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# Cationic low coordinated phosphorus compounds as ligands: recent developments

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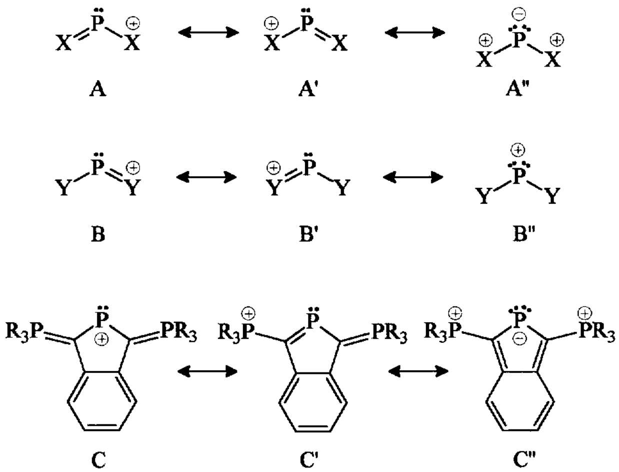
## 1. Introduction and scope

The Lewis-acid/base reaction between a ligand and a metal fragment to form a complex is one of the fundamental chemical reactions. In accord with their role as Lewis-bases, most ligands are neutral species or anions. However, cations may in principle also act as donors, and low coordinate phosphorus cations of the general formula $R_2P^+$ have received considerable interest as potential ligands [1]. The stability of these species depends vitally on charge delocalisation by incorporation of the phosphorus atom into a conjugated π-electron system, and salts of these cations actually represent the oldest examples of isolable compounds with genuine (pp)-π-bonds to phosphorus [1].

As suggested by Schmidpeter [1]c, $R_2P^+$ cations can be divided into two categories which differ in the charge distribution within the π-electron system. In type *A* cations, the positive charge is localised exclusively on the substituents. The phosphorus atom is neutral or has even a negative π-charge and is therefore expected to be a mainly nucleophilic centre. In contrast, the phosphorus atom in type *B* cations exhibits a positive π-charge and may be classified as an ambiphilic centre which exhibits both electrophilic and nucleophilic (lone pair) character. Typical representatives of type *A* cations are 2-phosphaallylic cations and phosphamethine cyanines [1]c, while type *B* ions are exemplified by aminophosphenium ions [1]b. Recently, Schmidpeter and Thiele [2] reported the synthesis of a novel heterocyclic bis-phosphonio-isophosphindolide cation whose electronic structure was described by the mesomeric formulae *C*–*C*″ containing both phosphenium (*C*) and phosphide type structures (*C*″). The two coordinate phosphorus may still be considered as an ambiphilic centre, although one with reduced electrophilic character, so that this novel heterocycle may be actually regarded as a hybrid between a class *A* and a class *B* cation.

The utilisation of the nucleophilic character of a phosphenium centre for complex



Scheme 1.

formation was demonstrated by the synthesis of a first cationic phosphenium complex by Parry et al. in 1978 [3]. Since then, a steady development of the coordination chemistry of aminophosphenium ions has taken place, stimulated by the perception that these cations are isolobal and isoelectronic (isovalent) analogues of singlet silylenes and carbenes whose complexes are of considerable theoretical and practical interest in the field of organometallic chemistry.

While the basics of aminophosphenium coordination chemistry have been addressed in earlier reviews [1a,b], it is the scope of this article to comment on recent developments in the coordination chemistry of ambiphilic phosphorus cations, including both type *B* (aminophosphenium) and *C* (bis-phosphonio-isophosphindolide) ions. The presented material will be divided into three major sections dealing with (i) achievements in synthesis of the free ligands and characterisation of their electronic structures, (ii) complex formation with Lewis-bases; and (iii) transition metal complexes. The description of the metal coordination chemistry will focus on cationic phosphenium complexes ("neutral metallophosphenium compounds" are considered beyond the scope of this article; cf. Ref. [1]b for differentiation between the cationic and neutral complexes) and bis-phosphonio-isophosphindolide complexes. It is the aim not only to give an account of the preparative chemistry of the complexes, but also to outline the parallels as well as differences in structure and bonding between isolobal/isoelectronic classes of compounds such as complexes of type *B* and *C* phosphorus cations, and carbene/silylene complexes.

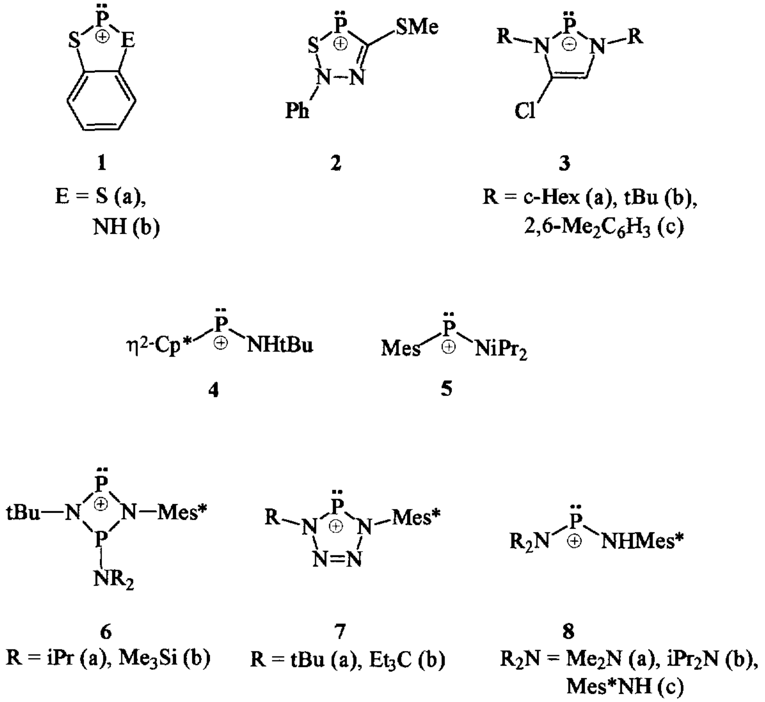
## 2. The ligands

### *2.1. Aminophosphenium ions and related systems*

### *2.1.1. Synthesis*

Earlier reviews [1]a,b have outlined three general routes to the synthesis of aminophosphenium ions, viz. (i) Lewis-acid induced phosphorus–halogen bond heterolysis, (ii) condensation reactions with trimethylsilyl triflate and (iii) substitution reactions at chlorophosphenium ions. The first route still seems to be the most widely applicable [4–11] and was in particular used for the synthesis of novel phosphenium salts containing heterocyclic cations such as the sulphur derivatives **1** [4,5], **2** [6] or the 1,3,2-diazaphospholenium ions **3** [7,8], which are isolobal analogues of "Arduengo"-carbenes. Novel acyclic cations comprise the N/C-substituted derivatives **4** [9], whose cationic phosphorus is stabilised by π-interactions with both the Cp*- and $NR_2$-groups, and **5** [10], where the P–C bond is essentially a σ-bond and the mesityl group does not participate in mesomeric charge stabilisation. As a variant of bond heterolysis, dechlorination of phosphorus compounds with $NaBPh_4$ has also been useful in some cases [11,12].

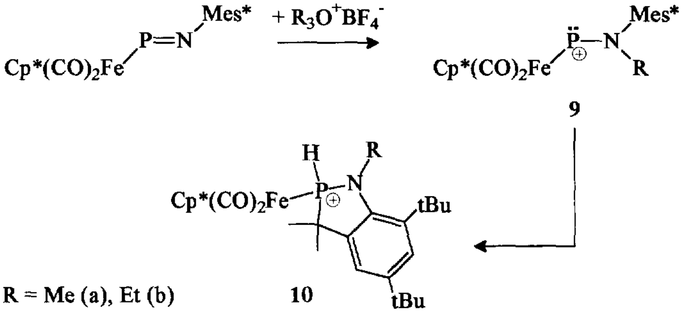
In addition, a variety of novel phosphenium ions were also prepared according to non-standard routes. [2+2] or [2+3] cycloaddition reactions of an iminophosphenium ion (see below) with aminoiminophosphines or alkyl azides gave the cyclic phosphenium cations **6** and **7** [13], of which the latter is a nitrogen analogue of the



Scheme 2.

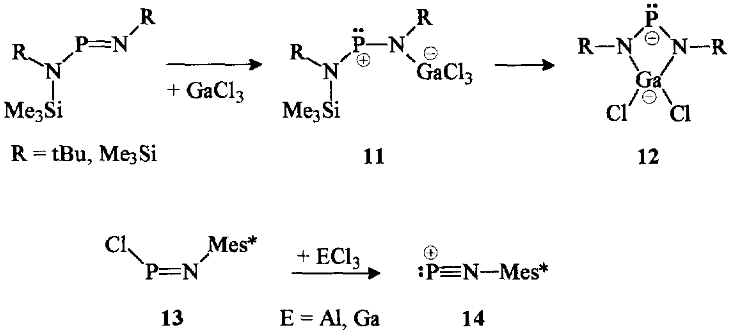
diazaphospholenium ions **3** and represents another isolobal equivalent of an Arduengo-carbene. Secondary aminophosphenium ions are accessible via protonation of the two-coordinate nitrogen in iminophosphines with strong Brønsted acids such as triflic acid; this reaction was first employed for the synthesis of a triflate salt of cation **4** [9], but seems also to be applicable for the synthesis of asymmetric diaminophosphenium ions of the type **8** [14]. Alkylation of a metallo-iminophosphine afforded the marginally stable transition metal substituted phosphenium ion **9** [15] which rearranges via CH-activation and formation of the metallophosphonium cation **10** in the same manner as a similar derivative reported earlier by Gladysz et al. [16].

Related to the alkylation and protonation of amino-iminophosphines is the adduct formation with $GaCl_3$ which proceeds in analogy to the long known reaction with $AlCl_3$ [1]a[14], to give first the acyclic zwitterion **11** which further cyclises to the four membered ring **12** [17]. Quite in contrast to amino-iminophosphines, the P-chloro-iminophosphine **13** reacts with both $AlCl_3$ [18] and $GaCl_3$ [19] via electrophilic attack at chlorine rather than nitrogen and subsequent P–Cl bond heterolysis to give the iminophosphenium cation **14** which is best described as a cationic phosphorus–nitrogen triple bond system which is isoelectronic and isolobal to a diazonium ion or a phosphaalkyne [18,20]. Nevertheless, the simultaneous presence of a phosphorus "lone-pair" and a low lying empty $\pi^*(PN)$-orbital, as well as the



Scheme 3.

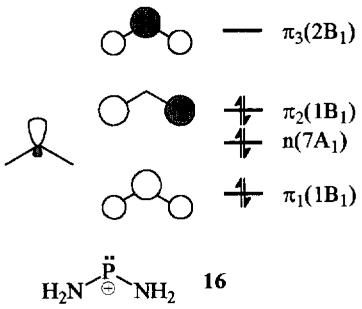
concentration of the positive charge at phosphorus [18], also resemble typical features of phosphenium ions. The phosphorus and carbon analogues of **14**, methylenephosphenium and diphosphazonium ions $[P{=}CR_2]^+$ and $[P{=}PR]^+$, are according to theoretical investigations [21] much less stable than **14** and were as yet not detected as (meta)stable species in condensed phases; however, some Lewis-base complexes of these species were recently characterised (see below). Cation **14** further reacted with Mes*EH (E = O, NH) via formal 1,2-addition to the triple bond to give the secondary aminophosphenium ions $[(\text{Mes*E})P(\text{NHMes*})]^+$ (E = NH (**8c**), O) [22].



Scheme 4.

### 2.1.2. *Physical properties, structure and bonding*

Theoretical studies. A number of recent studies focused on the electronic structures and stabilities of amino- and iminophosphenium ions. The planar geometries of $[HP(NH_2)]^+$ (**15**) and $[P(NH_2)_2]^+$ (**16**) and the description of **16** as a heteroallylic 3-centre-4π-electron system were confirmed on a higher level of theory [21,23]. In contrast to the generally assumed "carbenic" nature [24] of phosphenium ions which is reflected in their reactivity [1]a,b, **16** actually exhibits an "olefinic" frontier orbital sequence (Fig. 1) in which HOMO and LUMO are represented by the $\pi_2$- and $\pi_3^*$-orbitals of the heteroallylic π-electron system and the *n*-orbital (phosphorus "lone



16

Fig. 1. Schematic representation of frontier orbitals in **16**.

