



Syntheses and crystal structures of linear coordinated complexes of Ag⁺ with the ligands C(PPh₃)₂ and (HC{PPh₃}₂)⁺

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ABSTRACT

The cationic complexes [(Ph₃P)₂C]Ag(C(PPh₃)₂)X (**2**⁺, X = Cl, BF₄) with a linear arrangement of the ligands were obtained from the reaction of C(PPh₃)₂ (**1**) with the appropriate AgX in THF. The ³¹P NMR spectrum of the cation **2**⁺ exhibits a doublet with *J*(Ag,P) = 15.3 Hz. The cation was also formed when the adduct O₂C ← **1** was allowed to react with AgX in CH₂Cl₂ in the first step as shown by ³¹P NMR; however, deprotonation of the solvent finally produced the cation (HC{PPh₃}₂)⁺, (**H1**)⁺ quantitatively. In the absence of coordinating anions, the tricationic complex [(Ph₃P)₂CH]Ag(CH{PPh₃}₂)(BF₄)₃ (**3**), containing the cation (**H1**)⁺ as ligand, could be isolated by reacting AgBF₄ with the salt (**H1**)(BF₄). All compounds were characterized by IR and ³¹P NMR spectroscopy; the structures of the compounds **2**]Cl·1.25THF, **3**·5CH₂Cl₂, **3**·4C₂H₄Cl₂, and (**H1**)(BF₄) could be established by X-ray analyses.

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1. Introduction

The double ylide hexaphenylcarbodiphosphorane C(PPh₃)₂ (**1**) [1] has a bent conformation [2] and can be considered as a divalent carbon(0) atom which is stabilized by two neutral phosphine ligands, thus attaining eight electrons. **1** is equipped with two high lying occupied MO's at the carbon atom of σ and π symmetry (HOMO and HOMO-1) which is established by NBO analysis; the lone pairs of electrons are stabilized by negative hyperconjugation [3]. **1** is a strong Lewis base and for chemical reactions these lone pairs may be arranged in a carbene-like sp² (**1a**) or sp³ (**1b**) hybridization, as depicted in Scheme 1, and in principle coordination to one or two Lewis acids is possible.

In contrast, in N-heterocyclic carbenes (NHC), which also contain carbon atoms with sp² hybridization, the related p-orbitals are empty [4].

It is well established that **1** forms addition compounds of the type L ← **1** with various electron deficient species L. In main group chemistry adducts with the atoms or ions S, Se [5], I⁺ [6], H⁺, Cl⁺, and the Lewis acids InMe₃ and AlBr₃ [7] were obtained and confirmed by X-ray analyses. Complexes in which **1** acts as a ligand in transition metal chemistry are described with Ni(CO)_n (n = 2, 3) [8], ReO₃⁺ [9], CuCl [10], and with Cp⁺Cu [11]. In addition to these adducts, the silver complexes [ClAgC(PPh₃)₂] [10] and [Cp⁺AgC(PPh₃)₂] [11] were also mentioned but not confirmed by crystal structure determinations. One Au complex has also been

published recently in which **1** is bridging an Au–Au bond [12]. With the 16 electron heteroallenes E=C=E, the adducts E₂CC–(PPh₃)₂ (E = O, S) are formed under C–C bond formation [13], which could be characterized by X-ray analyses [14]; recently, we have also published addition compounds between Lewis acids and these adducts [14–19]. All the addition compounds L ← **1** are based on **1a** and have in common that the ylidic carbon atom still has an occupied p-orbital of π symmetry which may undergo further reaction with Lewis acids. **1** is a strong base and can easily take up a proton to produce the cation (**H1**)⁺; however, in some cases twofold protonation can occur resulting in the dication (H₂**1**)²⁺ [3,20,21] based on an sp³ carbon atom as expressed by **1b**. Solvents like THF, CH₂Cl₂, or MeCN can serve as sources for protons. Studies concerning the high proton affinity of **1** are in progress. The additional free pair of electrons at the cation (**H1**)⁺ enables it to serve as a ligand under special conditions. Thus, the structure of the triply charged cation [(Ph₃P)₂CH]Ag(CH{PPh₃}₂)³⁺ was reported by us recently [3]. The coordination chemistry of ylides was summarized in several review articles [22–24].

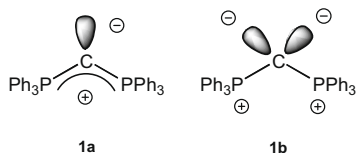
Here we report on the results of the reaction of **1** with AgCl, AgBF₄, and on an unusual behavior of its CO₂ adduct, O₂CC(PPh₃)₂ (O₂C ← **1**), with AgCl and AgBF₄ in various solvents.

