An Elemental Micro Cube elemental analyser was used for elemental analyses. [3]Ferrocenophanes **1a,b** were prepared as described.⁹ Cyclic voltammetry studies on 0.1 mM solutions of the samples in CH₂Cl₂ (dried over CaH₂, distilled and stored over 3 Å molecular sieves in argon atmosphere) containing [nBu₄N][PF₆] (concentration 0.1 M) as conducting salt were carried out under inert argon atmosphere (in the case of **2c** in a MBraun acrylic glovebox GB2202-C-VAC). The setup consisted of a three-electrode cell with a platinum disk as working electrode, a silver spiral as counter electrode, and a silver pseudo reference electrode. The potential was driven by a WaveDriver 20 bipotentiostat from Pine Research Instrumentation, and electrochemical data were recorded via AfterMath (Ver. 1.2.5966; Pine Instruments). The peak potentials of the redox processes were referenced using Fc/Fc⁺.

Ferrocenophane-phosphonium salts 2a[ECl₄] (E = Al, Ga). A mixture of **1a** (100 mg, 238 μ mol) and the appropriate metal trichloride (AlCl₃: 30 mg, 238 μ mol; GaCl₃: 40 mg, 238 μ mol) was mechanically agitated with a magnetic stir bar until the solid mixture adopted a homogeneous, dark red color. The crude products were obtained as oily or solid residue in \approx 90% yield after evaporation of any volatile

components. Single crystals of **2a**[AlCl₄] were obtained by dissolving the crude product in anhydrous CH₂Cl₂ (2 mL), layering with pentane (2 mL) and allowing for mixing of the two solvents by diffusion. A small amount of red crystals that had formed overnight was collected after decantation of the mother liquor and cautiously dried in vacuum (yield < 5%).

2a[AlCl₄]: ¹H NMR (CD₂Cl₂, 400 MHz, 303 K): δ = 4.72 (m, 4 H, Cp), 4.46 (m, 4 H, Cp), 3.85 (d, 2 H, ³J_{PH} = 15.8 Hz, CH₂), 1.04 (d, 18 H, ⁵J_{PH} = 0.8 Hz, *t*Bu). – ¹³C{¹H} NMR (CD₂Cl₂, 101 MHz, 303 K): δ = 100.5 (d, ²J_{PC} = 14.3 Hz, Cp), 71.9 (s, Cp), 68.8 (d, *J*_{CP} = 1.5 Hz, Cp), 66.7 (d, ²J_{PC} = 36.2 Hz, CH₂), 32.7 (d, ³J_{PC} = 3.5 Hz, NCC), 27.7 (d, ⁴J_{PC} = 1.9 Hz, CH₃). – ¹H, ¹⁵N gs-HMBC (CD₂Cl₂, 400 MHz, 303 K): δ ¹⁵N = -227 (d, ¹J_{PN} = 120 Hz). – ²⁷Al NMR (CD₂Cl₂, 104.3 MHz, 303 K): δ = 103.7 (Δ v_{1/2} = 16 Hz). – ³¹P{¹H} NMR (CD₂Cl₂, 163 MHz, 303 K): δ = 296.0. The high sensitivity precluded obtaining a satisfactory elemental analysis and conclusive MS data, but the homogeneity was proven by spectroscopic data.

2a[Ga_{1.5}Cl_{1.75}]: ¹H NMR (CD₂Cl₂, 400 MHz, 303 K): δ = 4.71 (m, 4 H, Cp), 4.45 (m, 4 H, Cp), 3.84 (d, 2 H, ³J_{PH} = 15.8 Hz, CH₂), 1.03 (d, 18 H, ⁵J_{PH} = 0.7 Hz, *t*Bu). – ¹³C{¹H} NMR (CD₂Cl₂, 101 MHz, 303 K): δ = 100.5 (d, ²J_{PC} = 14.3 Hz, Cp), 71.9 (s, Cp), 68.8 (d, *J*_{CP} = 1.5 Hz, Cp), 66.7 (d, ²J_{PC} = 36.2 Hz, CH₂), 32.8 (d, ³J_{PC} = 3.4 Hz, NCC), 27.9 (d, ⁴J_{PC} = 1.9 Hz, CH₃). – ¹H, ¹⁵N gs-HMBC (CD₂Cl₂, 400 MHz, 303 K): δ ¹⁵N = -226.9 (d, ¹J_{PN} = 98 Hz). – ⁷¹Ga NMR (CD₂Cl₂, 122 MHz, 303 K): δ = 248.3 (Δ v_{1/2} = 2.3 kHz). – ³¹P{¹H} NMR (CD₂Cl₂, 163 MHz, 303 K): δ = 295.8 (br). Anal. for C₂₀H₃₀Cl₄FeGa_{1.5}N₂P (596.82 g mol⁻¹): calcd. C 40.25, H 5.07, N 4.69; found C 38.46, H 4.81, N 4.46.¹¹ The high sensitivity precluded conclusive MS analysis.

