N-Heterocyclic Phosphenium, Arsenium, and Stibenium Ions as Ligands in Transition Metal Complexes: A Comparative Experimental and Computational Study

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Dedicated to Professor Gerd Becker on the Occasion of his 65th Birthday

Abstract. Reaction of 2-chloro-1,3,2-diazaarsolenes and -diazaphospholenes with Tl[Co(CO)$_4$] gives instable complexes of type [Co(ER$_2$)(CO)$_4$] which decarbonylated to yield [Co(ER$_2$)(CO)$_3$]. Spectroscopic and X-ray diffraction studies revealed that the tetracarbonyl complexes can be formulated as ion pair for E = P and as covalent metalla-arsine for E = As, and the tricarbonyl complexes as carbene-like species with a formal E=Co double bond. A similar reactivity towards Tl[Co(CO)$_4$] was also inferred for 1,3,2-diazastibolenes although the products were not isolable and their constitution remained uncertain. Evaluation of structural and computational data suggests that the weak and polarized Co−As bond in [Co(AsR$_2$)(CO)$_4$] can be characterized as an "inverse" M→L donor-acceptor bond. The computational studies disclosed further η^2(EN)-coordination of the EN$_2$C$_2$ heterocycle as an alternative to the formation of a carbene-like structure for [Co(ER$_2$)(CO)$_3$]. The η^2-complex is less stable for E = P but close in energy for E = As and more stable than the carbene-like complex for E = Sb.

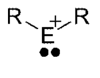
Keywords: Carbene analogues; Phosphenium complexes; Arsenium complexes; π-Acceptor ligands; Metal-ligand multiple bonding

Introduction

Phosphenium cations (**I**, E = P) have since their discovery some thirty years ago constantly remained in the focus of research [1]. A great deal of the interest in these species was − and still is − initiated by their ability to act as σ-donor/π-acceptor ligands in transition metal complexes **II** (E = P) with similar molecular and electronic structures as Fischer-carbene complexes [1, 2], and to stabilize electrophilic complexes with late metal atoms [3].

Stable cations with heavier dicoordinate group-15 elements such as arsenic (**I**, E = As [4−7]), antimony (**I**, E = Sb [8]), and bismuth (**I**, E = Bi [8]) have likewise been prepared, but coordination chemical studies involving these species are largely confined to the formation of complexes with Lewis bases [5, 9−11]. Well characterized carbene-analogue transition metal complexes **II** (E = As, Sb) with formal double bonds to As and Sb are as yet unknown, even if complexes [CpMo(CO)$_2$=EMe$_2$] (E = As, Sb) were identified by matrix isolation techniques [12], and metalla-arsine and -stibine complexes with pyramidal coordination at the pnicogen atom and formal M-E single bonds have been described [13, 14].

We have recently reported on the synthesis of stable *N*-heterocyclic arsenium and stibenium cations **III** (E = As, Sb) [15, 16]. Knowing that the corresponding phosphenium analogues (**III**, E = P) form transition metal complexes (**IV**, E = P) that are stabilized by a high degree of metal-phosphorus double bonding [17], we conceived that extension of this chemistry to ligands with heavier group 15 elements might allow to access as yet unprecedented stable arsenium and stibenium complexes. In this work we report on the generation of 1,3,2-diazaphospholenium, -arsolenium, and -stibolenium complexes **IV** (E = P, As, Sb; M = Co(CO)$_3$), the first structural characterization of an arsenium complex **IV** and a precursor **V** where the metal-ligand interaction is best described as "inverse" dative bond involving M→L charge transfer, and on computational studies aiming at a comparison of the ligand properties of the phosphenium, arsenium, and stibenium ligands in the complexes **IV** and **V**, respectively.