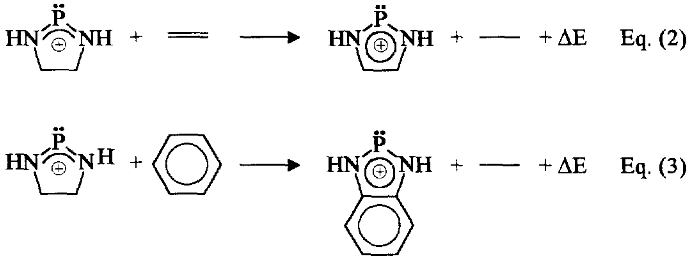
pair") lies 0.6 eV below the HOMO [21] (cations bearing alkyl substituents at nitrogen may well exhibit a genuine "carbenic" frontier orbital sequence because of inductive destabilisation of the "lone pair"; furthermore, phosphenium ions frequently act in chemical reactions as electrophiles [1]a,b so that the nature of the HOMO becomes less significant for a description of reactivities). The "cation stability" as measured by the calculated reaction energy of the group transfer reaction Eq. (1) (Table 1) [21] is as expected much higher for **16** than for **15**; similar relative stabilities were calculated for the aminosilylenes $HSi(NH_2)$ and $Si(NH_2)_2$ [25]. The large differences in cation stabilities for the ions $[HEP]^+$ (E=N, P, CH) [21] are in accord with the experimental stabilities; noteworthy is that the iminophosphenium ion $[HN{\equiv}P]^+$ is predicted to be more stable than the phosphenium ion **16**.

An aspect which has attracted some interest, but was debated rather controversially, is the stabilisation of cyclic phosphenium cations by cyclic π-electron delocalisation. Thus, while the poor π-acceptor properties of the diaminophosphenium unit were judged to render cyclic 6π-conjugation in the tetrazaphospholenium cation **7** unimportant [13], theoretical [5] as well as experimental arguments [4,5,26] seemed to support the presence of a delocalised "heteronaphthalenic" 10π-electron system in the benzophospholenium ions **1**. Formation of a conjugated 6π-electron system

Table 1
Relative cation stabilities of $[P(R^1)(R^2)]^+$ as reaction enthalpies $\Delta E$ of Eq. (1) (energies at MP4SDTQ(fc)/6–31+g*//RHF/6–31+g* level, from Ref. [21])

$$HP(R^1)(R^2)+[PH_2]^+ \rightarrow [P(R^1)(R^2)]^+ + HPH_2 + \Delta E$$

| $P(R^1)(R^2)$ | $\Delta E$ (kcal mol$^{-1}$)) |
|---|---|
| $PH_2$ | 0.0 |
| $HP(NH_2)$ | −66.4 |
| $P(NH_2)_2$ | −92.1 |
| PNH | −94.7 |
| PPH | −37.9 |
| $PCH_2$ | −27.5 |



| | ΔE (kcal/mol) |
|---|---|
| Eq. (2) | -21.4 |
| Eq. (3) | -16.6 |

Fig. 2. Calculated energies (in kcal/mol on HF/6-31g* + ZPE level, from Ref. [28]) of isodesmic reactions involving formation of 1.3.2-diaza(benzo)phospholenium cations.

was also postulated for cation **2** [27]. The calculated reaction enthalpies [28] of the isodesmic reactions of Eqs. (2) and (3) (Fig. 2) confirm that π-electron delocalisation contributes in principle to the stability of cations of type **1**, **3**. However, the listed stabilisation energies are considerably lower than those of isoelectronic phospholide or benzo-phospholide anions [28,29], suggesting that cations of type **1**, **3** have only weak aromatic character. An interesting bonding situation was further anticipated for the diazadiphosphetidinium cations **6** whose calculated geometries and electron populations [13] suggested a charge delocalisation within the four membered ring as expressed by the mesomeric structures **6′**–**6⁗** (Fig. 3).

X-ray crystallography. Several of the newly synthesised phosphenium cations were characterised by X-ray diffractometry. The results (Table 2) confirm the range of P–N distances extending from 1.56 to 1.65 Å known from earlier studies [1]a,b. The cation **14** which exhibits the shortest P–N distance is assigned a formal triple bond. The similarity of the P–N bond lengths in the mono-amino cations **4**, **5** to those of diaminophosphenium ions appeared somewhat surprising, since the concentration of P–N double bond character on one $R_2N$ group was expected to result in relative bond shortening [10], but is in accord with theoretical predictions [21]. Notable are the structures of the salts $[P(NHMes^*)_2][ECl_4]$ (E = Al [30], Ga [22]) which consist

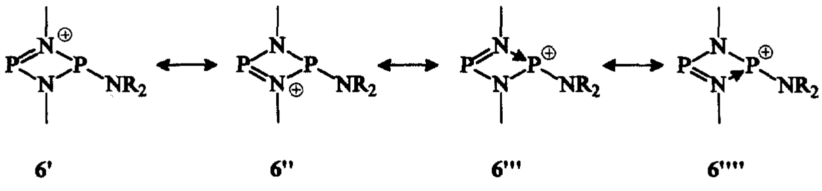
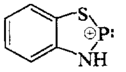
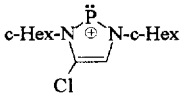
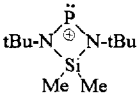
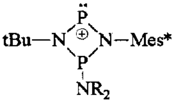
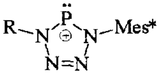


Fig. 3. Mesomeric structures describing the bonding situation of **6c** [13].

Table 2
Selected crystal structure data of phosphenium salts

| | Cation | Anion | P–N bond lengths (Å) | Closest $P^+$... anion contacts (Å) | Ref. |
|---|---|---|---|---|---|
| **1b** |  | $AlCl_4^-$ | 1.643(3) | 3.393(1)<br>3.405(2) | [5] |
| **3a** |  | $SbCl_6^-$ | 1.656(4)<br>1.673(4) | | [7] |
| **4** | $[(Cp^*)(tBuNH)P]^+$ | $AlCl_4^-$ | 1.620(2) | – | [9] |
| **5** | $[(i\mathrm{Pr}_2N)(Mes)P]^-$ | $AlCl_4^-$ | 1.617(5) | 3.296(3)<br>3.471(3) | [10] |
| |  | $GaCl_4^-$ | 1.56(2)<br>1.58(2) | 3.548(1)<br>3.982(2) | [11] |
| | $[(i\mathrm{Pr}_2N)_2P]^+$ | $GaCl_4^-$ | 1.587(12)<br>1.601(13) | 3.867(6)<br>3.976(6) | [11] |
| |  | $BPh_4^-$ | 1.623(3) | 3.48(P...C) | [12] |
| **6a** |  | $AlCl_4^-$ | 1.632(3)<br>1.636(3) | 3.413.65 | [13] |
| **7a** |  | $AlCl_4^-$ | 1.653(3)<br>1.654(3) | – | [13] |
| **8c** | $[(Mes^*NH)_2P]^+$ | $GaCl_4^-$, $AlCl_4^-$ | 1.617(3) | 3.853(2) | [22,30] |
| | $[(i\mathrm{Pr}_2N)(Mes^*NH)P]^+$ | $CF_3SO_3^-$ | 1.602(1)<br>1.602(1) | 2.809(2)<br>(N–H...O) | [14] |
| | $[Me_2NPN(AlCl_3)Mes^*]$ | – | 1.610(2)<br>1.615(2) | – | [14] |
| | $[(Me_3Si)_2NPN(GaCl_3)SiMe_3]$ | – | 1.590(5)<br>1.637(5) | – | [17] |
| | $[P{\equiv}NMes^*]^+$ | $AlCl_4^-$ | 1.475(8) | 3.163.273.52 | [18] |

of one-dimensional polymeric lattices resulting from NH· · ·Cl hydrogen bonding in connection with inter-ionic P· · ·Cl contacts.

NMR studies. $^{15}N$ NMR studies on a series of acyclic and cyclic diaminophosphenium ions [31] revealed a similar deshielding of $\delta^{15}N$ compared to trivalent aminophosphines as was previously found for $\delta^{31}P$ [1]a,b. The observed loose correlation between both quantities was interpreted to the effect that the variation in the shielding of both nuclei is dominated by paramagnetic contributions arising from $N(\pi){\rightarrow}P$ interactions. In contrast to the structural similarity of the P–N bonds in mono- and diaminophosphenium ions, both the $^{31}P$ and $^{14}N$ resonances of **6** are strongly deshielded [10]. The P–N triple bond character in $[Mes^{*}N{\equiv}P]^{+}$ (**14**) was further confirmed by analysis of solid state $^{31}P$ and $^{15}N$ NMR spectra [20]. A study of the solid state $^{31}P$ NMR spectra of $[(Mes^{*}E)P(NHMes^{*})][GaCl_4]$ (E = O, NH) revealed [22] that the phosphorus chemical shielding is not simply related with the formal charge at phosphorus, but is governed by the paramagnetic contributions to magnetic shielding, with magnitudes and orientation of the principal components of the shielding tensor obeying similar rules as had been previously established for neutral iminophosphines [32].

### 2.2. *Bis-phosphonio-isophosphindolide ions and related systems*

#### 2.2.1. *Synthesis*

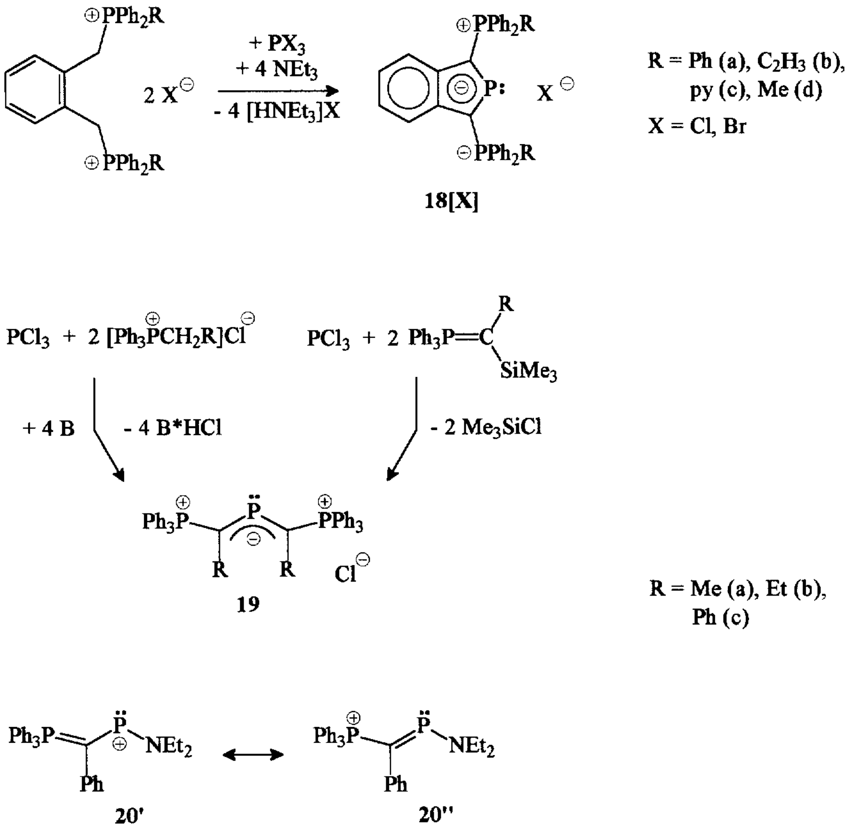
The first bis-phosphonio-isophosphindolide salt with the cation **18a** was prepared by Schmidpeter and Thiele via condensation of a bis-phosphonium salt with $PCl_3$ in the presence of $NEt_3$ [2]. The reaction is easily extended to derivatives with differently substituted phosphonio groups [29,33], the generation of monocyclic bis-phosphonio-phospholides starting from butenylidene-bis-phosphonium salts [33,34], and an arsenic analogue of **18a** [2]. The halide anions in the isolated salts are easily exchanged by anion metathesis reactions [2,29,33,35], and even salts with organometallic anions ($Co(CO)_4^-$, $CpM(CO)_3^-$ (M = Mo, W)) may be obtained with this procedure [35].

Although acyclic diphosphonio-phosphapropenides **19** are accessible from analogous condensation reactions of $PCl_3$ with two equivalents of mono-phosphonium salts, a better route to these compounds proved to be condensation with trimethylsilylated phosphonium ylides [34,36]. Cations such as **20**, whose two coordinate phosphorus atoms carry both an amido and an ylide substituent, are similarly accessible from condensation of an ylidyl-dichlorophosphine with a silylated amine [34,36]. However, with respect to their structures and reactivities these species should better be described as phosphonio-substituted phosphaalkenes (**20″**) rather than ylide-substituted aminophosphenium ions (**20′**) [36,37].