2. Results and discussion

In an earlier report about the reaction of **1** with AgCl in THF solution, the formation of the adduct [ClAgC(PPh₃)₂] was described [10]. However, we could not confirm these results; instead, treatment of **1** with AgCl in THF solution produced colorless crystals

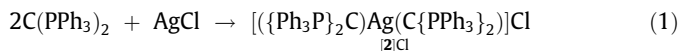
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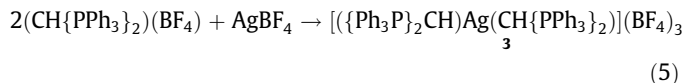
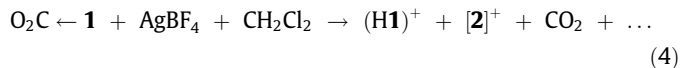
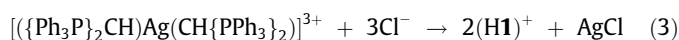
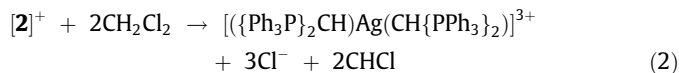
Scheme 1.

of the complex $[(\text{Ph}_3\text{P})_2\text{C}]\text{Ag}(\text{C}(\text{PPh}_3)_2)\text{Cl}$ ($[\mathbf{2}]\text{Cl}$) formed upon standing of the THF solution for several days at -18°C as shown in Eq. (1).



The ^{31}P NMR spectrum of the THF solution exhibits a doublet at 13.6 ppm arising from $^2J(^{107/109}\text{Ag}, ^{31}\text{P})$ coupling with a coupling constant of 15.3 Hz; no further doublet is recorded which could point to a 1:1 coordination complex. In the complex $[\text{Cp}^*\text{AgC}(\text{PPh}_3)_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) a related coupling constant of 12.2 Hz was found [11]. The cation $\mathbf{2}^+$ is the first complex in which two molecules of $\mathbf{1}$ coordinate at one metal ion. Additionally to the doublet, the ^{31}P NMR spectrum of a freshly prepared solution of $[\mathbf{2}]\text{Cl}$ in dichloromethane (DCM) exhibits a signal at 20.9 ppm (10:1 signal mole ratio) which is attributed to the cation $(\text{H}\mathbf{1})^+$. This signal ratio changed to 10:2 after 24 h and to 10:3 after 120 h. HCl abstraction from the solvent and protonation of the ylidic carbon atom of $[\mathbf{2}]\text{Cl}$ was suggested with intermediate formation of the trication $[(\text{Ph}_3\text{P})_2\text{CH}]\text{Ag}(\text{CH}(\text{PPh}_3)_2)^{3+}$ but which loses the weak nucleophile $(\text{H}\mathbf{1})^+$ upon reaction with the stronger nucleophile Cl^- present in solution (Eq. (3)). However, the complex $\mathbf{3}$, containing this trication, can be isolated in the absence of coordinating anions as shown below. The reaction of $\mathbf{1}$ with AgBF_4 in THF leads also to the cation $\mathbf{2}^+$ as shown by ^{31}P NMR spectroscopy; however, formation of a silver mirror indicates some decomposition. If the reaction was carried out in the dark colorless crystals of $[(\text{Ph}_3\text{P})_2\text{C}]\text{Ag}(\text{C}(\text{PPh}_3)_2)(\text{BF}_4)$ ($[\mathbf{2}]\text{BF}_4$) were obtained from THF solution upon cooling the solution to -18°C .

A similar ^{31}P NMR spectrum was observed when we reacted the adduct $\text{O}_2\text{C} \leftarrow \mathbf{1}$ with AgBF_4 in methylene chloride (DCM) or 1,2-dichloroethane (DCE). Immediately after combining the components, the spectrum exhibits a singlet at 20.0 ppm along with a doublet at 12.7 ppm and a coupling constant = 15.3 Hz according to the cation $\mathbf{2}^+$; however, within several hours the doublet disappeared in favor of the singlet, which was attributed to the cation $(\text{H}\mathbf{1})^+$. This cation is probably formed by a proton abstraction from CH_2Cl_2 by $\mathbf{2}^+$ and loss of CO_2 . The ratio of the two signals depends on the time between starting the reaction and measuring the spectrum. Crystals obtained from this solution were identified as $(\text{H}\mathbf{1})(\text{BF}_4)$. Addition of excess AgBF_4 to the CH_2Cl_2 solution of $\text{O}_2\text{C} \leftarrow \mathbf{1}$ gave a new signal in the ^{31}P NMR spectrum at 23.5 ppm. From this solution crystals of $\mathbf{3} \cdot 5\text{CH}_2\text{Cl}_2$ formed upon layering with *n*-pentane which in DCM solution show only a singlet at 23.5 ppm. The same results were obtained in DCE solution. Thus, halogenated hydrocarbons such as DCM, DCE, or chloroform act as sources for H^+ ions to produce the cation $(\text{H}\mathbf{1})^+$ as shown in Eqs. (2) and (3); the remaining CHCl fragment dimerizes to give the related olefin [20]. Kinetic studies of the deprotonation process of DCM by $\mathbf{1}$, $\text{O}_2\text{C} \leftarrow \mathbf{1}$, and addition compounds of $\mathbf{1}$ are in progress.



