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Effect of π-donating substituents on the dative or covalent character of adducts of some simple "enium" ions with PMe_3 and NMe_3

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Abstract

The charge distribution, molecular structure and bond cleavage of formal donor adducts of phosphenium, arsenium, and the isolobal selenenyl cations with trimethylphosphane and trimethylamine have been explored by quantum chemical methods on Hartree–Fock, DFT and MP2 level. According to our results, adducts of methyl substituted cations are mainly covalent and therefore should be better described as phosphonium or ammonium ions. Switching from methyl substituted "enium" ions to their π-donor substituted analogs increases the dative character of the central bond to an extent for which a description as donor adducts of phosphenium or arsenium ions appears appropriate, while their selenium congener still remains preferentially covalent.

Keywords: Donor-stabilization; Selenium; Phosphenium; Arsenium; Ab initio calculations

1. Introduction

The formation of donor adducts of "enium" ions of the main group elements has proven to be an elegant strategy to stabilize such reactive cationic species. Especially in group 15 numerous donor adducts of phosphenium, arsenium and stibenium ions have reported [1–11]. A general sketch illustrating the possible formulations of such adducts of "enium" ions of group 14/15/16 elements is depicted in Scheme 1. Of course it is debatable, whether such adducts still represent cryptic "enium" ions (**I**) or in contrast should be described as "onium" ions (**II**) or (**III**) of the respective donor atom [9,12]. In principle, for a situation in which the donor atom is more electronegative than the acceptor atom, the "enium" ion character should be more pronounced than for a more electropositive donor. Interestingly, in phosphane adducts of arsenium ions the donor atom is more electropositive (EN(P) = 2.06) than the acceptor atom (EN(As) = 2.20) [13], yet still they have been regarded as cryptic arsenium rather than phosphonium ions, which was also supported by their reactivity [1,2,7]. A situation which is even more paradox in terms of a donor adduct can be expected for phosphane adducts of selenenium ions which are isolobal to arsenium ions. In this element combination the donor atom is even more electropositive (EN(P) = 2.06) than the acceptor atom (EN(Se) = 2.48) [13]. Given the electronic influence of adjacent substituents and the various electronegativity scales that exist [13–16], the electronegativity difference is anyway too simple to describe the delicate bond polarity in these ions. Schoeller et al. provided a detailed analysis of the bond situation in donor adducts of the heterocarbenes of group 14 [17]. Moreover, they and others investigated donor adducts of phosphenium ions with one or more donors and phosphenium ions as part of low coordinated π-systems [10,12,18–20]. Of course also phosphorus ylids can be regarded as phosphane adducts of carbenes and iminophosphoranes as phosphane adducts of nitrenes [21–29]. More recently also the bond situation of donor stabilized phosphinidenes has been investigated [30].

In this paper we report an ab initio study to assess the covalent or dative character of formal adducts of alkyl and amino substituted phosphenium, arsenium and selenenium ions with PMe_3 and NMe_3. Our findings suggest that the

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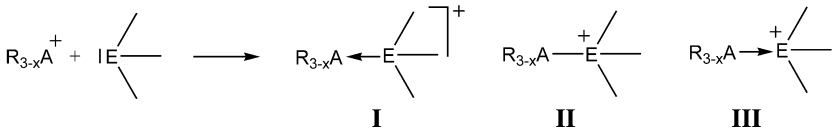


Scheme 1. E = donor, group 15 element; A = acceptor, group 14 element ($x = 0$), group 15 element ($x = 1$), group 16 element ($x = 2$).

balance between a predominantly covalent or dative character is very sensitive to the presence of π-donating substituents.