#### 2.2.2. *Physical properties, structure and bonding*

Theoretical studies. A qualitative description of the electronic structures of cyclic bis-phosphonio-isophosphindolide and acyclic bis-phosphonio-phosphapropenide ions was first suggested by Schmidpeter in terms of the mesomeric formulas **18′**–**18′′′′** [2] and **19′**–**19′′′** [36] (Fig. 4). With accentuation of the ylidic nature ($>C^{(-)}{-}P^{(+)}{\lessgtr}$) of the terminal P–C bonds, **19** represents a 2-phosphaallylic anion with a 3-centre-4-electron π-system and two phosphonio substituents which is isolobal and isoelectronic to a diaminophosphenium cation. On the same basis, **18** can be formulated as a "heteronaphthalenic" 10π-electron system which is isolobal to a diazaphospholenium cation [35].

These considerations were in principle confirmed by a quantum chemical analysis of the bonding in the parent bis-phosphonio-substituted (benzo)phospholides **21a,b** [29]. Examination of MO coefficients and population analyses suggested a qualita-



Scheme 5.

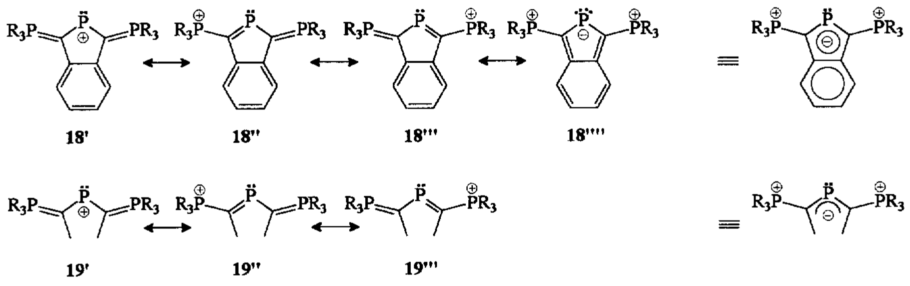
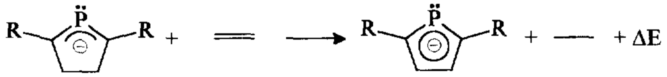


Fig. 4. Mesomeric structures describing the bonding situation bis-phosphonio-phosphapropenides and -isophosphindolides.

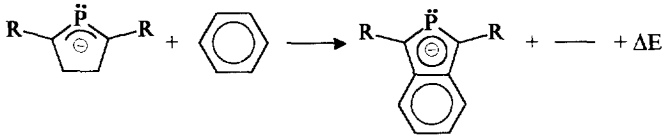
tively similar π-electron structure as in the aromatic 10- or 6-π-electron systems of the (benzo)phospholide anions **22a,b**, even if the extent of π-delocalisation is somewhat reduced. These conclusions were corroborated by the energies of the isodesmic reactions of Eqs. (4) and (5) which showed that the stabilising effect of π-delocalisation in the phosphonio substituted cations is less than in the anions Fig. 5, but nonetheless still greater than for the isolobal diazaphospholenium ions (cf. Fig. 2).

Crystal structure analyses. Crystal structures of two bis-phosphonio-isophosphindolide salts, **18a**[CpW(CO)$_3$] (R = Ph) [35] and **18b**[Br] (R = vinyl) [29], have been reported. Both structures consist of discrete, well separated anions and cations. The planarity of the fused heterocycles in the cations and the observed distribution of P–C and C–C bonds (Table 3) are in accord with a weakly delocalised 10π-electron system. As for aminophosphenium ions, the endocyclic P–C bond lengths lie between the expectation values of pure single and double bonds (heterophospholes display quite similar bond distances [38]). The exocyclic P–C bonds have similar



Eq. (4)

**21a, 22a**



Eq. (5)

**21b, 22b**

| | R | | ΔE (kcal/mol) |
|---|---|---|---|
| **21a** | $PH_3^+$ | Eq. (4) | -33.1 |
| **22a** | H | Eq. (4) | -64.5 |
| **21b** | $PH_3^+$ | Eq. (5) | -25.1 |
| **22b** | H | Eq. (5) | -59.4 |

Fig. 5. Calculated energies (in kcal/mol on HF/6-31g*+ZPE level, from Ref. [29]) for formation of (benzo)phospholide anions (**22a,b**) and bis-phosphonio-(benzo)phospholide cations (**21a,b**) in isodesmic reactions (4) and (5).

Table 3
Selected crystal structure data of bis-phosphonio-isophosphindolide salts $[(Ph_2PR)_2C_8H_4P]^+$ $X^-$ (all distances in Å, the atom numbering scheme is identical to the one of Fig. 6)

| | R | Anion $X^-$ | P(2)-C | P(1A)-C(1)/ P(3A)-C(3) | C(1)-C(3a)/ C(7)-C(7a) | C(3a)-C(7a) (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| **18a** | Ph | $CpW(CO)_3^-$ | 1.728(4)<br>1.729(4) | 1.747(4)<br>1.749(4) | 1.441(6)<br>1.449(6) | 1.423(6) | [35] |
| **18b** | $C_2H_3$ | $Br^-$ | 1.723(8)<br>1.740(7) | 1.735(8)<br>1.752(8) | 1.434(10)<br>1.439(11) | 1.406(11) | [29] |

distances as the corresponding bonds in phosphonium ylides of the type $R_3P^{(+)}$–C(R)=C(R′)–$O^{(-)}$ [39], in accord with the expected low ylidic character. A further prominent structural feature was noted in the steric protection of the two coordinate phosphorus (Fig. 6): the voluminous phosphonio moieties of both cations are arranged in such a way that the phosphorus "lone pair" lies in the middle of a narrow gap formed by two phenyl rings whose ring planes are nearly parallel and face each other at a distance of approximately 6.7 Å [29,35].

NMR studies. $^{31}P$ NMR chemical shifts for the two coordinate phosphorus in bis-phosphonio-phosphapropenides **19** ($\delta^{31}P = 290$–$304$ [34,36]) are similar to those of phosphonio-phosphaalkenes of type **20** [36,37], while the corresponding resonances of bis-phosphonio-isophosphindolides **18** are more shielded by 50–60 ppm and appear close to 240 ppm [2,29]. At the same time, $^2J_{PP}$ decreases from 165–170 Hz in **19** [36] to 90 Hz in **18** [2,29]. The $^{13}C$ chemical shifts of the carbon atoms next to the two coordinate phosphorus site in **18** ($\delta^{13}C$ 108–112 [2,29]) are less positive than in phosphinines ($\delta^{13}C$ 129–155 [40]a) or phospholides ($\delta^{13}C$ 129 in 3,4-$Me_2C_4H_2P^{(-)}$ [40]b). The deshielding with respect to the corresponding resonances of phosphonio-phosphaalkenes ($\delta^{13}C \approx 88$ [37]) or stabilised phosphonium ylides ($\delta^{13}C$ 78.3 for $Ph_3P^{(+)}$–$C_5H_4^{(-)}$) is in accord with the low ylidic character of the exocyclic P–C bond.

## 3. Complexes with Lewis bases

As a consequence of their pronounced Lewis-acid character, phosphenium cations form complexes with Lewis-bases B (Scheme 6a) [1]a,b. It has been shown that the feasibility of this reaction is favoured with increasing "base strength", but that

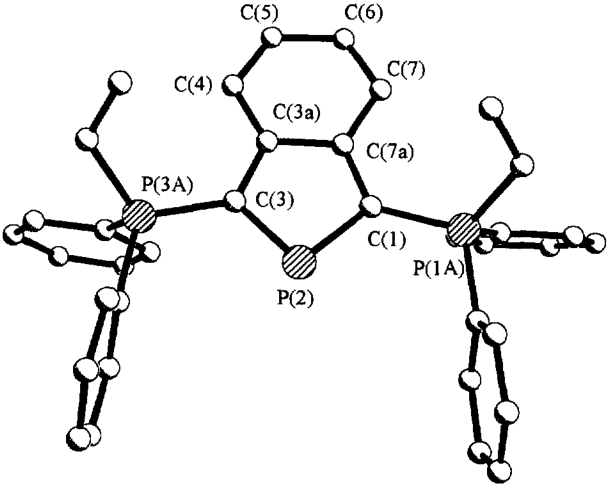
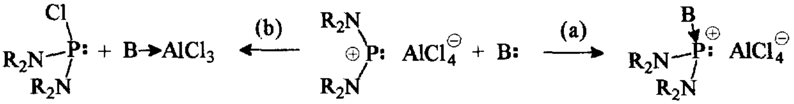


Fig. 6. Representation of the cation in crystalline **18b**[Br]*EtOH (from Ref. [29]).

competition between the cation and counterions such as $AlCl_4^-$ (which may undergo nucleophilic cleavage to give $AlCl_3$–base adducts, Scheme 6b) also plays a role [1]a,b[9]. Within the frame of the extended HSAB concept [41], the "base strength" can be correlated with the absolute electronegativity $\chi$ of B, while its preference to form an $AlCl_3$ or a phosphenium complex can be related with the absolute hardness ($\eta$): hard bases (pyridines) prefer interaction with the hard acid $AlCl_3$, while soft bases (phosphines) preferably bind to the soft phosphenium ion [1]a,b[9]. It appears logical, that in addition to these two factors, the absolute electronegativity of the phosphorus cation itself, i.e. its "acid strength", should also be of importance. Starting from the consideration that absolute electronegativities can be approximated in the frame of MO theory by the relation [41] $\chi = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$, the analysis of HOMO/LUMO energies of model cations [28] suggests that the tendency of different types of low coordinate phosphorus cations to engage in complex formations with Lewis bases should increase with $\chi$ in the order bis-phosphonio-isophosphindolide $< [P(NH_2)_2]^+ < [HP(NH_2)]^+ < [HN{\equiv}P]^+$.



Scheme 6.

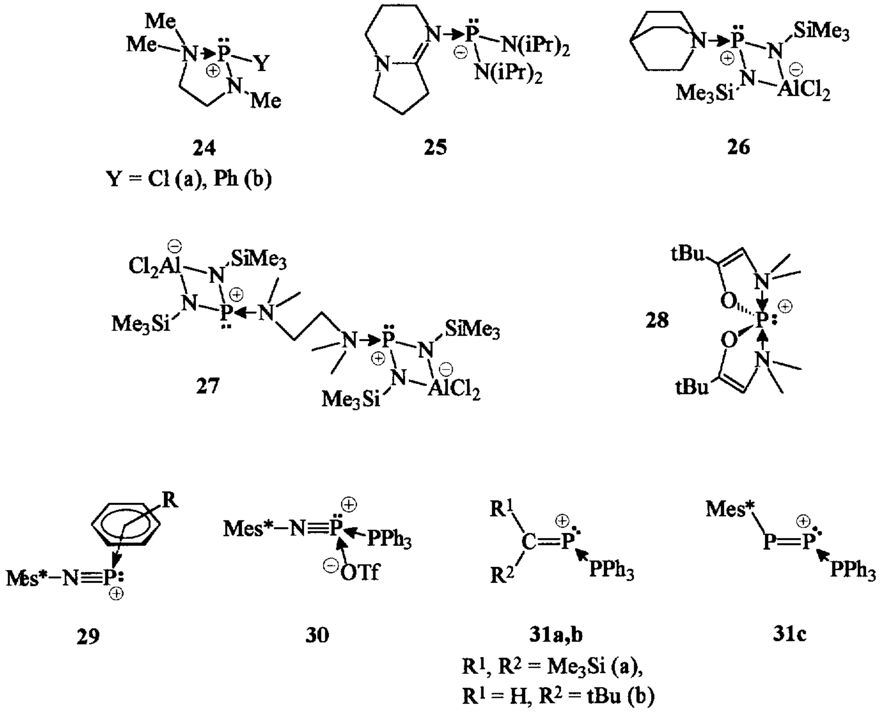
### 3.1. *Anion–cation interactions*

The most elementary manifestation of the Lewis-acid properties of low coordinate phosphorus cations is represented by acid-base interactions with their counterions. The extent of such interactions differs considerably for individual cation/anion pairs, but the experimentally observed trends are in accord with the predicted variations of $\chi$ for the model systems given above. Thus, in contrast to the other cations, bis-phosphonio-isophosphindolides (and -phosphapropenides) are formed via spontaneous heterolysis of a P–Cl(Br) bond even in the absence of an additional Lewis-acid and exhibit apparently no anion–cation interactions, even for anions as nucleophilic as $Cl^-$ or $Br^-$ [2,29]. Inter-ion interactions in diaminophosphenium salts appear to be negligible in the solid state (crystal structure studies revealed that the shortest inter-ion contacts involving the two coordinate phosphorus are beyond the sum of van der Waals radii [11–13], see Table 2), but the observed counterion dependent variation of $\delta^{31}P$ for $[(iPr_2N)_2P]X$ [$\delta^{31}P = 313$ ($X = AlCl_4^-$, $GaCl_4^-$); 308 ($X = BPh_4^-$)] as well as the pronounced difference in stabilities of the $GaCl_4$ and $BPh_4$ salts in $CH_2Cl_2$ solution suggest that ion pairing may be important in solution [11]. The greater Lewis-acidity of mono-aminophosphenium and iminophosphenium ions is reflected in the shorter inter-ion contacts in solid $[(iPr_2N)(Mes)P][AlCl_4]$ [10] and $[Mes^*N{\equiv}P][AlCl_4]$ [18] (cf. Table 2) which are well below the sum of van der Waals radii, and in the covalent character of the P–O bonds in the triflates $(tBuNH)(Cp^*)P(OTf)$ [9], $(iPr_2N)(Mes^*)P(OTf)$ [10] and $Mes^*N{=}P{-}OTf$ [42]. $\eta^2$-Coordination of an anion to a phosphenium centre was established for the compound $[t\mathrm{Bu}_2\mathrm{PSe}_2][\mathrm{P{\equiv}NMes^*}]$ leading to a description of the bonding as an intimate donor–acceptor complex of an iminophosphenium cation with a diselenophosphinate anion [43].