These findings prompted us to perform a direct synthesis of $[(\text{Ph}_3\text{P})_2\text{CH}]\text{Ag}(\text{CH}(\text{PPh}_3)_2)(\text{BF}_4)_3$ ($\mathbf{3}$) from AgBF_4 and $(\text{H}\mathbf{1})(\text{BF}_4)$ in DCM (Eq. (5)). The ^{31}P NMR of this solution showed only a singlet at 23 ppm indicating quantitative formation of $\mathbf{3}$. Both the compounds $[\mathbf{2}]\text{Cl}$ and $\mathbf{3}$ exhibit a $\text{Ag}-\text{C}-\text{P}$ sequence but apparently only the $^2J(\text{Ag},\text{P})$ coupling constant mediated by a sp^2 carbon atom is large enough to be resolved in ^{31}P NMR spectroscopy at room temperature.

The salt $\mathbf{3}$ is the first compound in which the cation $(\text{H}\mathbf{1})^+$ acts as a ligand towards a transition metal and selected crystal data of $\mathbf{3} \cdot 5\text{CH}_2\text{Cl}_2$ were published recently [3]. A similar Au complex was described earlier [12], but without crystal structure analysis. Cations as ligands in transition metal chemistry are rare and concentrate on few examples. The most common cationic ligand is NO^+ , but which can also be considered as the neutral NO molecule contributing three electrons to the electronic household of a metal in a complex or a cluster [25].

3. Crystal structures

To get more insight into the nature of the complexes and the bonding situation, X-ray analyses of $[\mathbf{2}]\text{Cl}$ and of two salts of $\mathbf{3}$, containing different solvent molecules, were performed. Colorless crystals of $[\mathbf{2}]\text{Cl} \cdot 1.25\text{THF}$ formed upon standing the THF solution of the reaction mixture at -18°C . Suitable colorless crystals of $\mathbf{3} \cdot 5\text{CH}_2\text{Cl}_2$ were obtained from CH_2Cl_2 solution by layering with *n*-pentane [3]; crystals of $\mathbf{3} \cdot 4\text{C}_2\text{H}_4\text{Cl}_2$ were obtained similarly from DCE solution. The unit cell of $\mathbf{3} \cdot 5\text{CH}_2\text{Cl}_2$ contains two crystallographically independent salt units; the unit cell of $\mathbf{3} \cdot 4\text{C}_2\text{H}_4\text{Cl}_2$ contains only one molecule. The DCE molecules and the BF_4 groups of $\mathbf{3} \cdot 4\text{C}_2\text{H}_4\text{Cl}_2$ are disordered. Colorless needles of the salt $(\text{H}\mathbf{1})(\text{BF}_4)$ were also isolated, which crystallizes without including solvent molecules. The structure of the cation of $[\mathbf{2}]^+$ is shown in Fig. 1. In Fig. 2 a view down the $\text{C}(\text{Ag})\text{C}$ axis of the cation $[\mathbf{2}]^+$ is shown; crystallographic data are collected in Table 1; distances and angles are found in Tables 2–4.

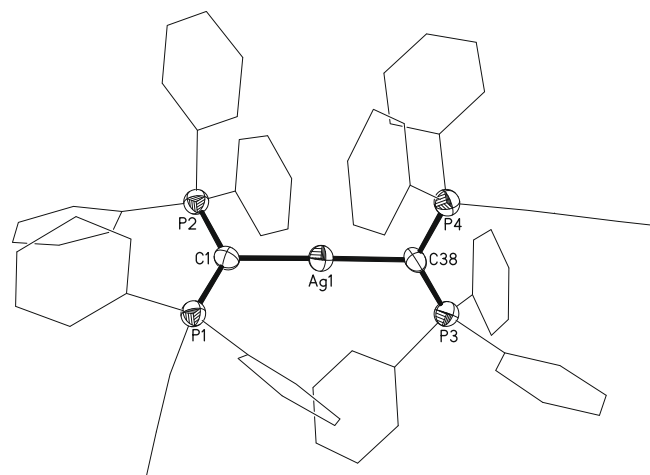


Fig. 1. Molecular structure of the cation of $[(\text{Ph}_3\text{P})_2\text{C}]\text{Ag}(\text{C}(\text{PPh}_3)_2)\text{Cl}$ ($[\mathbf{2}]\text{Cl} \cdot 1.25\text{THF}$) showing the atom numbering scheme. The ellipsoids are drawn at a 40% probability level. The H atoms at the phenyl rings, the anion, and the solvent molecules are omitted for clarity.