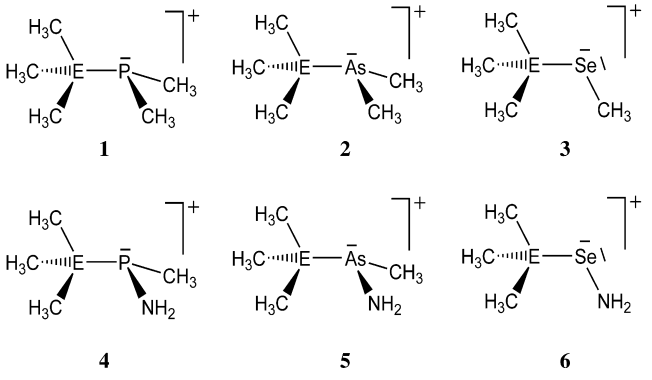
2. Results and discussion

To get a closer insight into the bond situation of formal donor adducts of phosphenium, arsenium, and the isolobal selenenyl cations we performed ab initio calculations on model systems of these compounds (Scheme 2). As model systems we considered the methyl substituted phosphenium, arsenium, and selenenyl cations stabilized by trimethylphosphane (**1–3a**) or trimethylamine (**1–3b**). Moreover we looked at ions in which one methyl group at the formal "enium" ion is replaced by an amino group representing a π-donating moiety (**4–6a,b**).

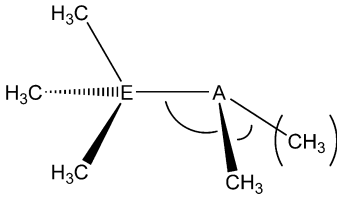
Ab initio calculations were performed using the program package GAUSSIAN 03 [31]. The geometries of structures (**1–6a,b**) have been optimized at HF, DFT and MP2 level using a 6-311G(d) basis set. In order to analyze the electronic situation in adducts (**1–6a,b**) the charge distribution within these ions has been analyzed using Mulliken population analysis (MPA) and natural population analysis (NPA) including the Wiberg bond index. The dative or covalent character of the donor bond has been assessed by comparing the energies of heterolytic and homolytic cleavage using the Haaland approach [32].

2.1. Molecular structure

Structural parameters have often been the experimental basis in discussing the bond situation in synthetically accessible donor adducts of enium ions [1–11]. A schematic sketch of the molecular structure of the methyl substituted



Scheme 2. Model systems used in our investigation (E = donor atom: P (**1–6a**), N (**1–6b**)).



Scheme 3. Illustration of geometric parameters relevant for the molecular structure of cations (**1–3a,b**) (E = donor atom: P, N; A = acceptor atom: P, As, Se).

cations (**1–3a,b**) is depicted in Scheme 3. Principal bond distances and angles of these structures resulting from geometry optimization at DFT (B3LYP) and MP2 level using a 6-311g(d) basis set are listed in Table 1. In all cases the central donor acceptor bond lengths are well below the sum of the van-der-Waals radii of the respective atoms. For the phosphane adducts the lengths of these bonds are just at (P–P (**1a**)) or slightly larger (P–As (**2a**)) than the sum of the covalent radii (2.20 Å (P–P), 2.32 Å (P–As)). Moreover, the P–Se bond in **3a** is shorter than the sum of the corresponding covalent radii (2.27 Å (P–Se)). These data suggest a regular single bond between the donor and acceptor atoms in the phosphane adducts **1–3a**. Generally, the donor acceptor bond distances obtained at DFT level are higher than those at MP2 level.

Table 1
Selected geometric parameters in methyl substituted **1–3a,b** at different levels of theory as indicated using a 6-311G(d) basis set

	E–A (Å)	E–A–CH_3 (°)	A–CH_3 (Å)	H_3C–A–CH_3 (°)	H_3C–E–CH_3 (°)
1a E = P					
B3LYP	2.239	99.5	1.860	101.3	107.9–108.2
MP2	2.199	98.5	1.846	100.9	108.1–108.3
1b E = N					
B3LYP	1.946	100.6	1.843	99.9	108.5–109.4
MP2	1.902	100.0	1.829	99.7	108.4–109.2
2a E = P					
B3LYP	2.374	97.0	1.987	98.7	107.7–107.8
MP2	2.333	96.1	1.970	98.3	107.9
2b E = N					
B3LYP	2.102	98.7	1.969	97.7	109.2–109.8
MP2	2.049	98.2	1.951	97.4	108.9–109.4
3a E = P					
B3LYP	2.244	99.7	1.986	–	108.5–109.0
MP2	2.221	98.1	1.970	–	108.6–109.1
3b E = N					
B3LYP	2.019	100.6	1.957	–	109.9–110.6
MP2	1.986	99.6	1.940	–	109.6–110.4