### 3.2. Interactions with neutral bases

Adduct formation between diaminophosphenium ions and neutral donors (phosphines, amines) is well established [1]a,b[9,44,45], but examples of such complexes have only recently been isolated and structurally characterised. They include the cyclic phospholidinium salts **24** [46] which can be regarded as intramolecular phosphenium ion – amine complexes, as well as the intermolecular mono- and diamine adducts **25**–**27** [47,48]. All these compounds exhibit pyramidal geometries at phosphorus with normal P–N(amino) bond distances (1.65–1.67 Å) and significantly longer dative P–N bonds (1.80–1.88 Å in the ionic derivatives **24b** [46]b, **25** [47] and 2.11–2.20 Å in the zwitterionic species **26**, **27** [48]). An interesting facet is added by the spirocyclic cation **28** [49] which represents a phosphenium ion stabilised by two intramolecular amine donors and displays a Ψ-tpb geometry at phosphorus with longer dative P–N bonds (2.05 and 2.06 Å) than the mono-adducts **24**, **25**.

The influence of acid strength on the adduct formation was addressed by a NMR



Scheme 7.

study of the reactions of phosphenium cations with pyridine [50]. The stability constants of the complexes indicated an increasing Lewis-acidity in the series $[(Et_2N)_2P]^+$ < 1,3-Me-1,3,2-diazaphospholenium < 5-Me-1,3,2-benzodithiaphospholium. Somewhat surprisingly, phosphenium ions are apparently stronger Lewis-acids than the corresponding homologous arsenium cations.

The potential of the iminophosphenium cation $[Mes^*N{\equiv}P]^+$ to form complexes with Lewis-bases was recently demonstrated by the syntheses of the arene complexes **29** [19] and the $PPh_3$-adduct **30** [22]. Crystal structure analyses of the former revealed an $\eta^6$-attachment of the phosphorus to the ring; the distances between phosphorus and the arene-centroid range between 2.69 and 3.03 Å and decrease with increasing π-donor capability of the arene [19]. In **30**, the interaction of the iminophosphenium phosphorus site with $PPh_3$ (P···P 2.62 Å) competes with the anion/cation interaction (P···OTf 2.30 Å), effecting displacement of the triflate anion relative to Mes*N=P–OTf [22]. While a $PPh_3$-adduct of $[Mes^*N{\equiv}P][AlCl_4]$ was found to be highly unstable [14], the recently reported cations **31a,b** [51] and **31c** [52] which represent $PPh_3$-adducts of the yet unknown methylenephosphenium and diphosphazonium cations, $[R_2C{=}P]^+$ and $[RP{=}P]^+$, respectively, displayed markedly higher stabilities, allowing characterisation by solution NMR data and X-ray crystal structure studies.

## 4. Metal complexes

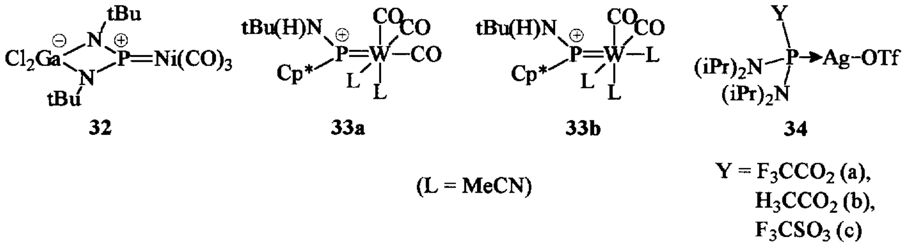
### 4.1. Cationic phosphenium complexes

#### 4.1.1. Synthesis

Known syntheses of cationic phosphenium complexes can be grouped into three fundamental categories. The first two approaches, (a) "direct synthesis" via displacement of a ligand in a metal complex by a phosphenium cation and (b) (Lewis) acid promoted abstraction of an anionic substituent from a coordinated trivalent phosphorus ligand, are well established [1]a,b while the third one, viz. ligand exchange in an already formed phosphenium complex under preservation of the phosphenium moiety, has emerged as a more recent development.

The direct complexation route was used for the synthesis of the novel Ni complex **32** from **12** and $Ni(CO)_4$ [17]. Likewise, reaction of $[Cp^*PNHtBu]^+$ (**4**) with $[(MeCN)_3W(CO)_3]$ in $CH_2Cl_2$ at −20 °C afforded the isolable phosphenium complex **33a**, which upon warming to ambient temperature reacted further via displacement of the *trans*-CO ligand by the previously liberated MeCN to give the new dicarbonyl complex **33b**. Alternatively, **33b** was directly accessible from reaction of **4** with $[(MeCN)_3W(CO)_3]$ at 60 °C in MeCN [9].

In contrast to the case of zerovalent metal compounds, reactions of $[(iPr_2N)_2P][OTf]$ with silver(I) salts yielded no phosphenium complexes, but resulted either in the formation of complexes **34** with neutral trivalent phosphorus ligands, or gave equilibria between such complexes and the free phosphenium cations [8]. Similar equilibria were also formed between the diazaphospholenium ion **3c** and

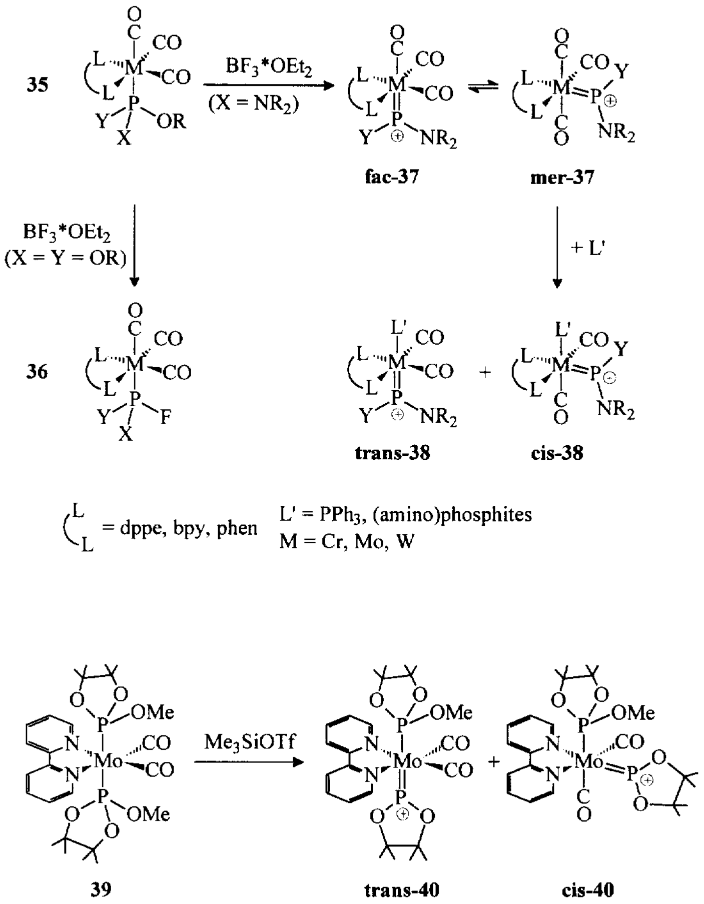


Scheme 8.

silver acetate or trifluoroacetate, while silver triflate gave no reaction at all. An X-ray crystal structure study [8] of **34a** revealed a distorted tetrahedral coordination geometry at phosphorus with rather short P–N (1.627, 1.663 Å) and P–Ag (2.349 Å) bonds, but a long P–O bond (1.707 Å), suggesting that the bonding situation can be described as in donor stabilised silylene complexes such as $[(CO)_nM{\leftarrow}SiR_2{\leftarrow}HMPT]$ [53], as a Lewis acid/base adduct of a cationic phosphenium complex with a trifluoroacetate anion.

Anion abstraction from a trivalent phosphorus ligand has been extensively used for the synthesis of cationic group 6 transition metal complexes [54–56]. Investigations of the reactivity of phosphite and aminophosphinite complexes **35** towards $BF_{3*}OEt_2$ revealed that phosphite complexes (X = Y = OR) reacted generally via OR/F exchange to give neutral fluorophosphine complexes **36**. Derivatives with at least one amino substituent at phosphorus preferably gave cationic phosphenium complexes **37** which were unequivocally characterised by IR and NMR spectroscopy, even if none of the products were isolated [54,56]. Further spectroscopic studies suggested that the *fac*-isomers were formed as the kinetic products which then rearranged into the thermodynamically more stable *mer*-isomers; the isomerisation is accelerated by addition of nucleophiles such as phosphines, ethanol or triflate ions [55,56]. Complexes **37** may further react with $PPh_3$ or excess aminophosphites with substitution of one CO ligand to give phosphine–phosphenium complexes **38** [57]. In remarkable contrast to the complexes **35**, methoxide abstraction from a coordinated phosphite was observed in the reaction of the dicarbonyl complex **39** with $Me_3SiOTf$ which afforded the cationic complexes **40** with O/O-substituted phosphenium ligands [57]. The (amino)phosphito–phosphenium complexes **38** and **40** exist either as pure *trans*-isomers, or as dynamic equilibrium mixtures of *cis*- and *trans* isomers, and it appears that the *cis*-configuration is electronically favoured and the *trans*-configuration sterically favoured [57,58].

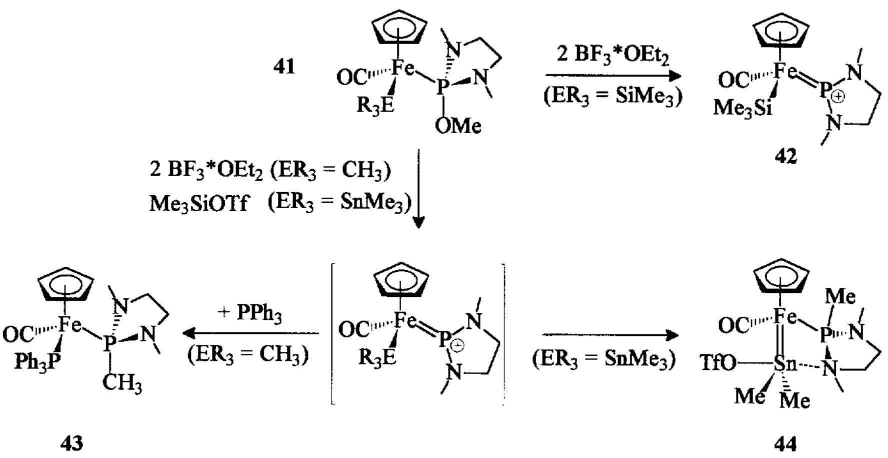
Attempts towards synthesis of novel phosphenium complexes of iron via reaction of the hetero-phospholidine complexes **41** with $BF_3^*OEt_2$ revealed a remarkable influence of the $ER_3$ substituent on the nature of the products. A stable phosphenium complex **42** was spectroscopically characterised but not isolated for $ER_3{=}SiMe_3$ only [59]a. For $ER_3{=}CH_3$ and $SnMe_3$, phosphenium complexes were postulated as transient intermediates which were stabilised via migration of a $CH_3$-group from iron to phosphorus ($ER_3{=}CH_3$) [59]a, or from tin to phosphorus ($ER_3{=}SnMe_3$)



Scheme 9.

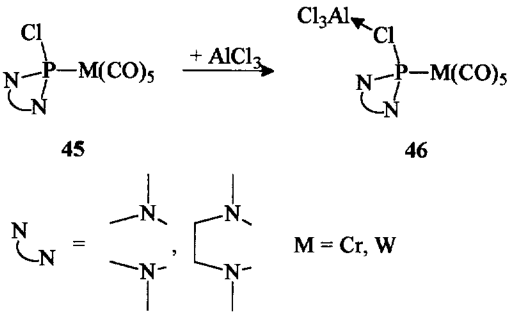
[59]b. Final products were the complexes **43**, and the doubly base stabilised stannylene complex **44** which was characterised by single crystal X-ray diffractometry [59]b. Similar migratory insertions of phosphenium ligands into metal carbon bonds were recently confirmed for some alkyl complexes of Mo and W [59]c.