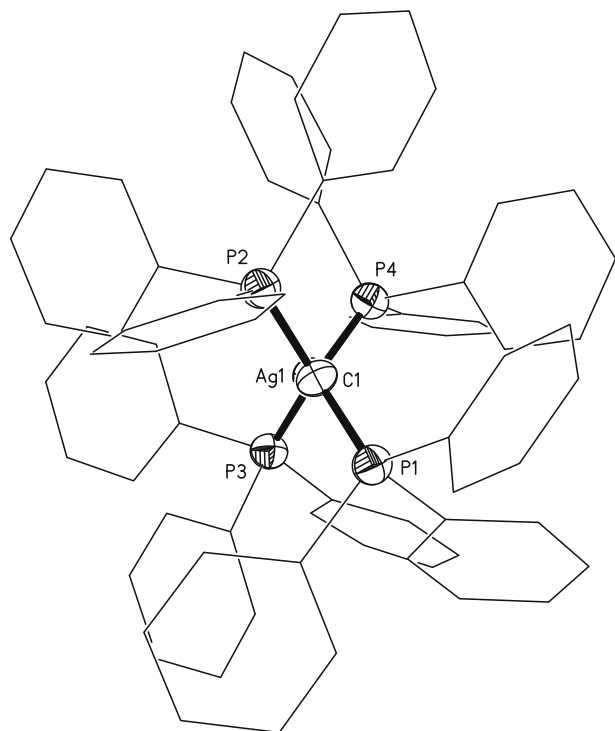


Fig. 2. View down the C(1)–Ag(1)–C(38) axis of $[2]Cl \cdot 1.25THF$; the H atoms at the phenyl rings are omitted for clarity.

3.1. Structure of $[2]Cl \cdot 1.25THF$

The structure of the cation of $[2]Cl \cdot 1.25THF$ is depicted in Fig. 1; the chloride counterion and the disordered THF molecules are not shown. The silver atom is essentially coordinated in a linear arrangement with a C–Ag–C angle of 177.5° . The Ag–C distances amount to 2.115(8) and 2.134(7) Å, which are actually longer than those in a related Arduengo type carbene complex $[(NHC)Ag(NHC)]^+$ (mean 2.073(4) Å) [26] but comparable (or slightly shorter) with those in the cation $[(OC)Ag(CO)]^+$ (2.14(3) Å), in which the CO groups act mainly as σ donor ligands [27]. The carbon atoms C(1) and C(38) are in a perfect planar environment with sp^2 hybridization, and the P_2CAg planes are twisted by 113° (67°), as shown in Fig. 2, suggesting steric interactions between the phenyl groups rather than electronic effects. The mean value of the P–C–P angles amounts to 128.8° , thus being slightly smaller than those in the free ligand. The P–C(1, 38) distances (mean 1.669(7) Å) have increased upon complex formation, which can be interpreted in terms of a reduction of the negative $p-\sigma^*$ hyperconjugation; similar effects were observed in other adducts of **1** at Lewis acids [7]. However, if the Lewis acid is a π acceptor such as ReO_3^+ [9] or the heterocumulenes CX_2 ($X = O, S$) [14], the related bond lengths increase by further 0.08–0.10 Å, thus reaching values of normal P–C single bonds.

3.2. Structures of $3 \cdot 5CH_2Cl_2$ and $3 \cdot 4C_2H_4Cl_2$

We have got the crystal structures $3 \cdot 5CH_2Cl_2$ and $3 \cdot 4C_2H_4Cl_2$, which differ in the nature and number of the solvents included and also in some parameters of the cations. The structure of $3 \cdot 5CH_2Cl_2$ was published earlier and is therefore not depicted here [3]. The trications of both salts are centrosymmetric with Ag^+ as the inversion center. The $(BF_4)^-$ counterions are disordered; one of them in $3 \cdot 5CH_2Cl_2$ in such that it could be refined in two positions. There are no remarkable contacts between the trications

and the anions or the solvent molecules. All solvent molecules are more or less disordered and three of the five DCM molecules of $3 \cdot 5CH_2Cl_2$ were refined in split positions. In $3 \cdot 4C_2H_4Cl_2$ all DCE molecules show disorder behavior. Whereas the selected bond lengths do not vary markedly in the two compounds, stronger deviations in bond angles (up to $6.1(3)^\circ$) are observed, which nicely demonstrate the influence of packing effects.

According to the centrosymmetry of the cations, the C–Ag–C angles are exactly linear. The two protons at the ylidic carbon atoms cause the Ag–C bond lengths to increase from 2.125 Å (mean value in **2**) up to 2.22 Å, which is one of the longest known bond lengths which normally range between 2.00 and 2.20 Å. The carbon atoms are in an approximately tetrahedral environment. However, the P(1)–C(1)–P(2) angles amount to approximately 120° , thus being close to that of a sp^2 carbon atom, but the sum of the angles Ag,C,P with exclusion of those to H(1) are 345° and far away from planarity. In the free cation $(H1)^+$ a planar HCP₂ arrangement is observed, but the P–C–P angle is larger (130°) than in $[2]^+$ and **3** and close to most of those in the addition compounds of **1** and various Lewis acids [7]. The P–C(1) distances in **3** amounting to 1.775 Å are about 0.08 Å longer than in the $(H1)^+$, and are about 0.10 Å longer than in **2** (mean 1.669(7) Å), indicating decreasing double bond character as is expected according the bonding to an sp^3 carbon atom. In general, the P–C distances increase in the row $1 < 2 < (H1)^+ < 3$.