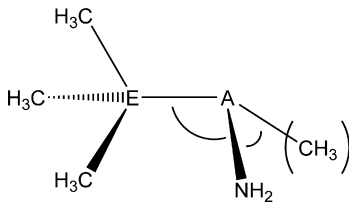
By contrast, the donor acceptor bond exceeds the sum of the covalent radii in the corresponding amine adducts in all cases. This difference is largest for the arsenium ion **2b** (r_{cov} (N–As): 1.97 Å) and smallest for **3b** (r_{cov} (N–Se): 1.92 Å), while phosphenium ion **1b** is just in the middle (r_{cov} (N–P): 1.85 Å). For the amine adducts **1–3b** the data reveal an elongated single bond between the donor and acceptor atoms. These findings suggest, that the amine donor is more loosely bound to the acceptor than the phosphane donor. A more detailed view of this point including energetic aspects will be addressed later in this paper.

An interesting aspect of the geometric parameters in cations **1–3a,b** is how they compare to related values in the uncoordinated amine or phosphane and the free ''enium'' ions. On adduct formation the Me–P–Me angle in PMe_3 increases from 99.3° at DFT level (98.8° at MP2) to values between 108° and 109° in **1–3a**. In contrary, the Me–N–Me angle in NMe_3 decreases from 111.7° at DFT level (110.1° at MP2) to values between 108° and 109° in the phosphenium and arsenium ions **1,2a** and remains almost unchanged in selenenium ion **3a**. The change of the R–E–R angle in ER_3 on adduct formation with $AR_{1(2)}$ decreases in the order A = P > As > Se, which indicates steric effects which are diminished by increasing the E–A distance or decreasing the number of substituents at A.

The H_3C–A–CH_3 angles in **1–3a,b** decrease on going from phosphane adducts to amine adducts and from phosphenium ions to arsenium ions. The dependence on the nature of the ''enium'' ion can be understood on the basis of isovalent nonhybridization which is more pronounced for As than P [33]. Moreover, the compared to P–C longer As–C bond reduces the repulsive interaction between the methyl groups and therefore allows smaller H_3C–A–CH_3 angles. Compared with the H_3C–A–CH_3 angles in the free $P(CH_3)_2^+$ and $As(CH_3)_2^+$ ions amine donors have a more pronounced effect than phosphane donors. Thus, the H_3C–A–CH_3 angle in $P(CH_3)_2^+$ decreases from 103.3° at DFT level (102.4° (MP2)) to 101.3° (100.9° (MP2)) in the phosphane adduct and further decreases to 99.9° (99.7° (MP2)) in the amine adduct. For $As(CH_3)_2^+$ (100.1°) at DFT level (99.3° (MP2)) a similar trend is observed. The stronger geometric changes induced by the amine donor compared with the phosphane donor suggest a stronger interaction (i.e. stabilization) of the ''enium'' ion by the former. In turn the elongated donor acceptor bonds in amine adducts compared to phosphane adducts suggests just the opposite, i.e., lower interaction and therefore stabilization of the ''enium'' ion by an amine donor compared with a phosphane donor.

Similar trends as for (**1–3a,b**) can be found for cations (**4–6a,b**) in which one methyl substituent is replaced by an amino group as depicted in Scheme 4. Relevant bond distances and angles of these structures resulting from geometry optimization at DFT (B3LYP) and MP2 level using a 6-311g(d) basis set are listed in Table 2. Compared to the methyl substituted **1–3a,b** the donor acceptor bond in cations (**4–6a,b**) is longer by 3–8 pm at DFT level and 2–5 pm at MP2 level. This elongation is more pronounced for the amine than for the phosphane adducts and stronger on DFT than MP2 level. Consequently, the donor acceptor bond lengths are all larger than the sum of the covalent radii of the respective atoms, except for the phosphane stabilized selenenium ion (**1a**). As in the methyl substituted **1–3a,b** the Me–E–Me angle in **4–6a,b** varies between 108° and 111° with the largest values found for the selenium ion. Also the H_3C–A–NH_2 angle in **4–6a,b** is frequently larger than the corresponding H_3C–A–CH_3 angle in **1–3a,b**, although the difference is rather small. The H_3C–A–NH_2 angle again decreases going from phosphane to amine donors and from phosphenium ions to arsenium acceptors. Generally, the structural changes found in adducts **1–6a,b** are rather small and may sometimes even be below the accuracy of the method. Therefore, simply based on geometric parameters a clear distinction between more covalent or dative bond character is unlikely to be resolved.