Comparison of the observed stabilities/reactivities of the phosphenium complexes **34**, **37**, **38**, **40** lead to the conclusions [9,54–58] that (i) cationic phosphenium complexes of Mo and W are more stable than those of Cr, (ii) the stability increases with increasing number of amino substituents at phosphorus, (iii) cyclic diazaphosphospholidinium or azoxaphospholidinium cations form more stable complexes than acyclic aminophosphenium cations and (iv) the complexes become more stable when the overall number and acceptor capabilities of π-acidic co-ligands decrease. Following the last argument, complexes $[(CO)_5MPY_2]^+$ are predicted to be less stable than **37**. This is indeed suggested by the outcome of the reactions of the



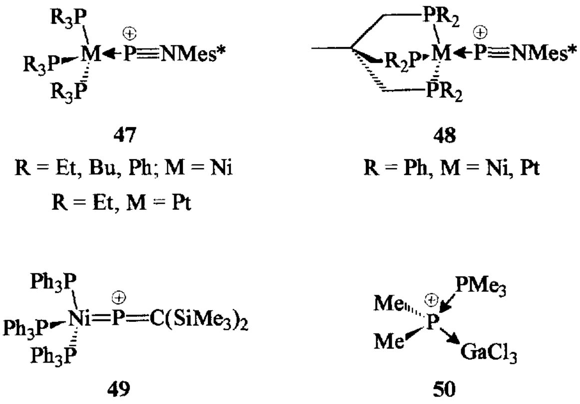
Scheme 10.

pentacarbonyl complexes **45** with $AlCl_3$, which afforded Lewis-acid/base adducts of proposed constitution **46**, rather than the (presumably unstable) cationic phosphenium complexes [60].



Scheme 11.

In contrast to the extensive studies on phosphenium complexes, the metal coordination chemistry of $[Mes^*N{\equiv}P]^+$ is less developed. To our knowledge, the only reported cationic complexes with this ligand are the Ni and Pt compounds **47**, **48** which were generated either via $AlCl_3$ promoted halide abstraction from $[(R_3P)_2M(\eta^1\text{-}P(Cl){=}NMes^*)]$ (M = Ni, Pt), or alternatively via direct complexation of in situ generated $[Mes^*N{\equiv}P][BPh_4]$ with complexes $[(R_3P)_nM]$ (M = Ni, Pt; $n$ = 3,4) [61]. The coordination properties of donor stabilised phosphorus cations were demonstrated in the reaction of $[Ph_3P\text{–}P{=}C(SiMe_3)_2]^+$ with $(Ph_3P)_2Ni(COD)$ which gave rise to the spectroscopically characterised cationic complex **49** via formal insertion of Ni into the P–P bond [51]a. Furthermore, the unusual cation **50** which was obtained from the reaction of $Me_2PCl$ with $GaCl_3$ was formulated, on the basis of a crystal structure determination, as a Ga complex of a phosphenium–phosphine adduct [62].



**47**

R = Et, Bu, Ph; M = Ni

R = Et, M = Pt

**48**

R = Ph, M = Ni, Pt

**49**

**50**

Scheme 12.

### 4.1.2. *Reactivity*

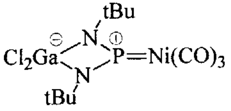
Apart from the mentioned ligand exchange and isomerisation reactions, the only other known type of reactivity includes the nucleophilic attack of anions at the phosphorus centre to give neutral complexes with trivalent phosphorus ligands [1]b[54].

### 4.1.3. *Physical properties*

X-ray structural investigations. Even though the first crystallographic studies were reported almost 15 years ago [1]a,b, the structural chemistry of cationic phosphenium complexes is still underdeveloped, and to date only five compounds have been characterised (Table 4). In all cases, the geometry at the phosphenium phosphorus atom is planar. The M–P(phosphenium) bonds in the Mo complexes **38a,b** [57] are 9–12% shorter than the M–P($PX_3$) bonds of ligands at the same metal centre, while for the Fe and Ni complexes **51** [1]b and **32** [17] the contraction is only 3–4%. A reverse trend is observed for the intra-ligand P–N distances, which are comparable to the distances in free phosphenium cations for **32** and **51**, while **38a,b** exhibit somewhat longer bonds which equal the P–N bond distances in the aminophosphite ligands in the same molecule [57].

NMR Spectroscopic Studies. Values for $\delta^{31}P$ of phosphenium complexes range from 200 to 350 ppm (see Table 5 for selected data). The shielding in complexes with comparable metal substitution patterns increases with increasing electronegativity of the substituents at phosphorus. Coordination shifts ($\Delta\delta = \delta$(complex) $- \delta$(free ligand)) vary from $-100$ to $+190$ ppm. Even if a general discussion of $\Delta\delta$ seems difficult, characteristic trends emerge for selected subsets of compounds with similar molecular constitutions. Thus, complexes $[L_2(CO)_3M{=}P(NR_2)_2]^+$ exhibit generally small values of $\Delta\delta$ ($<40$=ppm) which decrease in the sequence Cr > Mo > W [56],

Table 4
Selected crystal structure data of cationic phosphenium complexes (all distances in Å)

| | | Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|---|---|
| | Complex (a) | M–P ($PX_2$) | M–P ($PX_3$) | P–N ($PX_2$) | P–N ($PX_3$) | $S^b$ | Ref. |
| **51** | $[\{(Et_2N)_2P\}Fe(CO)_4]^+[AlCl_4]^-$ | 2.10(5) $^c$ | 2.183 $^d$ | | – | 3.8% | [1]a[1]b |
| | $[\{(MeO)_2P\}Mo\{P(OMe)_3\}_5]^+$ $F_3CCO_2^-$ | 2.229(4) | 2.44 $^c$ | – | – | 8.6% | [1]a[1]b |
| **32** |  | 2.123(3) | 2.189 $^d$ | 1.604(8)<br>1.616(5) | – | 3.0% | [17] |
| **38a** | *trans*-$[(phen)(CO)_2(PN_2)(PN_2O)Mo]^+$ $OTf^-$ | 2.254(1) | 2.495(1) | 1.642(5)<br>1.644(5) | 1.648(5)<br>1.662(5) | 9.7% | [57] |
| **38b** | *trans*-$[(bpy)(CO)_2(PNO)(PNO_2)Mo]^+$ $OTf^-$ | 2.238(4) | 2.529(4) | 1.65(1) | 1.63(1) | 11.5% | [57] |

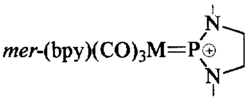
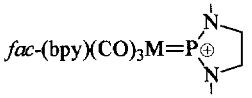
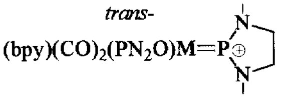
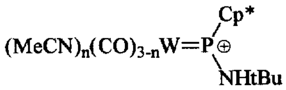
[a] phen = phenanthrene, bpy = 2,2′-bipyridine, $PN_2$ = 1.3-$Me_2$-1,3,2-diazaphospholenium, $PN_2O$ = 2-MeO-1,3-$Me_2$-1,3,2-diazaphospholene, PNO = 3-*t*Bu-1,3,2-Oxazaphospholenium, $PNO_2$ = 1-MeO-3-*t*Bu-1,3,2-Oxazaphospholene.

[b] Bond shortening factor $S = 100^*\{r(M-PX_2)-r(M-PX_3)\}/r(M-PX_3)$.

[c] Average value.

[d] Standard bond distances for M–P bonds in aminophosphite complexes, from Ref. [70].

Table 5
Selected $^{31}$P NMR data of cationic phosphenium complexes

| Cationic complex[a] | | $\delta^{31}$P (complex) | $\Delta\delta$[b] | $^1J$(M$^{31}$P) (Hz) | Ref. |
|---|---|---|---|---|---|
|  *mer*-(bpy)(CO)$_3$M=P$^{\oplus}$ | M = Cr Mo W | 277.3<br>268.2<br>242.6 | +13.3<br>+4.2<br>−21.4 | 561.1 | [55,56] |
|  *fac*-(bpy)(CO)$_3$M=P$^{\oplus}$ | M = Cr Mo W | 263.8<br>252.2<br>233.7 | −0.2<br>−11.8<br>−30.3 | 441.7 | [55,56] |
|  *trans*-(bpy)(CO)$_2$(PN$_2$O)M=P$^{\oplus}$ | M = Cr Mo W | 248.6<br>242.2<br>222.2 | −15.4<br>−21.8<br>−41.8 | 518.8 | [57] |
|  (MeCN)$_n$(CO)$_{3-n}$W=P$^{\oplus}$(Cp*)(NHtBu) | n =0<br>1 | 297.9<br>268.3 | +191.2<br>+161.6 | 404<br>583 | [9] |

[a] bpy = 2,2′-bipyridine, PN$_2$O = 2-MeO-1,3-Me$_2$-1,3,2-diazaphospholene.
[b] $\Delta\delta = \delta$(complex) − $\delta$(free phosphenium cation).

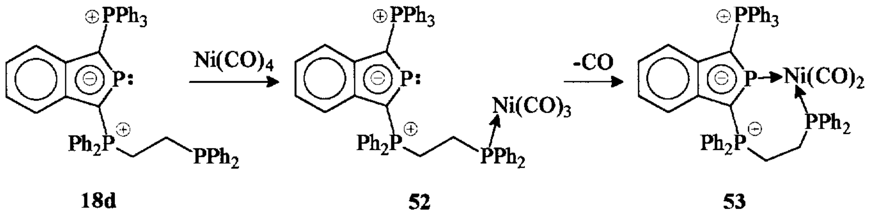
showing a similar influence of the metal as is known for phosphine complexes. Replacement of a CO by less π-acidic ligands in $[L_2L'_n(CO)_{3-n}M{=}P(NR_2)_2]^+$ ($n$ = 0,1) or $[(MeCN)_{2+n}(CO)_{3-n}M{=}P(Cp^*)(NHtBu)]^+$ ($n$ = 0,1) induces an algebraic decrease of $\Delta\delta$; the pronounced positive coordination shifts for the latter are attributed to a change from $\eta^2$-(free cation) to $\eta^1$-attachment (complex) of the Cp*-ligand [9].

Characterisation of phosphenium complexes by metal NMR spectroscopy is restricted to a single $^{95}$Mo NMR study of a few derivatives of the type $[(bpy)(CO)_2LMo{=}PX_2)]^+$ [63]. However, an extensive body of $J(^{183}W,^{31}P)$ data has been collected by analysis of $^{183}$W satellites in $^{31}$P NMR spectra [9,54–59]. The available $\delta^{95}$Mo values display essentially the same trends as $\delta^{31}$P values, viz. a deshielding of the metals in cationic phosphenium complexes as compared to neutral phosphine complexes which further decreases with replacement of CO by phosphite ligand [63]. Coupling constants $^1J(M,^{31}P)$ adopt characteristically large values for both Mo and W complexes, and their magnitude appears to be a sensitive probe for the effects of structural variations. Algebraic increases in $^1J(M,^{31}P)$ are observed not only with increasing electronegativity of the substituents at phosphorus (which is a common phenomenon in $^{31}$P NMR spectroscopy), but also with decreasing π-acidity of the *trans*-ligand in an octahedral complex, or with a decrease in the total number of CO ligands in the complex and were attributed to an increase in M–P double bond character [9,54–59].

## 4.2. Bis-phosphonio-isophosphindolide complexes

### 4.2.1. Synthesis

Investigations of the coordination properties of class C cations are so far restricted to bis-phosphonio-isophosphindolides, and all known complexes were obtained by the direct complexation route. Most reactions were performed with the triphenylphosphonio substituted derivative **18a** whose complexation behaviour deviates markedly from that of aminophosphenium cations: while the latter form stable cationic complexes with carbonyl derivatives of zerovalent metals of the chromium, iron or nickel triades, but not with $Ag^+$, **18a** does not react with $Mo(CO)_6$, $W(CO)_3(MeCN)_3$, $Fe_2(CO)_9$ or $Ni(CO)_4$ [35], but forms complexes with univalent coinage metal cations (the few investigations involving different bis-phosphonio-isophosphindolides revealed very similar reactivities) [33,35,64,65]. The reluctance to form metal carbonyl complexes was attributed to the steric protection of the two coordinate phosphorus (see Fig. 1) rather than to electronic effects; presumably, an $M(CO)_n$ fragment with a spherically (tetrahedral, tbp or octahedral) coordinated metal cannot approach the coordination site (the phosphorus "lone pair") due to steric interferences between the CO ligands and the flanking $Ph_3P$-moieties [35]. Experimental support for this hypothesis was recently derived from the reaction of **18d** with $Ni(CO)_4$ which afforded the isolable chelate complex **53** via the spectroscopically detectable intermediate **52**. Here, the initial coordination of the pendant phosphine moiety enables a constructive rather than a repulsive interaction of the metal with one of the phosphonio groups which results in a synergistic stabilisation of the complex **53** by both the chelate effect and the release of steric hindrance [66].