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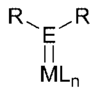

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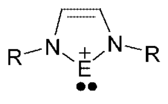

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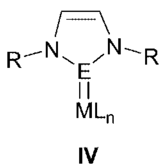

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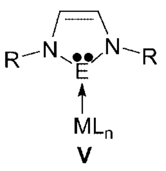

V

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Results and Discussion

Complex syntheses

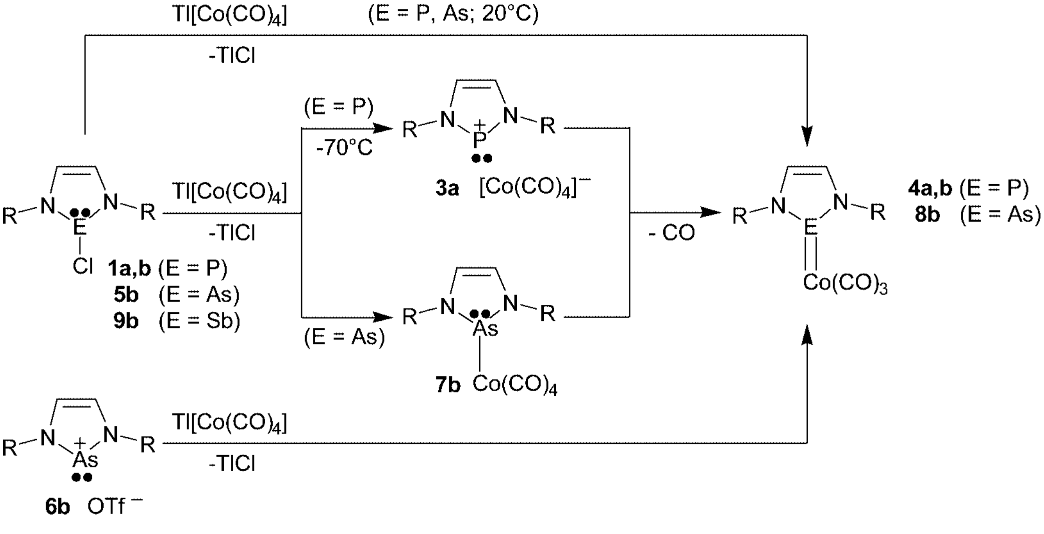
Although earlier work by *Nakazawa* et al. demonstrated the use of strongly back-donating 16 valence electron [M(CO)$_3$(bipy)] fragments (M = Mo, W; bipy = 2,2′-bipyridine) for a highly efficient stabilization of phosphenium complexes [2, 18], we have previously established that *N*-tBu substituted 1,3,2-diazaphospholenes fail to react with [W(CO)$_3$(bipy)(MeCN)], presumably because of sterical reasons [17]. The desired 1,3,2-diazaphospholenium complexes were, however, easily accessible when *N*-aryl substituted diazaphospholene precursors were used [17]. Surprisingly, neither *N*-tBu nor *N*-aryl substituted 2-chloro-1,3,2-diazaarsolenes or −stibolenes nor the corresponding cations reacted with [M(CO)$_3$(bipy)(MeCN)]. Similar negative results were observed when other neutral transition metal complexes such as [W(CO)$_5$(C$_8$H$_{14}$)] or [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] were employed. Facing this general failure to prepare complexes of the As- and Sb-centered cations with neutral metal fragments, we turned to reactions with metal carbonylate anions, anticipating that enhanced electrostatic attraction between the reactants might provide an additional driving force for complex formation. To this end, the reactions of the 2-chloro-substituted heterocycles **1, 5, 9** (scheme 2) with Tl[Co(CO)$_4$] were studied.