By contrast, a noteworthy feature of structures **4–6a,b** affects the A–NH_2 bond lengths. Generally these values are in the single bond region of the respective element



Scheme 4. Illustration of geometric parameters relevant for the molecular structure of cations (**4–6a,b**) (E = donor atom: P, N; A = acceptor atom: P, As, Se).

Table 2
Selected geometric parameters in methyl substituted **4–6a,b** at different levels of theory as indicated using a 6-311G(d) basis set (R = CH_3)

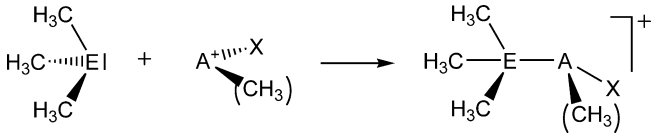
	E–A (Å)	E–A–R (°)	E–A–N (Å)	A–R (Å)	A–N (Å)	R–A–N (°)	R–E–R (°)
4a E = P							
B3LYP	2.293	98.2	99.1	1.849	1.689	102.8	107.7–108.5
MP2	2.234	97.8	97.2	1.836	1.692	102.8	108.0–108.9
4b E = N							
B3LYP	2.025	98.1	101.7	1.838	1.663	100.1	109.4–110.9
MP2	1.954	97.9	100.9	1.824	1.659	100.0	109.1–110.5
5a E = P							
B3LYP	2.418	96.3	92.0	1.978	1.852	99.5	107.6–108.7
MP2	2.364	95.6	91.0	1.960	1.845	99.6	107.8–108.8
5b E = N							
B3LYP	2.170	96.5	97.2	1.965	1.801	97.7	109.8–111.1
MP2	2.093	96.2	96.4	1.945	1.796	97.9	109.3–110.7
6a E = P							
B3LYP	2.272	–	92.2	–	1.875	–	108.8–110.2
MP2	2.241	–	90.6	–	1.871	–	109.0–110.2
6b E = N							
B3LYP	2.102	–	99.7	–	1.772	–	110.8–111.4
MP2	2.041	–	97.7	–	1.773	–	109.3–110.7

combination. However, more interesting than the absolute value of these distances is the trend that for the same "enium" ion the A–NH_2 bond distance is shorter for the amine adduct than for the phosphane adduct. This difference is smallest for phosphorus (3 pm (2%)) increases for arsenic (5 pm (3%)) and amounts to 11 pm (6%) for selenium. This trend can be rationalized considering negative hyperconjugation as in related cases [34–39]. Such a hyperconjugative interaction competes with the σ-donor-stabilization of the amine/phosphane and is more likely for polar donor acceptor bonds and is therefore weakest for the (formally) unpolar homonuclear bond in **1**.

2.2. Energy of formation

As discussed above, the structural details of adducts **1–6a,b** reveal a marked difference for trimethylamine or trimethylphosphane acting as a donor. In order to assess the relative stability of these adducts we calculated the free reaction enthalpy (ΔG_f) for the formation of adducts **1–6** from the respective "enium" ions and trimethylphosphane or trimethylamine (Scheme 5). The results of this comparison for a temperature of 298.15 K and a pressure of 1.00 bar are summarized in Table 3. The adduct formation with respect to "enium" ion and donor is exergonic in all cases. For the phosphane adducts the ΔG_f values are generally more negative, i.e. the stabilization on adduct formation is larger, than for the corresponding amine adducts. For a given substituent the energy released on adduct formation is largest for the selenenium ion, decreases for the phosphenium ion and is smallest for the arsenium ion.