Scheme 13.

The known bis-phosphonio-isophosphindolide complexes with coinage metals can be divided into (a) mononuclear complexes where the cation binds to the metal via the phosphorus "lone pair" similar to the phosphenium complex (*CI* in Fig. 7), and (b) dinuclear complexes with a $\mu^2$(P)-bridging coordination of the cation to two metals (*CII*; the lines connecting the P and M are not meant to represent 2-centre-2-electron bonds; for a discussion of the bonding cf. Section 4.3). The metal coordination geometries in all complexes can be described as (pseudo)linear or trigonal planar, and the remaining ligands are arranged in such a way as to minimise steric interactions with the bis-phosphonio-isophosphindolide moiety.

Phosphenium analogue class *CI* complexes were first observed in reactions of salts [**18a**][X] with AuCl. Depending on the anion, the reactions proceed either in a 1:1

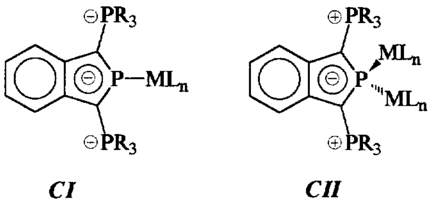
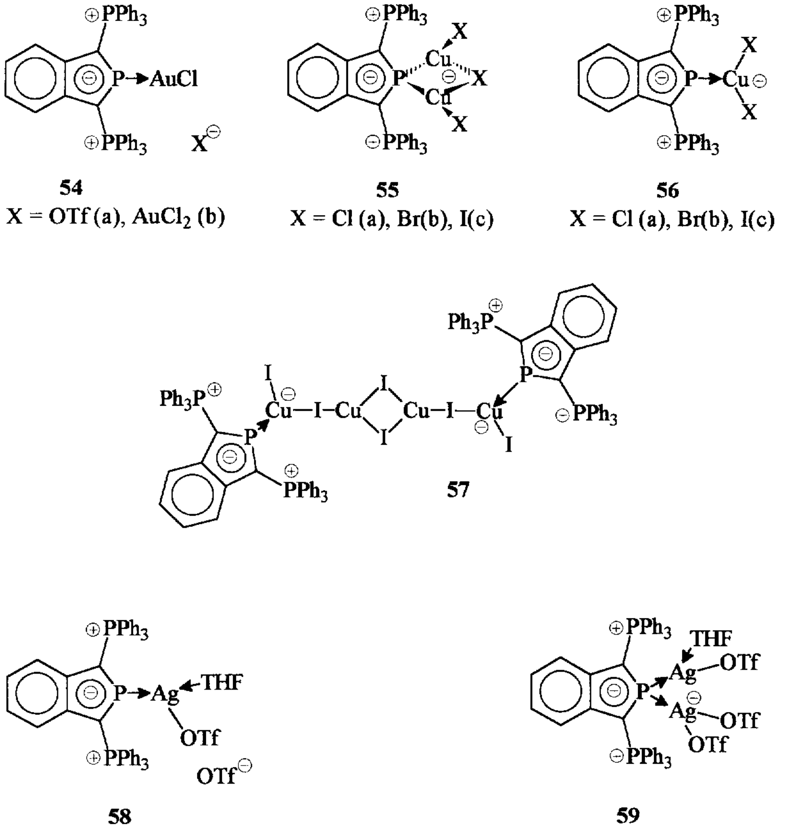


Fig. 7. Schematic representation of principle types of bis-phosphonio-isophosphindolide complexes.

(X=OTf) or 1:2 ratio (X=Cl, Br) to afford the complexes **54a,b** [35]. Formation of dinuclear complexes was not observed with AuCl, however, reactions of [**18a**][OTf] with one or two equivalents of in situ generated $[(Ph_3P)Au][BF_4]$ provided spectroscopic evidence for the presence of both mononuclear and dinuclear complexes in which the two coordinate phosphorus atom of the cation carries one or two $[Au(PPh_3)]^+$ units, respectively [67].

A clear preference for the formation of class *CII* products was observed in the



Scheme 14.

reactions of [**18a**][Cl, Br] with CuCl and CuBr which afforded the dinuclear complexes **55a,b** even in cases where equimolar ratios of the reactants were employed [33,64]. Although both products were isolated as stable solids and characterised by X-ray crystal structures [33,64,67], $^{31}P$ NMR investigations indicated that they are partially dissociated in solution and exist in a dynamic equilibrium with small amounts of free **18a** and other species which were tentatively formulated as the mononuclear complexes **56a,b** [67]. Even if similar equilibria were also detected for the reaction of [**18a**][I] with CuI, a crystal structure investigation revealed in this case a composition of the isolated reaction product as a 1:1 mixture of a salt-like component $[\mathbf{18a}]_2[Cu_4I_6]$ with a tetranuclear complex **57** [68]. The latter may be regarded as a 2:2 adduct of CuI and a complex $[(\mathbf{18a})CuI_2]$, suggesting that a mixture of the two remaining equilibrium components had precipitated, and not the *CII* type complex.

Rapidly exchanging dynamic equilibria between free bis-phosphonio-isophosphindolide ions, mononuclear and dinuclear complexes were likewise observed in reactions of [**18a,b**][OTf] with silver salts AgY. For Y = OTf, enrichment of either complex was feasible by appropriate adjustment of the stoichiometry, and the two products **58**, **59** were isolated by low temperature crystallisation from THF solutions and characterised by crystal structure analyses [65]. The results of NMR studies suggested that the metal coordination sphere of **58** remains unchanged in solution, while **59** exhibits dynamic averaging of the two metal environments. For $Y = CF_3CO_2$, complexation of the cation remained incomplete even in the presence of a large excess of silver salt. Although isolable products could not be obtained, dynamic NMR studies revealed that the dissociation of the observed dinuclear complex **60** occurred via cleavage of the $\mu^2$-coordinated bis-phosphonio-isophosphindolide, leading to the reaction sequence given in Fig. 8 and further to the conclusion

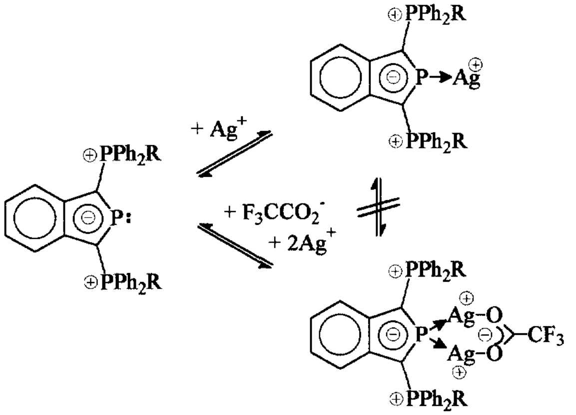


Fig. 8. Schematic presentation of the equilibria observed in the reaction of cation **18b** (R = vinyl) with $CF_3CO_2Ag$ [65]. With the exception of the bridging trifluoroacetate in [60], additional ligands at silver are omitted.

that **60** contains in addition to the bis-phosphonio-isophosphindolide a second bridging ligand (presumably a $\mu^2$-(O,O′)-trifluoroacetate) [65].

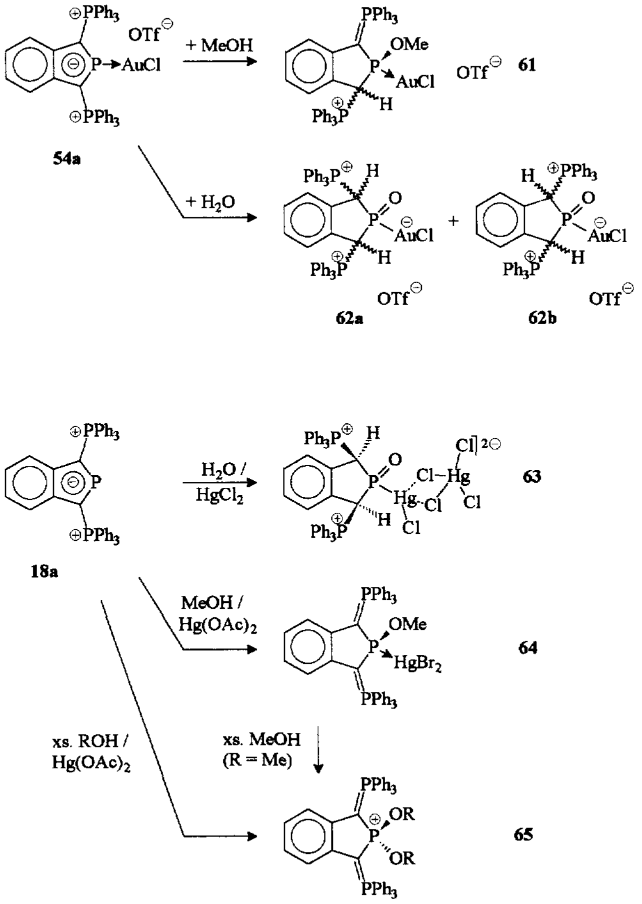
Studies of the reactivity of cation **18a** with $HgCl_2$ and $Hg(OAc)_2$ in aprotic solvents gave no evidence for the formation of spectroscopically detectable or even isolable complexes, however, the nature of the products observed after addition of $H_2O$ or alcohols strongly suggested that such (presumably not very stable) complexes are actually formed in very low concentration, and may be trapped in a subsequent reaction with H-acidic compounds [69].

### 4.2.2. *Reactivity*

Reactivity studies of bis-phosphonio-isophosphindolide complexes revealed two characteristic reaction modes, viz. ligand exchange under displacement of the coordinated cationic ligand, and addition reactions to the unsaturated π-electron system.

The gold complex **54a** reacts with equimolar amounts of $(Et_2N)_2C{=}NH$, $F^-$ or HMPT, either via quantitative displacement of the coordinated phosphorus cation, or via formation of a dynamic equilibrium between the complex and the free cation [35]. Similar equilibria occurred in reactions of [**18a**]X (X = Cl, Br) with AuCl or CuX [35,64], and of **18a**[OTf] with AgOTf [65] (vide supra), and exclusive complexation of the anion of **18a**[X] was observed in reactions of [**18a**]X (X = Cl, Br) with $HgCl_2$ [69] or $HgI_2$ [2]. The outcome of all reactions can be explained in terms of a competition between the phosphorus cation and the available neutral, or anionic, donors for the Lewis-acidic metal [35]. Assuming that the observed ratios between free and coordinated phosphorus cations reflect the difference in donor strengths of the competing Lewis-bases [35], the donor properties should increase in the following order: $\text{HMPT} < F^- <$ **18a** $\approx Cl^-, Br^- < (Et_2N)_2C{=}NH, PPh_3$ in gold complexes [35], $\text{OTf} < CF_3CO_2^- \approx$ **18a** $< OAc^-, SO_4^{2-}$ in silver complexes [65], and **18a** $< Cl^-, Br^-, I^-$ in mercury complexes. Apparently, the cation **18a** behaves as anticipated on the grounds of its positive charge and the low basicity of the $sp^2$-hybridised phosphorus, as a rather weakly donating ligand.

Methanolysis of the gold complex **54** proceeded via diastereoselective addition of MeOH to the coordinated cation to give the phosphite complex **61**, whereas with water two of three possible diastereomers of the phosphinito complex **62** were formed [35]. Copper complexes of **18a** displayed no similar reactivity [64], but a diastereoselective water addition which gave the dinuclear complex **63** as the final product was observed in the three component reaction between [**18a**][OTf], $HgCl_2$ and $H_2O$, and [**18a**]Br reacted with MeOH and $Hg(OAc)_2$ via formal transfer of $MeO^-$ to the two coordinated phosphorus site to yield the neutral complex **64**. Both reactions were assumed to proceed via mercury complexes of **18a** which evaded spectroscopic detection but were trapped by further reaction with $H_2O$ or MeOH [69]. Crystalline **64** consists of monomeric complexes with three-coordinate mercury rather than the usually encountered halide bridged dimers; presumably, the dimerisation, which is associated with a change from trigonal planar to tetrahedral coordination at Hg, is prohibited due to a similar steric protection of the coordination site as in the cation **18a** [69]. Reaction of **18a**/$Hg(OAc)_2$ or **64** with excess alcohols gave phosphonium cations **65** [69], the overall conversion **18a**→**65** resembling the oxidative methanolysis of $\lambda^3$-phosphabenzenes [40]a.