3.3. Structure of $(H1)(BF_4)$

Cation and anion of $(H1)(BF_4)$ are linked by weak H bridges. The anion is disordered in two positions (0.6:0.4) in which F(1) could be refined for both positions. Although this salt was not described so far, cation and anion were frequently reported with other counterions; that's why the structure is not depicted here. The P–C–P angle of $130.2(2)$ and the mean P–C and P–C_{ph} bond lengths of 169.9(1) and 180.7(1), respectively, correspond to those found in other compound with the same cation [3,7,28]. The difference of 0.11 Å in P–C bonds reflect the partial $p-\sigma^*$ double bond to the ylidic carbon atoms and the normal single bond to the phenyl carbon atoms.

4. Conclusion and outlook

The bent structure of the carbon ligand **1** suggests proximity to N-heterocyclic carbenes (NHC); both form addition compounds with various Lewis acids. In adducts with NHC's an empty p-orbital at the donating carbon atom allows d–p (π) back bonding which, however, is rather small but not negligible. This is established by theoretical calculations [30].

In addition compounds of **1**, however, the filled p-orbital at the carbon atom changes the properties dramatically. For low valent transition metals a repulsion between this and filled d-orbitals is expected, whereas for metals in high oxidation states the possibility of a four electron donating ligand is given [9,29]. Indeed, the number of low valent transition metal carbonyl complexes with **1** as ligand is limited as yet to two Ni derivatives [8]; for other $(CO)_xM \leftarrow 1$ compounds no structural proofs are given and their existence is questionable. Furthermore, an electrophilic attack at the second HOMO orbital of $L \leftarrow 1$ adducts can occur. In principle two types of complexes are to be expected if **1** acts as a two electron donor to produce 1:1 adducts as shown in Scheme 2. In **A**, a planar arrangement with an sp^2 carbon atom is operative, whereas a pyramidal arrangement with an sp^3 carbon atom and a free pair of electrons as in **B** should also be taken into account.

From theoretical considerations, electron rich Lewis acids **L** should prefer a type **B** geometry whereas for electron poor acids

Table 1
Crystal data and structure refinement details.

	2-1.25THF	3-5CH ₂ Cl ₂	3-4C ₂ H ₄ Cl ₂	(H1)(BF ₄)
Formula	C ₇₉ H ₇₀ AgClO _{1.25} P ₄	C ₇₉ H ₇₂ AgB ₃ Cl ₁₀ F ₁₂ P ₄	C ₈₂ H ₇₈ AgB ₃ Cl ₈ F ₁₂ P ₄	C ₃₇ H ₃₁ BP ₂ F ₄
M _w (g/mol)	1306.64	1868.15	1839.33	624.51
a (Å)	20.918(2)	13.044(1)	11.484(1)	10.717(2)
b (Å)	23.940(1)	13.384(2)	13.505(1)	11.405(2)
c (Å)	16.317(2)	26.411(3)	14.304(1)	14.515(2)
α (°)		94.20(2)	93.29(1)	79.27(1)
β (°)	111.62(1)	103.78(2)	93.25(1)	77.79(1)
γ (°)		109.91(1)	111.54(1)	63.94(1)
Crystal size (mm)	0.2 × 0.14 × 0.07	0.41 × 0.31 × 0.26	0.26 × 0.24 × 0.14	0.21 × 0.21 × 0.08
Volume (Å ³)	7596(1)	4149.8(2)	2052.9(3)	1548.9(5)
Z	4	2	1	2
D _{calc} (g/cm ³)	1.142	1.495	1.488	1.339
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P2 ₁ /c (Nr. 14)	P $\bar{1}$ (Nr. 2)	P $\bar{1}$ (Nr. 2)	P $\bar{1}$ (Nr. 2)
Diffractionmeter	IPDS I (Stoe)	IPDS I (Stoe)	IPDS II (Stoe)	IPDS II (Stoe)
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Temperature (K)	193	193	193	193
μ (cm ⁻¹)	4.2	7.1	6.6	1.9
2θ _{max} (°)	52.36	52.27	52.50	52.74
Index range	-25 ≤ h ≤ 25 -29 ≤ k ≤ 29 -20 ≤ l ≤ 20	-16 ≤ h ≤ 16 -16 ≤ k ≤ 16 -32 ≤ l ≤ 32	-14 ≤ h ≤ 14 -16 ≤ k ≤ 16 -17 ≤ l ≤ 17	-13 ≤ h ≤ 13 -14 ≤ k ≤ 19 -17 ≤ l ≤ 17
Number of reflections collected	74757	40800	29876	22567
Number of independent reflections (R _{int})	14910 (0.2487)	15195 (0.1039)	8204 (0.0623)	6180 (0.0631)
Number of observed reflections with F ₀ > 4σ(F ₀)	3098	6092	5319	3431
Parameters	737	1041	530	429
Absorption correction	Numerical	Numerical	Numerical	Numerical
Structure solution	Direct methods	Direct methods	Patterson method	Direct methods
Refinement against F ²	SHELXS-97 [33] SHELXL-97 [36]	SIR-92 [34] SHELXL-97 [36]	SHELXL-PLUS [35] SHELXL-97 [36]	SIR-92 [34] SHELXL-97 [36]
H atoms	Calculated positions with common displacement parameter	Calculated positions with common displacement parameter	Calculated positions with common displacement parameter; H(1) was refined free	Calculated positions with common displacement parameter
R ₁	0.0649	0.0611	0.0801	0.0395
wR ₂ (all data)	0.1441	0.1528	0.2332	0.0816
Maximum electron density left (e Å ⁻³)	0.74	1.43	1.72	0.61