The nature of the substituent adjacent to the "enium" ion has a significant influence on the enthalpy of formation. While for the all-methyl substituted adducts of the phosphenium and arsenium ion the preference of the phosphane adduct is about 10 kcal/mol, attachment of the π-donating amino substituent lowers this difference to 4–5 kcal/mol. Generally the ΔG_f values compiled in Table 3 reflect the donor–acceptor interaction plus other contributions such as geometric reorganization on adduct formation. Since an NH_2 and a CH_3 are isoelectronic units, the energy contribution for reorganization will be however very similar. Therefore the lower ΔG_f values for the amino substituted ions **4–6** relative to their methyl substituted counterparts **1–3** should mainly reflect the donor–acceptor interaction. Accordingly, the lower values found for the amino substituted ions indicate that the central donor–acceptor interaction is weakened by the amino substituent and therefore the nature of the donor becomes less relevant.



Scheme 5. Formation adducts **1–6a,b** from "enium" ions and donor (E = P, N; X = CH_3, NH_2, A = P, As, Se).

Table 3
ΔG_f values (kcal/mol) of the formation of adducts **1–6** according to Scheme 5 calculated at DFT level using a 6-311G(d) basis set and corrected for 298.15 K and 1 bar

	X	PMe_3-adduct		NMe_3-adduct	
		ΔG_f (kcal/mol)		ΔG_f (kcal/mol)	
E = P	CH_3	−61.3	**1a**	−51.3	**1b**
	NH_2	−33.2	**4a**	−29.0	**4b**
E = As	CH_3	−57.4	**2a**	−47.0	**2b**
	NH_2	−32.2	**5a**	−27.3	**5b**
E = Se	CH_3	−108.9	**3a**	−83.8	**3b**
	NH_2	−67.9	**6a**	−50.7	**6b**

2.3. Charge distribution

An interesting detail of the bond situation in **1–6** is the charge distribution within these cations. The natural charges for each atom in adducts (**1–6a,b**) have been calculated using NPA at DFT and MP2 level. Charges obtained by Mulliken population analysis at HF, DFT and MP2 levels of theory have also been computed and show similar trends but are not discussed here. Moreover, Wiberg bond indices (WBI) have been computed as a formal measure of bond order [40]. A comparison of the NPA values (DFT, MP2) for phosphenium ions (**1a,b**) and (**4a,b**) is summarized in Table 4.

In the phosphane adduct of the alkyl substituted phosphenium ion (**1a**) the positive charge at the electron accepting phosphorus atom is only half as much as in the free phosphenium ion. The positive charge at the donating phosphorus atom in **1a** is in turn substantially increased compared to the free PMe_3 in which the phosphorus atom shows a natural charge of 0.76 at DFT level (0.78 at MP2). In the corresponding amine adduct (**1b**) the positive charge at the electron accepting phosphorus atom is also lowered,

Table 4
Calculated NBO charges of selected atoms in **1a,b** and **4a,b** at different levels of theory as indicated using a 6-311G(d) basis set

	E_{Don}	P_{Acc}	P_{Cat}	PCH_3[a]	PNH_2[a]	WBI
1a E = P						
B3LYP	1.16	0.62	1.20	−0.19	–	0.909
MP2	1.20	0.62	1.33	−0.20	–	0.867
1b E = N						
B3LYP	−0.52	1.01	1.20	−0.20	–	0.580
MP2	−0.51	1.03	1.33	−0.21	–	0.544
4a E = P						
B3LYP	1.12	0.84	1.28	−0.20	−0.34	0.823
MP2	1.17	0.84	1.28	−0.22	−0.35	0.807
4b E = N						
B3LYP	−0.52	1.17	1.28	−0.21	−0.31	0.486
MP2	−0.51	1.19	1.28	−0.22	−0.32	0.470

[a] Charges of hydrogen atoms summed into heavy atoms.

however much less than in phosphane adduct **1a**. The charge at the formally donating nitrogen atom is slightly more negative than in the uncomplexed NMe_3 in which the nitrogen atom shows a natural charge of −0.50 at DFT and MP2 level. Replacing one of the methyl groups at the formal phosphenium center in **1a,b** by a π-donating amino group increases the positive charge at the phosphenium center and slightly reduces the charge at the donating phosphorus atom in **4a** while the charge at nitrogen of the amine donor in **4b** remains unchanged. Throughout this series the charges at the carbon atoms adjacent to the phosphenium centers remain almost unaffected by changing the donor or the geminal substituent.