Scheme 15.

The feasibility of coordinated bis-phosphonio-isophosphindolides to add alcohols or $H_2O$ implies a chemical activation in the coordination sphere, since a similar reactivity is unobservable for the free ligands. The origin of this activation is presumably the enhancement of electrophilic character at phosphorus which follows the formation of the P→M dative bond and should facilitate attack of a nucleophile as the initial step of the addition reaction [35].

### 4.2.3. *Physical properties*

Crystal structures. Selected crystal structural data of both mono- and dinuclear bis-phosphonio-isophosphindolide complexes [33,35,64,65] are collected in Table 6. The mononuclear (class *CI*) complexes **54**, **57**, **58** reveal similar planar coordination

Table 6
Selected crystal structure data of bis-phosphonio-isophosphindolide complexes

| | | Bond lengths (Å) | | | | |
|---|---|---|---|---|---|---|
| | Complex | M–P | P–C ($PC_2$) | M–P (std.) [a] | $S$[b] | Ref. |
| **54** | $[\{(Ph_3P)_2C_8H_4P\}AuCl]^+OTf^-$ | 2.207(2) | 1.707(6)<br>1.721(7) | 2.272 | 2.9% | [35] |
| **57** | $[\{(Ph_3P)_2C_8H_4P\}_2Cu_4(\mu\text{-}I)_4I_2]$ | 2.199 | 1.719<br>1.733 | 2.252 | 2.4% | [68] |
| **58** | $[\{(Ph_3P)_2C_8H_4P\}Ag(THF)(OTf)]^+OTf^-$ | 2.338(1) | 1.715(3) | 2.419 | 3.3% | [65] |
| **55b** | $[\mu\text{-}\{(Ph_3P)_2C_8H_4P\}Cu_2(\mu\text{-}Br)Br_2]$ | 2.255(2)<br>2.351(1) | 1.728(7)<br>1.730(7) | – | – | [64] |
| **55a** | $[\mu\text{-}\{(Ph_3P)_2C_8H_4P\}Cu_2(\mu\text{-}Cl)Cl_2]$ | 2.194(2)<br>2.628(2) | 1.722<br>1.732 | – | – | [33]6[8] |
| **59** | $[\mu\text{-}\{(Ph_3P)_2C_8H_4P\}Ag_2(THF)(OTf)_2]$[c] | 2.377(3)<br>2.393(3)<br>2.416(6)<br>2.419(3) | 1.727(10)<br>1.732(10)<br>1.741(10)<br>1.742(19) | – | – | [65] |

[a] Standard bond distances for M–P bonds in $PPh_3$ complexes, from Ref. [70].
[b] Bond shortening factor $S = 100^*\{r(M-P) - r(M-P, \text{std.})\}/r(M-P, \text{std.})$.
[c] Two independent molecules per unit cell.

geometries at phosphorus as phosphenium complexes, but display neither particularly short P–M bonds, nor an elongation of intra-ligand P–C bonds; in fact, the P–M distances are only 2–4% shorter than standard values of $PPh_3$ complexes [70] (**57** features even longer P–Cu bonds than $[(Cy_3P)_2Cu_2(\mu\text{–}Cl)_2]$ ($r_{CuP} = 2.18$ Å [71])), and the intra-ligand P–C and C–C distances deviate insignificantly from the values of the free cation. The metal coordination geometries can be described as linear (**54**), regularly trigonal planar (**57**) and (distorted) T-shaped planar (**58**) with the Ψ-*trans* and -*cis* positions with respect to phosphorus in **58** being occupied by a THF molecule and a triflate anion, respectively. The metal coordination planes form dihedral angles of 74° (**57**) and 88° (**58**) with the isophosphindole ring planes and are predictably arranged in a way as to minimise any contacts between the adjacent $Ph_3P$-moieties and the other ligands on the metal.

The dinuclear (class *CII*) complexes **55a,b**, **59** display on average even longer P–M bonds, while intra-ligand bond lengths are still comparable to those of the free cations. In contrast to the symmetrically $\mu^2$-bridging coordination of the cationic ligand in **59** with two equal Ag–P bonds, the $PCu_2X$ cores of **55a** (X = Cl), **b** (X = Br) exhibit remarkably short Cu–Cu distances, as well as a unique asymmetry. The two Cu–P and Cu–X bonds are considerably different in length, and the ligand plane no longer bisects the Cu–P–Cu angle but is tilted away from the more distant metal [33,64]. Similar structural features are known for copper aryls with $\mu^2$-bridging aryl moieties [72], and these structural analogies inspired the suggestion [33,64] that the metal–ligand interactions in the present complexes can be explained by a similar model (see below). As in the mononuclear complexes, the directing effect of the ligand stereochemistry on the metal geometry becomes manifest in the preference for three-coordination with planar, distorted trigonal or T-shaped geometries, and a nearly orthogonal arrangement of the metal coordination plane with respect to the isophosphindole ring.

NMR Spectroscopy. Due to the kinetic lability of the complexes, meaningful NMR data can only be obtained from spectra recorded at low temperatures [35,64,65]. $^{31}$P coordination shifts $\Delta\delta$ are generally negative. Values for mononuclear complexes range from $\Delta\delta = -25$ for the Ni-complex **53** [66] to $\Delta\delta = -45$ to $-60$ for complexes of coinage metals [35,65,68]. Coordination shifts of dinuclear complexes are still more negative and are further sensitive to the presence of additional bridging ligands; silver complexes without additional bridging ligands beside the $\mu^2$-bis-phosphonio-isophosphindolide feature more negative values ($\Delta\delta = -140$ to $-150$ [65]) than doubly bridged complexes ($\Delta\delta = -100$ to $-110$ for $[\{\mu^2\text{-}\mathbf{18a}\}Ag_2(\mu^2\text{-}CF_3CO_2)]^{2+}$ [65], $-105$ to $-95$ for $[\{\mu^2\text{-}\mathbf{18a}\}Cu_2(\mu^2\text{-}X_2)X_2]$ [64,68]). The gold complex **54** displayed a negative $^{13}$C coordination shift ($\Delta\delta = -10$ [35]). Magnitudes of $^1J(^{109}Ag,^{31}P)$ (750 to 831 Hz) in mononuclear silver complexes are comparable to those in $[(R_3P)AgX]$, while dinuclear complexes display smaller couplings (440 to 520 Hz), in accord with the higher phosphorus coordination number and larger bond distances [65]. Determination of $\delta^{109}$Ag for two mono- and one dinuclear complex revealed markedly higher metal shieldings ($\delta^{109}Ag = 502$, 528 for mononuclear, 764 for dinuclear complexes [65]) as in phosphine or phosphite complexes ($\delta^{109}Ag = 1000\text{–}1500$ [73]), indicative of a rather small perturbation of the $d^{10}$ electron configuration at $Ag^+$ due to both low coordination numbers and weak donor capabilities of the ligands [73].

### *4.3. The nature of the phosphorus–metal bond in complexes of phosphenium and bis-phosphonio-isophosphindolide cations*

The basic principles of the phosphorus–metal bonding in phosphenium complexes can be developed by focusing, for reasons of simplicity, on the interaction of a diaminophosphenium cation with an octahedral 16e-transition metal fragment. Relevant orbital interactions (Fig. 9a) include combination of the metal-LUMO with the phosphenium-(HOMO-1) ("lone pair"), and of the phosphenium-LUMO with one of the occupied orbitals of the former $d(t_2g)$-set (interactions of the phosphenium-HOMO with empty d-orbitals can be neglected because of the vanishing coefficients at phosphorus). In simple terms, the two interactions constitute a dative $L \rightarrow M$ $\sigma$- and a retrodative $M \rightarrow L$ $\pi$-bond, leading to the commonly accepted description of a formal double bond similar to carbene or nitrosyl complexes [1]a,b. This concept was successfully utilised for the explanation of the special structural (short metal phosphorus bonds, *trans*-effect) and spectroscopic features (IR data, $^1J(M,P)$ coupling constants) as well as chemical properties (ligand exchange, isomerisation) of phosphenium complexes [9,54–58].

Since any flow of electron density from the ligand to the metal further sharpens the electron deficit at phosphorus, the formation of a $L \rightarrow M$ $\sigma$-bond may be considered as an inherently destabilising influence. Compensation of this effect can be achieved either by "intramolecular" $M \rightarrow L$ back donation, or by "intermolecular"

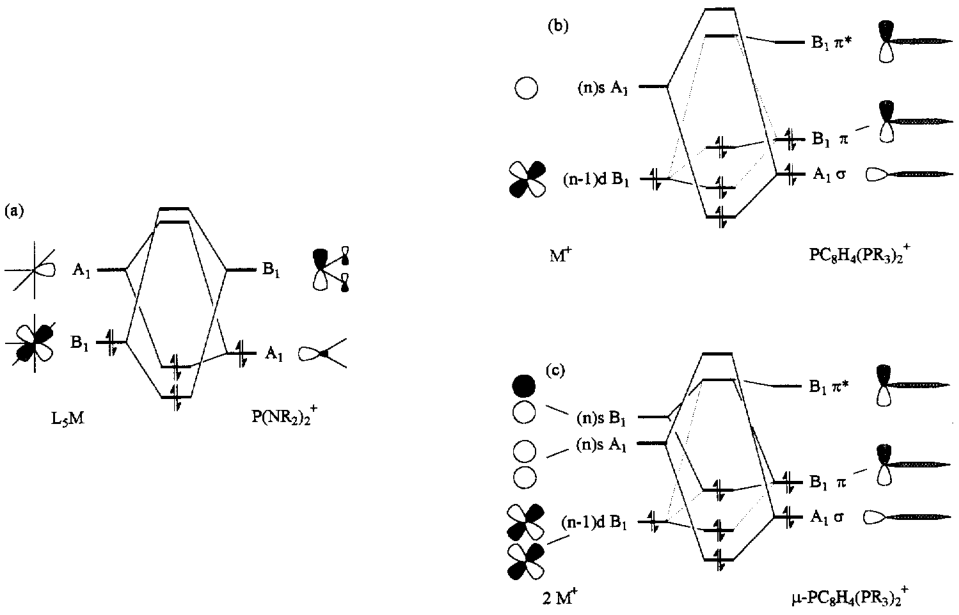


Fig. 9. Schematic representation of correlation diagrams showing the frontier orbital interactions between (a) a 16e-$ML_5$ fragment and a diaminophosphenium ion, (b) a $PC_8H_4(PR_3)_2^+$ (bis-phosphonio-isophosphindolide) cation and one $M^+$ ($d^{10}$) metal ion, and (c) a $PC_8H_4(PR_3)_2^+$ cation and two $M^+$ ($d^{10}$) metal ions. The ring system of the $PC_8H_4(PR_3)_2^+$ ions is thought to be perpendicular to the drawing plane, and for σ- and π-orbitals only the lobe at the two coordinate phosphorus is shown.

anion capture and formation of a neutral complex with a trivalent phosphorus ligand [8,54]. In this respect, the π-basicity rather than the σ-acidity of the metal fragment must be considered as the decisive factor for the stability of a cationic phosphenium complex [8], and the efficacy of stabilising influences such as low formal oxidation state and high atomic number of the metal, or low π-acidity of co-ligands [9,56,57], can be traced to the stabilisation of the $M \rightarrow P$ π-bond. As this interaction further implies population of the P–N antibonding $\pi_3$-orbital of the phosphenium ligand, strengthening of the P–M bond will result in simultaneous weakening of the intra-ligand P–N bonds, thus explaining the inverse trends of M–P and P–N bond distances in phosphenium complexes which culminate in the equality of phosphenium and phosphite P–N distances in the complexes **38a,b** [57]. Seen from a different angle, the interplay between M–P and intra-ligand π-bonding also explains why stable cationic complexes of phosphenium ions with weakly π-donating RO-substituents can be obtained whereas the free cations are unstable [57]. If the metal fragment exhibits sufficient π-basicity, the electronic stabilisation of the complex is dominated by M–P rather than intra-ligand π-bonding (this effect is further enhanced by the stronger σ-withdrawing effect of an RO-group [56]), so that the loss of electronic stabilisation due to the lower π-donor capability of an RO- as compared to an $R_2N$-group becomes less critical.