Reaction of equimolar amounts of the solid *P*-chlorodiazaphospholene **1a** and Tl[Co(CO)$_4$] in CH$_2$Cl$_2$ at −70 °C and slow warming to ambient temperature produced solid TlCl and a red solution which was stable for a short time before decomposing under evolution of CO. As the ^{31}P{^{1}H} NMR spectrum of the initial solution displayed the signal of the cation **2a** formed by loss of chloride from **1a** [19], and both IR (ν(CO) at 1889 cm^{-1}) and ^{59}Co NMR spectra (sharp signal at δ^{59}Co −2979) revealed the presence of [Co(CO)$_4$]$^-$ [20], the initial product was formulated as ionic 1,3,2-diazaphospholenium cobaltate **3a**. Considering the absence of any broadening of the ^{59}Co NMR line or splitting of the single IR-active F$_2$ ν(CO) mode, the spectral data point to a very low degree of intermolecular interaction which might perturb the local T$_d$ symmetry in the anion [20]. This suggests that the solution structure of **3a** is presumably best described as a solvent separated ion pair.

The cleavage of CO from **3a** was accompanied by the appearance of a new ^{31}P NMR signal at lower field (δ^{31}P 234.7) and two new IR bands at 2015 and 1948 cm^{-1}. These data suggest conversion of **3a** into a single product which was formulated as the carbene-analogue tricarbonyl complex **4a**. Direct formation of **4a** was observed when **1a** and Tl[Co(CO)$_4$] were reacted at ambient temperature in toluene, and treatment of **1b** with Tl[Co(CO)$_4$] under the same conditions yielded the analogous complex **4b**. Both **4a,b** were isolated as red, slightly air and moisture sensitive crystalline solids and their constitution was confirmed by analytical and spectroscopic data and single-crystal X-ray diffraction studies.

The reaction of Tl[Co(CO)$_4$] with the 2-chloro-1,3,2-diazaarsolene **5b** at room temperature in MeCN proceeded, in the same way as with **1a**, via elimination of TlCl and formation of a red solution which decomposed slowly under evolution of CO if stored for prolonged time above −30 °C. In contrast to the reaction of **1a**, crystallization at −25 °C allowed to isolate a moderate yield of the initial product. Since the reaction occurred without liberation of CO and the IR spectrum displayed a pattern of three ν(CO) bands ($\bar{\nu}$ = 2004, 1934, 1928 cm^{-1}) which is in accord with an assignment to the three IR-active modes (2 a$_1$ + e) of a complex [Co(CO)$_4$(L)] having local C$_{3v}$ symmetry, the product was formulated as the metalla-1,3,2-diazaarsolene **7b**. The marked deviation of the IR data of **7b** from those of [Co(CO)$_4$]$^-$ suggest that, unlike as in **3a**, a substantial covalent interaction between As and Co is present. This proposal was confirmed by a single-crystal X-ray diffraction study of **7b**.

In solution, **7b** decarbonylated easily to afford the carbene-analogue complex **8b** which was identified by spectro-



Scheme 2 (R = tBu (**1a**, **3a**, **4b**), Mes (**1b**, **4b-9b**)).

scopic data and a single-crystal X-ray diffraction study. The same species was also identified by ^{1}H NMR and IR studies as product of the reaction of Tl[Co(CO)$_4$] with the diazaarsolenium triflate **6b** [16]. The most significant spectral data comprise the blue shift for the ν(CO) bands ($\tilde{\nu}$ = 2023, 1964 cm^{-1}) with respect to **4b** ($\tilde{\nu}$ = 2015, 1945 cm^{-1}).

Finally, reaction of Tl[Co(CO)$_4$] with the 2-chloro-1,3,2-diazastibolene **9b** in d$_8$-toluene or hexane at −78 °C afforded a precipitate of TlCl and a red solution whose color first faded and then turned black when the solution was warmed to room temperature. Although no isolable product was obtained, ^{1}H NMR spectra disclosed formation of a transient species which decayed rapidly to afford a diazadiene, (MesN=CH-)$_2$, and further unidentifiable products. IR spectra showed two strong ($\tilde{\nu}$ = 2062, 1977 cm^{-1}) and two further weak ν(CO) bands ($\tilde{\nu}$ = 2002, 1942 cm^{-1}) attributable to transient products. By analogy to the reactions of **1a,b** and **5b**, we interpret the available data in terms of the presence of a mixture of a tetracarbonyl complex (minor product) and a tricarbonyl complex (major product) which undergo dynamic exchange via CO-transfer on the NMR time scale (thus explaining the presence of a single set of signals) but are distinguishable on the IR time scale. Evidence for a similar dynamic equilibrium between the As-complexes **7b** and **8b** was provided by line broadening and coalescence effects in the ^{1}H NMR spectra of solutions of partially decarbonylated **7b**.