Similar trends can be observed for the analogous adducts of arsenium ions (Table 5). Again the positive charge at the arsenic atom is lowest for the alkyl substituted phosphane adduct **2a** and shows a value which is ca. 50% of that in the free arsenium ion. Switching to an amine donor as in **2b** increases the positive charge at As to roughly 80% of that in the free arsenium ion. Replacing one methyl group at the arsenium center with an amino group also increases the charge at As in phosphane adduct **5a** to somewhat more than 60% of that in the corresponding free arsenium ion. Consequently the charge at the arsenic atom is highest for the amine adduct of the amino-substituted arsenium ion (**5b**) in which the charge at As amounts to roughly 90% of the free arsenium ion.

For the adducts of formal selenenium ions with trimethylphosphane (**3a**) the charge at Se is reduced to less than 20% compared to the free selenenium ion (Table 6). The charge at the phosphorus atom in turn is increased to the highest values found in this series of compounds. Also the NMe_3 donor substantially reduces the positive charge at the Se atom (**3b**), however far less than the PMe_3 donor (**3a**). Interestingly, the charge at the nitrogen atom in **3b** and **6b** is slightly more positive than in free NMe_3. Replacement of the methyl group at selenium with an amino group roughly doubles the positive charge to a third of that of the uncomplexed cation (**6a**). Again the positive charge at Se is highest for the amino substituted and amine stabilized cation **6b**.

Table 5
Calculated NBO charges of selected atoms in **2a,b** and **5a,b** at different levels of theory as indicated using a 6-311G(d) basis set

	E_{Don}	As_{Acc}	As_{Cat}	$AsCH_3$[a]	$AsNH_2$[a]	WBI
2a E = P						
B3LYP	1.14	0.68	1.36	−0.20	–	0.874
MP2	1.18	0.69	1.41	−0.21	–	0.833
2b E = N						
B3LYP	−0.52	1.07	1.36	−0.22	–	0.532
MP2	−0.51	1.09	1.41	−0.23	–	0.495
5a E = P						
B3LYP	1.11	0.89	1.34	−0.21	−0.36	0.810
MP2	1.16	0.89	1.34	−0.23	−0.37	0.787
5b E = N						
B3LYP	−0.52	1.23	1.34	−0.22	−0.34	0.453
MP2	−0.51	1.26	1.34	−0.24	−0.36	0.437

[a] Charges of hydrogen atoms summed into heavy atoms.

Table 6
Calculated NBO charges of selected atoms in **3a,b** and **6a,b** at different levels of theory as indicated using a 6-311G(d) basis set

	E_{Don}	Se_{Acc}	Se_{Cat}	$SeCH_3$[a]	$SeNH_2$[a]	WBI
3a E = P						
B3LYP	1.27	0.16	0.91	−0.04	–	1.025
MP2	1.31	0.16	0.90	−0.05	–	0.964
3b E = N						
B3LYP	−0.45	0.55	0.91	−0.06	–	0.701
MP2	−0.44	0.57	0.90	−0.07	–	0.648
6a E = P						
B3LYP	1.27	0.34	0.92	–	−0.22	0.976
MP2	1.32	0.33	0.85	–	−0.23	0.929
6b E = N						
B3LYP	−0.45	0.73	0.92	–	−0.19	0.586
MP2	−0.44	0.75	0.85	–	−0.21	0.562

[a] Charges of hydrogen atoms summed into heavy atoms.

In summary, electron transfer from the donor to the "enium" centers in this series is strongest for phosphane donors towards $^{+}Se–R$. Somewhat reduced but still substantial is the electron transfer from PMe_3 to $^{+}AsR_2$ and $^{+}PR_2$. Generally, amino substitution increases the charge at the formal "enium" center and marginally lowers the charge at the phosphane donor. When acting as a donor the charge of the phosphorus atom in PMe_3 increases dramatically, however the charge of the nitrogen atom in NMe_3 remains almost unaffected. In line with this the Wiberg bond indices for the central bond are in the range 0.8–1.0 for the phosphane adducts while they are much lower for the corresponding amine adducts (0.4–0.7). The charge distribution alone would suggest a description as phosphonium ions rather than as stabilized "enium" ions in phosphane adducts **1–6a**. Generally, the values obtained with the MP2 method are slightly higher than those obtained with B3LYP.