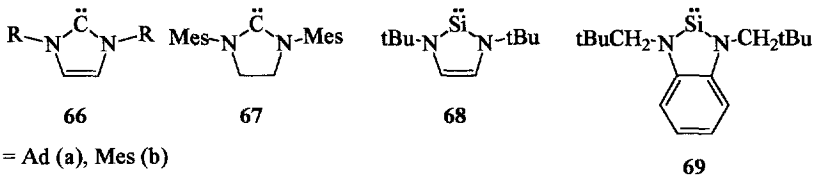
The bonding between a bis-phosphonio-isophosphindolide and a single $d^{10}$ metal cation in *CI*-type complexes can also be pictured by a superimposition of L→M-σ- and M→L-π-contributions. However, the situation gets somewhat complicated since the ligand possesses an additional energetically high lying π-orbital which exhibits the same symmetry as the LUMO and may therefore interact with the same metal orbitals (Fig. 9b). Owing to the weaker electrophilicity of the ligand and the repulsive aspect of the interaction between filled π-orbitals on metal and ligand, M→P back donation and therefore M–P double bond character should be less pronounced than in phosphenium complexes. This agrees in principle with the fact that bis-phosphonio-isophosphindolides form, in contrast to phosphenium ions, stable complexes with weakly π-basic coinage metal ions which reveal neither particular shortening of M–P bonds nor significant changes in intra-ligand bond lengths or electronic transition energies (reported π–π* transition energies in the silver complex **58** are similar to those of the free ligand [65]). On the other hand, the scaled reactivities of bis-phosphonio-isophosphindolide complexes with different metals in nucleophilic additions (vide supra), and the apparent low stability of the mercury complexes [69] (the high Lewis-acidity of $Hg^{2+}$ should render these complexes very stable if the M–P bonding was described as a pure σ-bond) seem to reflect differences in the extent of M→P back donation and suggest that, even if M–P double bond character may be low, it is not negligible.

For a description of the M–P bonding in dinuclear class *CII* complexes it is reasonable to focus first on the case of two $d^{10}$ metal ions with a symmetrically bridging ligand, where the main orbital interactions occur between occupied ligand $A_1(\sigma)$ and $B_1(\pi)$-orbitals with appropriate symmetry combinations of empty metal $(n)$s-orbitals, and between a antisymmetric combination of occupied metal $(n-1)$d-orbitals with the empty ligand $B_1(\pi^*)$-orbital (Fig. 9c). In principle, the ligand could form two dative L→M bonds by utilising the phosphorus "lone pair" and two electrons out of the π-system, which are further stabilised by M→L back bonding. Such a situation is encountered in bimetallic complexes with $\mu^2$(P)-bridging phospholide or diphospholide ligands, and is known to lead to rather short M–P distances as well as a significant reorganisation of intra-ligand bonds as a consequence of the breakdown of the delocalised π-electron system [74]; furthermore, the M–M antibonding character of the L→M(π) and M→L(π*) interactions should disfavour short inter-metal distances.

In contrast, dinuclear bis-phosphonio-isophosphindolide complexes are characterised by rather long P–M bonds, negligible changes in intra-ligand bond lengths and comparatively short inter-metal distances. These features can be explained if we assume that, as in the mononuclear complexes, the M–P bonding is dominated by the L→M σ-interaction. The bonding in the $M_2P$ core may thus be rationalised in analogy to the topologically related copper or silver aryls and aryl cuprates, where two metals are bridged by $\mu^2$(C)-coordinated aryl moieties, in terms of a 2-electron-3-centre bond which is further stabilised by interactions between the metals and the π-electron system [72]. A similar description was also proposed for the bonding of a $\mu^2$(P)-bridging phosphinine in the dinuclear complex $[Ir_2(1,5\text{-cod})_2(\text{niphos})_2][SbF_6]_2$ (niphos = 2-pyridylphosphinine) [75]. The asymmetric coordination mode of the $\mu^2$-bis-phosphonio-isophosphindolide in the copper complexes **55a,b** is further precedented by a similar asymmetry of the aryl bridges in the tetrameric copper aryl $[(2,4,6\text{-}i\text{Pr}_3C_6H_2)Cu]_4$ [76] and suggests an unequal distribution of $\sigma$- and $\pi$-bonding contributions between the two Cu–P bonds [64]. The observed bond distances are in accord with the initial assumption that an increase of $\pi$-contributions results in a weaker (longer) bond. When the interactions of the $P_2Cu$ moiety with the additional bridging halide ion are also considered, it appears that elongation of the P–Cu bond is associated with a shortening of the Cu–($\mu$)Br bond to the same metal, and the whole $PCu_2X$ moiety can be envisaged as an intimate contact ion pair between a phosphenium-like [(bis-phosphonio-isophosphindolide)CuX]$^+$ and a $[CuX_2]^-$-fragment which are held together by additional (weaker) M–P($\pi$)- and M–X($\sigma$)-interactions [64].

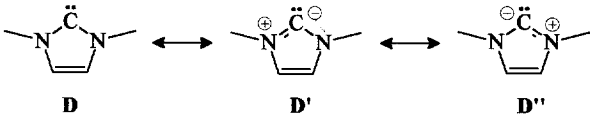
## 5. Aminophosphenium and bis-phosphonio-isophosphindolide ions vs carbenes and silylenes: an isolobal comparison

Quite in contrast to phosphenium ions, the isolobal and iso(valence)electronic carbenes [77] and silylenes were long regarded as unstable species which can only be intercepted in trapping experiments. This view was changed only a few years ago with the report of the first isolable "Arduengo"-carbene **66a** [78]a. Since then, a variety of stable carbenes, among them the C–C saturated analogue **67** [78]b and silylenes (**68,69** [79]) have been prepared. In the frame of isolobal and isoelectronic relationships, these derivatives can be compared with diazaphospholidinium and diazaphospholenium cations, and further, based on the isolobal/isoelectronic analogy between ylide ($>C^{(-)}\text{–}P^{(+)}\leqslant$) and imide ($>N\text{–}C(Si)\leqslant$) fragments, with bis-phosphonio-isophosphindolide cations. In order to emphasise the validity and significance of this (at first glance purely formal) concept, it seems appropriate to attempt a brief comparative analysis of the bonding situation and coordination properties of the two classes of compounds.



Scheme 16.

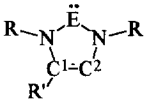
Structure and bonding in carbenes and silylenes of type **66–68** was addressed in both experimental and theoretical studies [80]. The results were discussed controversially, but it appears now that the dominant contribution to the thermodynamic stabilisation of both C–C saturated and unsaturated carbenes is N→C $\pi$-donation into the formally empty p-orbital of the divalent carbon, which may be described in the VB picture by the mesomeric structures D–D″ [80]. The C–C unsaturated heterocycles gain additional stability from cyclic π-delocalisation [80]. Aside from the pure thermodynamic aspect, both effects reduce significantly the Lewis-acidity of the carbene centre [80]b. Qualitatively similar, but smaller effects were predicted for the silylenes of type **68**. In terms of molecular structures, the electron delocalisation leads to an experimentally observable contraction of the C(carbene)–N or Si(silylene)–N bonds, and some further bond length equalisation in the C–C unsaturated compounds of type **66, 68** [80].



Scheme 17.

While on first glance this bonding model is, as anticipated, identical to that of phosphenium cations, there remain some important differences in the extent of the delocalisation effects. Thus, although contribution by structures D′ and D″ is crucial for carbenes, D is still the dominant mesomeric formula [80]b. In contrast, diaminophosphenium cations are normally addressed as heteroallylic 4π-systems [21,23], suggesting that π-bonding is clearly enhanced and the weight of resonance structures B′, B″ increases or even dominates. Likewise, the degree of cyclic π-delocalisation is markedly higher in diazaphospholenium ions than in carbenes or silylenes, as indicated by the more pronounced bond length equalisation in the phosphorus cation **3** compared to the neutral compounds **66a**, **68** (Table 7). A concise description of the π-electron structure seems to be intricate [80]a, but the lower degree of π-interaction in carbenes (silylenes) may be easily rationalised in the frame of the simple VB picture. Formulation of the ylidic structures D′, D″ in the carbon (silicon) system requires charge separation which makes these formulae higher in energy than D. In the phosphorus system only a shift of the positive charge is required, so that all three formulae are closer in energy and the weight of structures B′, B″ is increased

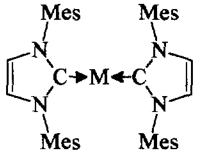
Table 7
Selected crystal structure data of carbene analogue five membered heterocycles



| | | | | Bond distances (Å) | | |
|---|---|---|---|---|---|---|
| | E | R | R′ | N–C$^1$/C$^2$ | C$^1$–C$^2$ | Ref. |
| **3a** | P$^+$ | *c*-Hexyl | Cl | 1.363(6)<br>1.370(6) | 1.357(7) | [7] |
| **66a** | C | Adamantyl | H | 1.382(2)<br>1.386(2) | 1.338(3) | [78]a |
| **68** | Si | *t*-Butyl | H | 1.400(9) | 1.347(21) | [79]a |

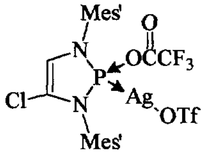
(π-donation from nitrogen to the central atom should be further facilitated by the higher electronegativity of $P^+$ as compared to neutral C or Si).

The predicted low electrophilicity of aminocarbenes [77,80] also dominates their coordination properties. Thus, carbenes **66a,b** form complexes with Mg and Zn alkyls, $GeI_2$ or $AlH_3$ [77], whose comparatively long M–C(carbene) distances suggest that the M–C bond may be described as a pure C→M single bond. With stronger π-basic metals such as Ni(0) and Pt(0), M→C contributions gain importance, and the homoleptic complexes **70a,b** display unique short M–C bonds and an elongation of C(carbene)–N distances with respect to the free ligand which are indicators for partial M–C double-bond character [81]a. The differences between imidazoyl-carbenes and isoelectronic diazaphospholenium cations are elucidated by the different behaviour of the carbene **66c** and the phosphorus cation **3c** towards $Ag^+$. While the former gives rise to a both kinetically and thermodynamically stable homoleptic complex **70c** [81]b, the latter only forms an unstable base stabilised adduct **71** [8], indicating that the phosphorus cation is both a stronger Lewis-acid and a weaker Lewis-base than the neutral carbene.



**70**

M = Ni (a), Pt (b), $Ag^+$ (c), $Cu^+$ (d)



**71**

(Mes' = 2.6-$Me_2C_6H_3$)

Scheme 18.

Complexes of aminosilylenes are hardly known, the only notable exception being $[(\mathbf{68})_2Ni(CO_2)]$ which was obtained by reaction of **68** with $Ni(CO)_4$ [82]. Its structural and spectroscopic features suggest weak Si–Ni double bond character, but the reported IR and NMR data indicate that the π-acidity of the silylene is comparable to $PPh_3$ [82] rather than CO or phosphenium cations. Silylenes with substituents other than $NR_2$ are stronger electrophiles, and the chemistry of their complexes [53,83] is characterised by the same competition between "intramolecular" and "intermolecular" stabilisation as that of phosphenium complexes. Stable silylene complexes are observed when the electron deficit at silicon is compensated by a combination of a highly π-basic metal fragment and strong π-donor/weak σ-acceptor substituents (thiolate groups or organometallic fragments), while otherwise intermolecular stabilisation by formation of base adducts $B \rightarrow R_2Si \rightarrow ML_n$ occurs. In principle, these adducts are isolobal and isoelectronic to complexes such as **34** and **36** which contain trivalent phosphorus ligands with nucleofugic substituents (OTf, F) and can be designated as adducts of cationic phosphenium complexes with anionic bases. Both types of compounds may be further regarded as isolobal analogues of carbenoids, and the increased weakening of the P(Si)–base and concomitant strengthening of the P(Si)–M interaction in the series "base stabilised phosphenium complex" – base stabilised silylene complex – ionic phosphenium complex / base free silylene complex can be seen as reversal [8] of the "transition metal assisted ionisation" [84] of a carbenoid.

The low electrophilicity of aminocarbenes and -silylenes suggests that their complexes might exhibit a closer kinship with complexes of bis-phosphonio-isophosphindolide rather than phosphenium ions. In fact, L→M σ-interactions dominate the M–L bonding in both cases, but the observed low stability of bis-phosphonio-isophosphindolide complexes with $Ag^+$ or $Cu^+$ as compared to the carbene complexes **70c,d** suggests that carbenes are stronger σ-donors than the phosphorus cations, presumably as a consequence of the overall positive charge of the latter. On the other hand, the formation of dinuclear complexes which is observed for bis-phosphonio-isophosphindolides but not for the carbenes suggests that the phosphorus cations are better π-donors, most likely as a consequence of a higher extent of cyclic π-electron delocalisation. Consequently, bis-phosphonio-isophosphindolides can be characterised with respect to their coordination properties as hybrids between true phosphenium cations (=carbene analogues) and phospholide anions which may utilise both the phosphorus lone pair and the π-electron system for metal binding.

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