Crystal structure studies. The molecular structures of the 1,3,2-diazaarsolene complexes **7b** and **8b** are displayed in Figures 1 and 2, respectively. The molecular structures of the diazaphospholenium complexes **4a,b** are very similar to the latter and are not shown. All crystals consist of isolated mononuclear complexes that exhibit no significant intermolecular interactions. Selected bond distances and angles for all four complexes are listed in Table 1.[1]

The phosphenium complexes **4a,b** crystallize in the space group P2$_1$/n and P2$_1$/c, respectively. The phosphorus and cobalt atoms have distorted trigonal planar and tetrahedral coordination, respectively. The Co−P bond in **4a** is slightly longer than in **4b** (2.0450(5) vs. 2.0018(4) Å), reflecting presumably the larger steric bulk of *N*-tBu as compared to *N*-Mes groups and a concomitantly increased steric congestion between the phosphenium fragment and the ancillary CO ligands. Both bond lengths deviate not significantly from those in the known complexes [(CO)$_3$Co=P(O-C$_6$H$_2$tBu$_3$)(Cp*)] (Co−P 2.010(19) Å [21]) and [(CO)$_3$Co=P(O-C$_6$H$_2$tBu$_3$)(C$_2$(Ph)Co$_2$(CO)$_6$)] (Co−P 2.009(3) Å [22]) and suggest that the metal-ligand interaction may be described as in other neutral phosphenium complexes [1, 2] as a formal double bond. The remaining bond distances and angles in **4a,b** (apart from those in *N*-tBu and *N*-Mes substituents) differ not significantly. The P−N and N−C bonds in the diazaphospholene rings are slightly longer and the C=C bonds shorter than in the cation **2a** (P−N 1.658 − 1.665 Å, N−C 1.368 − 1.377 Å, C=C 1.341 − 1.353 Å [19]). Although these deviations are small (approx. 2 pm for P−N and 1 pm for N−C and C=C bonds), their direction and magnitude matches the complexation induced changes in bond lengths in cationic diazaphospholenium tungsten complexes [17] and may in line with the generally acknowledged model of bonding in aminophosphenium complexes [2] be interpreted by assuming that the strong M-P π-interaction introduces a massive reduction in cyclic intraligand π-delocalization.

Table 1 Selected bond distances (in Å) and angles (in °) for the complexes **4a,b**, **7b**, and **8b**. The numbering scheme for all three compounds is identical to the one used in Figures 1 and 2.

	4a	**4b**	**7b**	**8b**
Co(1)-P(1)/As(1)	2.0450(5)	2.0018(4)	2.7263(4)	2.129(1)
Co(1)-C(1A)	1.760(2)	1.784(2)	1.789(3)	1.777(1)
Co(1)-C(1B)	1.772(2)	1.773(2)	1.790(3)	1.774(4)
Co(1)-C(1C)	1.775(2)	1.781(2)	1.796(3)	1.774(4)
Co(1)-C(1D)			1.822(3)	
P(1)/As(1)-N(2)	1.6835(14)	1.6720(12)	1.846(2)	1.811(2)
P(1)/As(1)-N(5)	1.6838(13)	1.6733(13)	1.835(2)	1.807(3)
N(2)-C(3)	1.387(2)	1.391(2)	1.394(3)	1.381(4)
C(3)-C(4)	1.330(2)	1.332(2)	1.330(3)	1.355(5)
C(4)-N(5)	1.388(2)	1.394(2)	1.396(3)	1.381(4)
N(5)-As(1)/P(1)-N(2)	90.33(7)	89.17(6)	85.40(8)	85.5(1)
N(5)-As(1)/(P(1)-Co(1)	135.10(5)	133.83(5)	111.59(6)	141.6(1)
N(2)-As(1)/P(1)-Co(1)	134.50(5)	136.59(5)	103.15(6)	132.9(1)
Σ_{angles}(P1/As1)	359.9(2)	359.6(2)	300.1(2)	360.0(3)