2.4. Cleavage of the A–D bond

Earlier, Haaland established a formalism to categorize a bond as either dative or covalent [32]. To classify the donor–acceptor bond in (**1–6a,b**) according to these categories we analyzed the reaction energies of homolytic and heterolytic cleavage of this bond (Scheme 6). The results of the corresponding calculations relative to path 1 are summarized in Tables 7 and 8.

Interestingly, heterolytic cleavage of the P–P bond in **1a** according to the description as phosphane adduct of a phosphenium ion is not the energetically favored pathway. The energetically most favored fission process is the homolytic cleavage of the P–P bond in **1a**. According to Haalands criteria this means in turn, that the P–P bond in **1a** is not a dative bond but a "normal" covalent bond, which corrob-

Table 7
Calculated relative energies for the different cleavage pathways of the donor acceptor bond in the methyl substituted ions **(1–3a,b)** in kcal/mol using a 6-311G(d) basis set at the level as indicated

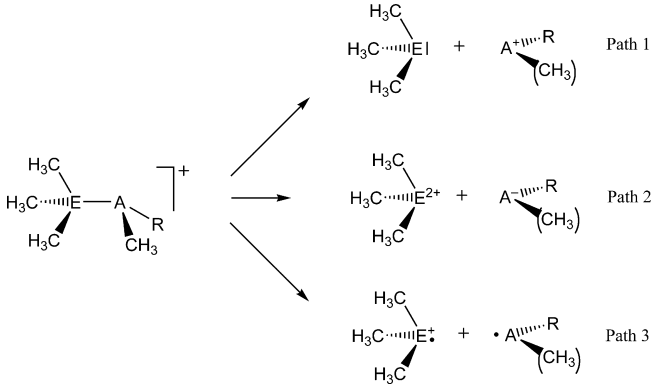
	1 (A = P)		**2** (A = As)		**3** (A = Se)	
	Path 2	Path 3	Path 2	Path 3	Path 2	Path 3
a (E = P)						
HF	314.5	−22.3	318.2	−18.8	235.6	−72.4
B3LYP	306.9	−6.3	311.0	−3.5	231.8	−54.6
MP2	312.2	−6.7	313.3	−5.4	232.8	−56.6
b (E = N)						
HF	361.1	−29.2	364.8	−25.7	282.2	−79.3
B3LYP	340.2	−10.5	344.3	−7.7	265.1	−58.8
MP2	355.0	−4.0	356.0	−2.7	275.5	−53.8

Path 1 was arbitrarily set to 0 in all cases.

Table 8
Calculated relative energies for the different cleavage pathways of the donor acceptor bond in the amino substituted ions (**4–6a,b**) in kcal/mol using a 6-311G(d) basis set at the level as indicated

	4 (A = P)		**5** (A = As)		**6** (A = Se)	
	Path 2	Path 3	Path 2	Path 3	Path 2	Path 3
a (E = P)						
HF	350.2	9.3	343.9	5.9	277.5	−38.4
B3LYP	344.7	25.1	341.2	23.3	280.1	−19.5
MP2	354.5	29.3	347.3	25.5	287.9	−14.0
b (E = N)						
HF	396.8	2.4	390.5	−1.0	324.1	−45.3
B3LYP	378.0	20.9	374.5	19.1	313.4	−23.7
MP2	397.2	32.1	390.0	28.2	330.7	−11.2

Path 1 was arbitrarily set to 0 in all cases.