Ferrocenophane-phosphonium-Mn(CO)₄ complexes. A mixture of the appropriate *P*-halogeno-1,3,2-diazaphospha-[3]ferrocenophan (**1a**: 100 mg, 238 μ mol; **1b**: 100 mg, 213 μ mol) and Na[Mn(CO)₅] (**8a**: 700 mg, 321 μ mol; **8b**: 600 mg, 275 μ mol) was dissolved in anhydrous Et₂O (10 mL). After the evolution of CO (Caution! toxic!) had ceased, the mixture was stirred for additional 10 min and then evaporated to dryness. The residue was extracted with pentane (5 mL) and the formed suspension filtered through a layer of Celite.

Complex 8a: The filtrate was evaporated to a volume of 2 mL and the resulting solution stored at -27 °C. Dark red crystals formed which were collected by filtration and dried in vacuum. Yield 92 mg (70%); ¹H NMR (C₆D₆, 400 MHz, 303 K): δ = 3.98 (m, 4 H, Cp), 3.84 (m, 4 H, Cp), 3.2 (m, 2 H, CH₂), 3.18 (m, 2 H, CH₂), 0.92 (s, 18 H, *t*Bu). – ³¹P{¹H} NMR (C₆D₆, 400 MHz, 303 K): δ = 320 (br). – IR (solid, ν CO): $\tilde{\nu}$ = 2059 (m), 1981 (m), 1963, (s) 1918 (s) cm⁻¹. – Anal. for C₂₄H₃₀FeMnN₂O₄P: calcd. C 52.20, H 5.48, N 5.07; found C 51.82, H 5.57, N 5.01.

Complex 8b: The filtrate was evaporated to dryness and the residue dissolved in MeCN (2 mL). Storage of the solution at -27 °C afforded 78 mg (yield 65%) of **9b** as ark red crystals. ¹H NMR (C₆D₆, 400 MHz, 303 K): δ = 4.01 (m, 2 H, Cp), 3.93 (m, 2 H, Cp), 3.83 (m, 2 H, Cp), 3.65 (m, 2 H, Cp), 0.25 (s, 18 H, TMS). – ³¹P{¹H} NMR (C₆D₆, 400 MHz, 303 K): δ = 290 (br). – IR (solid, ν CO): $\tilde{\nu}$ = 2042 (m), 1970 (m), 1932, (s) 1920 (s) cm⁻¹. – Anal. for C₂₀H₂₆FeMnN₂O₄PSi₂: calcd. C 43.18, H 4.71, N 5.04; found: C 43.05, H 4.88, N 4.89.

Crystallography. X-ray diffraction studies were carried out using a Bruker Kappa Apex II diffractometer equipped with a Duo CCD-detector and a KRYO-FLEX cooling device with Mo-K α radiation (λ = 0.71073 Å) at *T* = 150(2) (**2a**[AlCl₄]) or 130(2) K (**8a,b**), respectively. The structures were solved by direct methods (SHELXA^{29a}) and refined with a full-matrix least-squares scheme on *F*² (SHELXL-2014^{29b}). Semi-empirical absorption corrections were applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms with a riding model. CCDC-1942456 (**2a**[AlCl₄]), CCDC-1942458 (**8a**) and CCDC-1942457 (**8b**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational studies. All calculations were carried out with the Gaussian 09³⁰ and MRCC³¹ program packages. Full geometry optimization was performed for all molecules at ω B97X-D/6-311+G**³² and B3LYP-D3/6-311+G**³³ levels, followed by calculation of harmonic vibrational frequencies at the same levels to establish the nature of the

stationary points obtained. Minima are characterized by only positive eigenvalues of the Hessian. Solvation effects were modelled by applying the implicit PCM (Polarizable Continuum Model) method³⁴ during the geometry optimizations. Excitation energies of the cations were obtained from time-dependent DFT calculations at the B3LYP/6-311+G** level of theory, second-order algebraic diagrammatic construction (ADC(2)),³⁵ or second-order coupled-cluster singles and doubles (CC2)³⁶ approaches, respectively, using the ω B97X-D/6-311+G** optimized molecular structures. The orbitals for complete active space calculations were chosen from the HF/6-31G* orbitals (the shapes and energies are displayed in Table S4). The Multiwfn program³⁷ was used to determine the bond critical points and the IQmol program³⁸ for visualization of molecules and molecular orbitals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Crystallographic details for [2a]AlCl₄, **8a**, **8b**; plots of NMR and IR spectra for [2a]AlCl₄, [2a]Ga_{1.5}Cl_{5.75}, **8a**, **8b**; UV-VIS spectrum of [2a]AlCl₄; cyclic voltammetry studies of the reduction of [2a]Ga_{1.5}Cl_{5.75}; results of DFT and CASSCF calculations (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors acknowledge financial support by the German Research Foundation (DFG) through grant no. GU 415/16-1, PI 353/10-1 and grant no OTKA NN 113772, and the EU-COST network CM1302 “Smart Inorganic Polymers” (SIPs). LN is grateful for the Alexander von Humboldt Foundation for the re-invitation grant. We further thank B. Förtsch for elemental analyses, and J. Trinkner and Dr. W. Frey (both Institute of Organic Chemistry, University of Stuttgart) for the recording of mass spectra and the collection of X-ray data sets, respectively.

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