The crystals of the metalla-arsine **7b** (space group P$\bar{1}$) are composed of molecular complexes with a central cobalt atom in a distorted trigonal bipyramidal coordination sphere (Fig. 1). All equatorial and one axial coordination sites are occupied by carbonyl groups and the second axial site by the As-atom of the diazaarsolene unit. The equatorial Co−C bonds are equal and by approx. 4 pm shorter

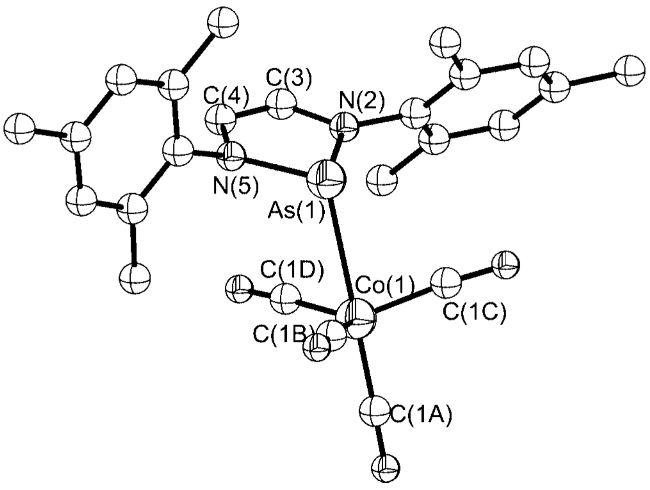


Fig. 1 Molecular structure of **7b**. Thermal ellipsoids are drawn at 50 % probability level, and H atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 1.

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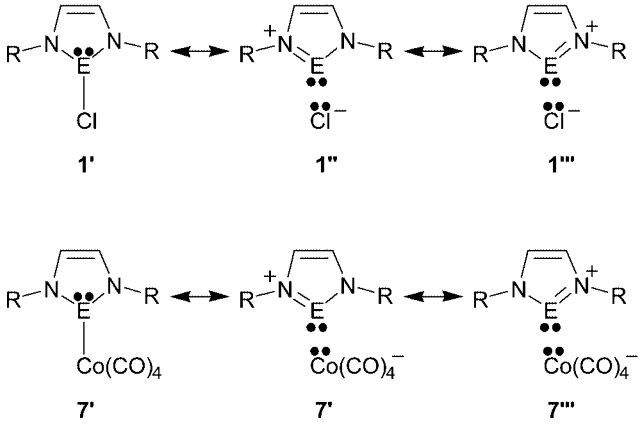
[1] In order to facilitate the discussion of structural features, we applied a universal numbering scheme for all compounds which is in some cases different from the one used in the cif-files.

than the axial one; all Co$-$C bonds are longer than in $[Co(CO)_4]^-$ (avg. distance in known tetracarbonyl cobaltates 1.75(4) pm [23]) but similar as in metalla-germanes of the type $[R_3Ge-Co(CO)_4]$ or $[R_2Ge(Co(CO)_4)_2]$, respectively [24, 25]. A most remarkable feature of **7b** is the extremely long Co$-$As bond (2.7264(4) Å) whose distance substantially exceeds those in cobalt complexes of tertiary arsines (As$-$Co 2.33(4) Å [23]) or cobalta-arsines $[L_nCo-AsR_2]$ (Co$-$As 2.39(3) Å [23]). The As(1) atom exhibits a pyramidal coordination geometry (sum of bond angles 300°) and the diazaarsolene ring is not exactly planar as in **4a** [16] but exhibits a very flat envelope conformation similar to that in the *P*-chloro-diazaphospholene **1a** [19]. The endocyclic As$-$N (avg. 1.840(2) Å) and C$-$N bonds (avg. 1.395(2) Å) are longer and the C=C bond (1.330(3) Å) is shorter than in the cation **6b** (avg. distances: As$-$N 1.832(2), C$-$N 1.349(2), C=C 1.362 Å [16]), thus indicating a higher π-bond localization [16, 19] in **7b**.