Scheme 6. Hypothetic cleavage reactions of the donor bond in (**1a,b**) and (**4a,b**) (A = P) (**2a,b**) and (**5a,b**) (A = As), and (**3a,b**) and (**6a,b**) (*A* = Se) (E = P, N; R = CH_3, NH_2).

orates the description as phosphanylphosphonium ion rather than as donor stabilized phosphenium ion. For the amine adduct **1b** the situation is basically the same. Homolytic cleavage is favored over heterolytic cleavage which makes the central N–P bond preferentially covalent rather than dative. This picture changes however completely on attachment of a π-donating amino group at the phosphenium ion (**4a,b**). This substituent stabilizes the adjacent cationic center to an extent which makes the heterolytic cleavage according to path 1 the energetically most favored pathway for both amine and phosphane adducts. Therefore a description of donor adducts of π-donor substituted phosphenium ions with dative bonds appears appropriate.

For formal adducts of arsenium ions the situation is very similar. In the adducts of the methyl substituted arsenium ion **2a,b** the central N–As or P–As bond is mainly covalent, while replacing one methyl group at arsenic with an amino group increases the dative character of the bond (**5a,b**). For the amino substituted amine adduct **5b** this is however only recognized if electron correlation is included.

In contrast, a different situation is found for formal donor adducts of selenenium ions. Here for methyl (**3a,b**) and amino (**6a,b**) substituted cations the energetically most favored fission process is the homolytic cleavage of the P–Se bond. Interestingly, the heterolytic cleavage of the P–Se bond in **3** and **6** according to the formal electronegativity difference is the energetically least favored pathway. According to Haalands criteria this means, that the P–Se bond in these cations is not a dative bond but a "normal" covalent bond, which corroborates the description as selenenylphosphonium ion rather than as donor stabilized selenenium ion. Again amino substitution lowers the preference of the homolytic cleavage pathway by *ca.* 40 kcal/mol. However this is insufficient to change the character of the central bond in **6** from covalent to dative.

3. Conclusion

Based on geometric parameters, charge distribution and the Haaland formalism the conclusion appears justified that the bond situation of the formal amine and phosphane adducts of phosphenium, arsenium and selenenium ions is rather covalent than dative for the methyl substituted systems. In contrast, for amino substituted phosphenium and arsenium ions the π-donating substituent imparts predominantly dative character to the central bond and therefore justifies the term donor–acceptor bond. Consequently, π-donor substitution at the "enium" ion seems to be a precondition for reversible adduct formation and not only for the practical reason that the starting "enium" ion is generated more easily. Interestingly, the so far structurally characterized adducts of arsenium and phosphenium ions are all π-donor substituted ones. Moreover we found, that a phosphane donor is better capable of stabilizing the investigated "enium" ions than an amine donor based on the ΔG_f values of these adducts. Immediate conclusions from our results to real donor stabilized "enium" ions might however be limited by solvation effects, which have not been included in this study.

4. Computational details

Quantum chemical calculations were carried out using the GAUSSIAN03 suite of programs [31], employing a 6-311G(d)

basis set [41–44] on Hartree–Fock, MP2 and DFT(B3LYP) level [45,46]. All reported geometries have been optimized starting from C1 symmetry on HF, MP2 and B3LYP level. Stationary points were confirmed as minima on the potential surface by second-derivative calculations. The reported ΔG_f values of adducts **1**–**6** have been calculated at DFT level using a 6-311G(d) basis set and were corrected for 298.15 K and 1 bar. Energy values of homo- and heterolytic cleavage reactions refer to the optimized fragments on HF, MP2 and B3LYP level with a 6-311G(d) basis set. For the radical species involved in the homolytic cleavage the magnitude of the spin contaminations in the UHF, UMP2 and UB3LYP wave functions has been assessed by comparison of the computed $\langle S^2 \rangle$ values with $S(S+1)$. These values differ by 0.3–0.6% on UB3LYP level and 0.7–2.3% with UHF/UMP2. Therefore our results indicate that spin contamination is negligible in this case. Population analyses were performed on the optimized structures at B3LYP and MP2 level (both with 6-311G(d) basis set) using the natural bond order (NBO) method implemented in GAUSSIAN03.

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Appendix A. Supporting Information

For compounds **1–6a,b** output summaries including complete data of harmonic vibrational frequencies at B3LYP level (6-311G(d) basis set); optimized geometries, total energies (*E*, in hartree) have been provided as supplementary material.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.03.045.

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