Table 2
Selected bond lengths (Å) and angles (°) in [2]Cl-1.25THF.

Bond lengths (Å)			
Ag(1)–C(1)	2.115(8)	Ag(1)–C(38)	2.134(7)
P(1)–C(1)	1.656(7)	P(1)–C(2)	1.803(8)
P(1)–C(8)	1.829(8)	P(2)–C(14)	1.796(8)
P(2)–C(1)	1.690(7)	P(2)–C(20)	1.821(8)
P(2)–C(26)	1.813(8)	P(2)–C(32)	1.822(8)
P(3)–C(38)	1.667(7)	P(3)–C(39)	1.813(8)
P(3)–C(45)	1.799(8)	P(3)–C(51)	1.791(8)
P(4)–C(38)	1.663(7)	P(4)–C(57)	1.815(8)
P(4)–C(63)	1.811(9)	P(4)–C(69)	1.821(9)
Bond angles (°)			
C(1)–Ag(1)–C(38)	177.5(3)	C(1)–P(1)–C(2)	116.3(4)
C(1)–P(1)–C(8)	110.9(4)	C(1)–P(1)–C(14)	115.1(4)
C(2)–P(1)–C(8)	105.5(4)	C(2)–P(1)–C(14)	106.8(4)
C(8)–P(1)–C(14)	100.7(4)	C(1)–P(2)–C(20)	109.9(4)
C(1)–P(2)–C(26)	114.8(4)	C(1)–P(2)–C(32)	116.9(4)
C(20)–P(2)–C(26)	104.2(4)	C(20)–P(2)–C(32)	104.4(4)
C(26)–P(2)–C(32)	105.5(4)	C(38)–P(3)–C(39)	114.4(4)
C(38)–P(3)–C(45)	115.6(4)	C(38)–P(3)–C(51)	110.9(4)
C(39)–P(3)–C(45)	108.0(4)	C(39)–P(3)–C(51)	105.7(4)
C(45)–P(3)–C(51)	100.9(4)	C(38)–P(4)–C(57)	113.0(5)
C(38)–P(4)–C(63)	116.1(4)	C(38)–P(4)–C(69)	111.8(4)
C(57)–P(4)–C(63)	106.6(4)	C(57)–P(4)–C(69)	103.1(4)
C(63)–P(4)–C(69)	105.0(4)	Ag(1)–C(1)–P(1)	117.9(4)
Ag(1)–C(1)–P(2)	113.6(4)	P(1)–C(1)–P(2)	128.5(5)
Ag(1)–C(38)–P(3)	119.8(5)	Ag(1)–C(38)–P(4)	110.9(4)
P(3)–C(38)–P(4)	129.1(5)		

a planar arrangement as in **A** is expected. However, as yet, only type **A** compounds were found and the only candidate for an electron rich L and an arrangement as in **B**, the complex [(CO)₃Ni(C{PPh₃})₂], exhibits a perfect sp² donating carbon atom [8]. The preference for **A** is probably due to a p–σ* back bonding into P–C_{phenyl} σ* orbitals (negative hyperconjugation) accompanied by the space requirement of the sterically demanding phenyl rings. Calculations have shown that the energy difference between **A** and **B** in the case of [(CO)₃Ni(C{PPh₃})₂] is very small, amounting to only 1.1 Kcal/mol [31]. Thus, the planar structure arises from steric and packing effects.

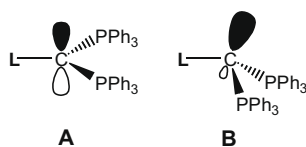
From recent results we found that most of the adducts of **1** with main group or transition metal fragments are powerful deprotonation agents to finally produce the cation (HC{PPh₃})₂⁺ (H1)⁺ probably via the related cations [L ← C(H){PPh₃}]⁺ (L ← H1)⁺, the protonated species **B**, as intermediates. Calculations of the proton affinities of some addition compounds **A** produced the surprising results that they are nearly as high as the proton affinity of **1**; a rearrangement to the pyramidal array **B** may be responsible for this effect [31]. In the presence of other nucleophiles, liberation of the cation (HC{PPh₃})₂⁺ from the protonated species **B** may occur which is less strongly bonded. However, in one case with Ag⁺ in the presence of weakly coordinating counterions as described in this contribution we could isolate a silver complex in which this cation acts as a complex ligand to produce the new trication of **3** [3]. A challenge for the future will be to study this type of compounds

Table 3
Selected bond distances (Å) and angles (°) in **3**-5CH₂Cl₂/**3**-4C₂H₄Cl₂.