If one considers all structural features, the bonding situation in **7b** resembles that in 2-chloro-diazaphospholenes **1**. The unique P$-$Cl bond lengthening in these compounds was attributed to ionic bond polarization ($P^{\delta+}-Cl^{\delta-}$) and lead to a description as donor/acceptor complexes of a diazaphospholenium cation and a chloride anion [19]. The polarization may be rationalized in the VB picture by assuming that the high cation stability of a diazaphospholenium fragment stabilizes the ionic canonical structures **1″**, **1‴** (scheme 3) relative to the covalent structure **1′** and thus emphasizes ionic bonding contributions and charge transfer to the chlorine atom. Adapting this picture suggests that the bonding in **7b** can be likewise described by bond/no-bond resonance between the canonical structures **7′** $-$ **7‴**. Assuming that the observed bond lengthening points as in the case of **1** to a considerable contribution by the ionic structures, the Co$-$As bond adopts substantial character of an "inverse" donor-acceptor bond involving charge transfer from cobalt atom into the empty p(As)-orbital of a diazaarsolenium cation.



Scheme 3

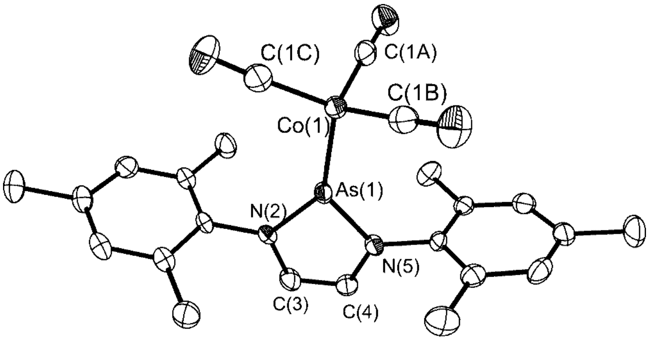


Fig. 2 Molecular structure of **8b**. Thermal ellipsoids are drawn at 50 % probability level, and H atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 1.

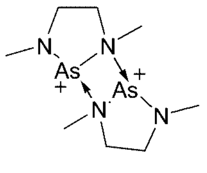
Crystals of the arsenium complex **8b** (space group $P2_1/c$) contain molecules (Fig. 2) with similar structural features as the lighter congeners. Apart from the As$-$Co and As$-$N bond lengthening and the decrease of the N$-$As$-$N angle which reflect the larger atomic radius of an arsenic as compared to a phosphorus atom, all bond distances in the EN_2C_2-rings (E = P, As) and $Co(CO)_3$ moieties of **8b** and **4b** are equal within experimental error, and all atoms in the AsN_2C_2 ring of **8b** still display planar coordination (sum of angles 360°). The As$-$Co bond in **8b** (2.129(1) Å) is by 36 pm (11 %) shorter than the average single bond in $[L_nCo-AsR_2]$ (2.39(3) Å [23]), and by 60 pm (22 %) shorter than the unusually long bond in **7b**. Evaluation of further structural variations in the diazaarsolene units of **8b** and **7b** reveals a small but distinguishable shortening of As$-$N bonds in the former by approx. 3 pm whereas shifts in C$-$N and C=C distances are not considered significant.

All features suggest clearly that the bonding between the cobalt and arsenic atoms in **8b** may be described as in phosphenium complexes [1, 2, 17] as a formal double bond resulting from superposition of a dative L→M σ-bonding and a retro-dative M→L π-bonding interaction between a 16VE $Co(CO)_3^-$ and a diazaarsolenium fragment. The shortening of the As$-$N bonds in **8b** with respect to **7b** suggests that as in diazaphospholenium complexes [17] residual intraligand π-delocalization may contribute to stabilize the positive charge on the As-atom.