Bond distances (Å)			
Ag(1)–C(1)	2.209(6)/ 2.221(5)	P(1)–C(1)	1.770(7)/ 1.791(6)
P(1)–C(2)	1.808(8)/ 1.803(6)	P(1)–C(8)	1.806(6)/ 1.811(6)
P(1)–C(14)	1.796(7)/ 1.816(6)	P(2)–C(1)	1.779(7)/ 1.779(6)
P(2)–C(20)	1.783(7)/ 1.813(6)	P(2)–C(26)	1.793(7)/ 1.806(6)
P(2)–C(32)	1.806(6)/ 1.801(6)	C(1)–H(1)	0.81(7)/0.93(6)
Bond angles (°)			
C(1)–Ag(1)– C(1a)	180/180	C(1)–P(1)–C(2)	108.2(4)/ 114.3(3)
C(1)–P(1)–C(8)	113.2(4)/ 108.3(3)	C(1)–P(1)–C(14)	113.1(4)/ 112.4(3)
C(2)–P(1)–C(8)	104.4(3)/ 108.8(3)	C(2)–P(1)–C(14)	110.4(4)/ 107.8(3)
C(8)–P(1)–C(14)	107.2(3)/ 104.8(3)	C(1)–P(2)–C(20)	108.8(4)/ 114.1(3)
C(1)–P(2)–C(26)	111.6(4)/ 111.1(3)	C(1)–P(2)–C(32)	113.9(3)/ 109.4(3)
C(20)–P(2)– C(26)	108.5(3)/ 110.9(3)	C(20)–P(2)– C(32)	103.9(4)/ 103.6(3)
C(26)–P(2)– C(32)	109.7(3)/ 107.3(3)	Ag(1)–C(1)–P(1)	113.4(4)/ 116.8(3)
Ag(1)–C(1)–P(2)	111.0(4)/ 109.9(2)	P(1)–C(1)–P(2)	119.9(4)/ 118.7(3)
Ag(1)–C(1)–H(1)	97(6)/99(4)	P(1)–C(1)–H(1)	103(6)/104(4)
P(2)–C(1)–H(1)	110(6)/105(4)		

Table 4
Selected bond distances (Å) and angles (°) in the cation of (H1)(BF₄).

Bond distances (Å)			
P(1)–C(1)	1.696(2)	P(1)–C(2)	1.809(2)
P(1)–C(8)	1.812(2)	P(1)–C(14)	1.802(2)
P(2)–C(1)	1.701(2)	P(2)–C(20)	1.811(2)
P(2)–C(26)	1.796(2)	P(2)–C(32)	1.810(2)
C(1)–H(1)	0.85(3)		
Bond angles (°)			
C(1)–P(1)–C(2)	114.9(1)	C(1)–P(1)–C(8)	109.2(1)
C(1)–P(1)–C(14)	113.7(1)	C(2)–P(1)–C(8)	103.9(1)
C(2)–P(1)–C(14)	109.4(1)	C(8)–P(1)–C(14)	104.8(1)
C(1)–P(2)–C(20)	114.1(1)	C(1)–P(2)–C(26)	111.7(1)
C(1)–P(2)–C(32)	111.5(1)	C(20)–P(2)–C(26)	104.4(1)
C(20)–P(2)–C(32)	105.6(1)	C(26)–P(2)–C(32)	109.0(1)
P(1)–C(1)–P(2)	130.2(2)	P(1)–C(1)–H(1)	117(2)
P(2)–C(1)–H(1)	113(2)		



Scheme 2.

more systematically and to prove the existence of type **B** compounds by exploring suitable Lewis acid components L. (H1)(BF₄) will be an important source for the introduction of the weak nucleophile (H1)⁺.

5. Experimental

All operations were performed under an argon atmosphere in dried and degassed solvents using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use.

The IR spectra were run on a Nicolet 510 spectrometer. For the ³¹P NMR spectra we used the instruments Bruker AC 200 and 300 and the chemical shifts are expressed in ppm relative to 85% H₃PO₄. Elemental analyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg (Germany). The carbodiphosphorane **1** was prepared according to the modified literature procedure [32], and its adduct O₂C ← **1** was obtained by bubbling thoroughly dried CO₂ into a solution of **1** in toluene [14]. Commercially available AgBF₄ was used without further purification.

5.1. Preparation of [2]Cl

To a suspension of 0.076 g of AgCl (0.53 mmol) in about 4 ml of THF was added 0.570 g of **1** (1.06 mmol) and the mixture was stirred for about 1 h in the dark. A colorless precipitate of [2]Cl formed, which was separated by filtration. The filtered solution was stored at –18 °C, which produced further amounts of [2]Cl·1.25THF as colorless crystal; yield 75%. [2]Cl is slightly soluble in THF but dissolves very good in DCM. ³¹P NMR (CH₂Cl₂): 13.6 ppm (d, ²J(^{107/109}Ag, ³¹P) = 15.3 Hz); a similar shift was observed in THF solution. IR (Nujol mull, cm⁻¹): 1480 s, 1435 vs, 1308 w, 1209 m, 1157 vs, 1103 vs, 1069 m, 1028 w, 1011 w, 997 m, 802 s, 779 w, 758 s, 748 s, 710 vs, 696 vs, 569 w, 525 m, 517 vs, 511 s, 503 m. Anal. Calc. for C₇₉H₇₀AgClO_{1.25}P₄: C, 72.62; H, 5.40. Found: C, 71.45; H, 5.47%.

5.2. Preparation of [2]BF₄

To a solution of 0.550 g of **1** (1.03 mmol) in about 4 ml of THF was added 0.12 g of AgBF₄ (0.61 mmol) and the mixture was stirred for about 1.5 h in the dark. The colorless solution was filtered from some beige material. Storing of the solution at –18 °C produced colorless crystals of [2]BF₄ in about 55% yield. ³¹P NMR (THF): 13.8 ppm (d, ²J(^{107/109}Ag, ³¹P) = 15.3 Hz).

5.3. Preparation of 3-5CH₂Cl₂ and 3-4C₂H₄Cl₂

A mixture of 0.845 g (1.36 mmol) of (H1)(BF₄) and 0.132 g of AgBF₄ (0.68 mmol) were dissolved in about 5 ml of CH₂Cl₂ and stirred for 2 h. The resulting clear colorless solution was layered with *n*-pentane; crystals of 3-5CH₂Cl₂ separated after several days in about 80% yield. ³¹P NMR (CH₂Cl₂) 22.9 ppm: IR (Nujol mull, cm⁻¹): 1587 w, 1484 m, 1439 s, 1337 w, 1281 w, 1263 w, 1221 w, 1195 m, 1100 vs br, 1061 vs br, 996 s, 948 m, 909 m, 828 m, 798 s, 724 s sh, 687 s, 543 m, 509 m, 500 s, 489 s. Anal. Calc. for C₇₄H₆₂AgB₃F₁₂P₄: C, 61.57; H, 4.19. Found: C, 60.83; H, 4.36%. A similar procedure in DCE gave crystals of 3-4C₂H₄Cl₂ in about 70% yield. ³¹P NMR (DCM): 23.6 ppm.

5.4. Preparation of (H1)(BF₄)

To a solution of 1.00 g of (H1)I (1.51 mmol) in CH₂Cl₂ was added a solution of 0.293 g of AgBF₄ (1.51 mmol) in the same solvent. Immediately after combining the solutions, a precipitate of AgI formed which was filtered off. From the solution, the salt (H1)(BF₄) was precipitated by addition of *n*-pentane; the precipitate was filtered and dried in vacuum; yield 95%. ³¹P NMR (CH₂Cl₂): 20.1 ppm. ¹H NMR (CDCl₃): 1.76 (t, CH, ²J(P,H) = 5.38 Hz), 7.2–7.6 (m, Ph). IR (Nujol mull, cm⁻¹): 1586 w, 1586 w, 1478 m, 1436 s, 1309 w, 1270 m, 1159 vs, 1098 s, 1056 vs, 997 m, 798 s, 744 vs, 709 s, 694 vs, 567 m, 517 s, 501 s.

5.5. Reaction of AgBF₄ with O₂C ← **1** in CH₂Cl₂

A mixture of 0.170 g (0.87 mmol) AgBF₄ and 1.013 g of O₂C ← **1** (1.74 mmol) was dissolved in about 10 ml of CH₂Cl₂. After 20 min

the ^{31}P NMR spectrum showed singlets at 20.3 (H1^+) and 17.7 ppm and a doublet at 12.8 ppm ($^2J(\text{Ag},\text{P}) = 15.3$ Hz) (2^+) in 1:1.1:0.2 ratios, respectively; these ratios changed to 1:0.6:1.1 after 1 h, 1:0.4:1.7 and 1:0:1.9 after 5 h. Prolonged standing of the solution led to diminishing of the signal of 2^+ in favor of that of the cation (H1^+), which remained as only signal after 2 d. From the solution, crystals of (H1)(BF_4) were isolated in about 30% yield (not optimized) upon layering with *n*-pentane. The IR spectrum is identical with that of (H1)(BF_4) obtained from (H1)I and $\text{Ag}(\text{BF}_4)$.

6. Supplementary material

CCDC 708842 ($[\text{2}]\text{Cl}\cdot 1.25\text{THF}$), 612361 ($\text{3}\cdot 5\text{CH}_2\text{Cl}_2$), 708843 ($\text{3}\cdot 4\text{C}_2\text{H}_4\text{Cl}_2$), and 708844 ((H1)(BF_4)) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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