Although the formation of dative/retro-dative double bonds has precedence in phosphenium complexes, the molecular structures of the dimeric dication **10** [26] and the complex **11** [13] (Scheme 4) suggest that the lone-pair of an adjacent sulfur or nitrogen atom may provide a more favorable donor site for interaction of an arsenium moiety with a Lewis acid than the lone-pair at arsenic atom. In consideration of these results it cannot be ruled out that the preference for a carbene-analogue structure for **8b** is largely determined by the steric influence of the *N*-aryl substituents which renders the nitrogen lone-pairs inaccessible for attack by a Lewis acid.

Computational studies

In order to permit a profound discussion of structure and bonding in *N*-heterocyclic phosphenium, arsenium, and sti-



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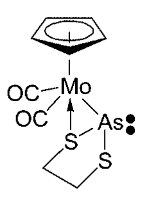

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benium complexes, computational studies were carried out. To cut down computation times, model compounds carrying *N*-H substituents were used and interaction between ionic species with counter-ions or solvent molecules were neglected. Molecular structures of all compounds were obtained from energy optimizations, using the B3LYP density functional method [27] employed in the GAUSSIAN 98 suite [28] with sdd basis sets augmented by one set of polarization functions at all heavy atoms. The final structures of the metalla-diazaphospholene **3c**, -arsolene **7c** and -stibolene **13c** are displayed in Fig. 3, and those of the carbene-analogue complexes **4c**, **8c**, **14c** and their isomers **4′c**, **8′c**, **14′c** with η^2-bound heterocyclic ligands in Fig. 4. All structures shown represent according to vibrational analyses local minima on the energy hypersurface. Selected bond distances of the complexes and the free cations **2c**, **6c**, and **12c** are listed in Table 2 and results of NBO population analyses [29] in Table 3.

The computed bond lengths of **4c** and **7c** (Tab. 2) are, regardless of the simplified structures of the model compounds, in close agreement with the experimental data of **4a,b** and **7b** (Tab. 1); the only notable discrepancy comprises the overestimation of the Co−As distance in **7c**. We attribute this deviation to the neglect of inductive substituent effects in the model compounds and the inappropri-

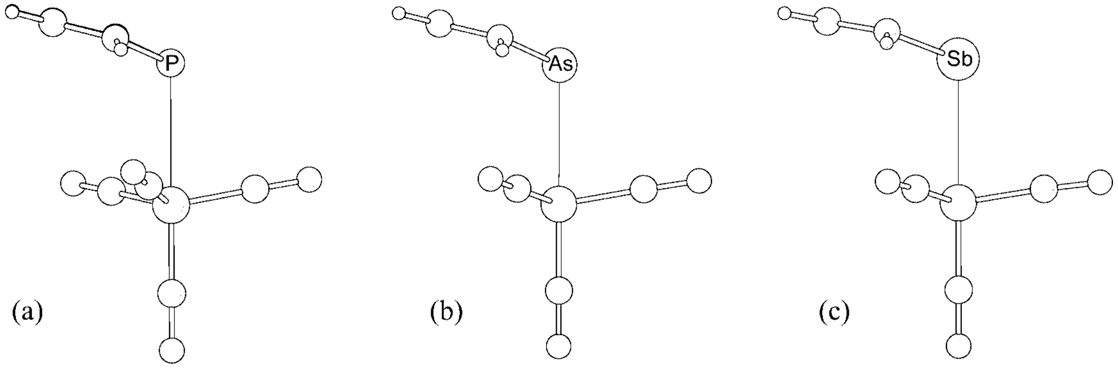


Fig. 3 Representation of the computed molecular structures of the tetracarbonyl complexes **3c** (a), **7c** (b), and **13c** (c). Selected bond lengths and angles are listed in Table 2.

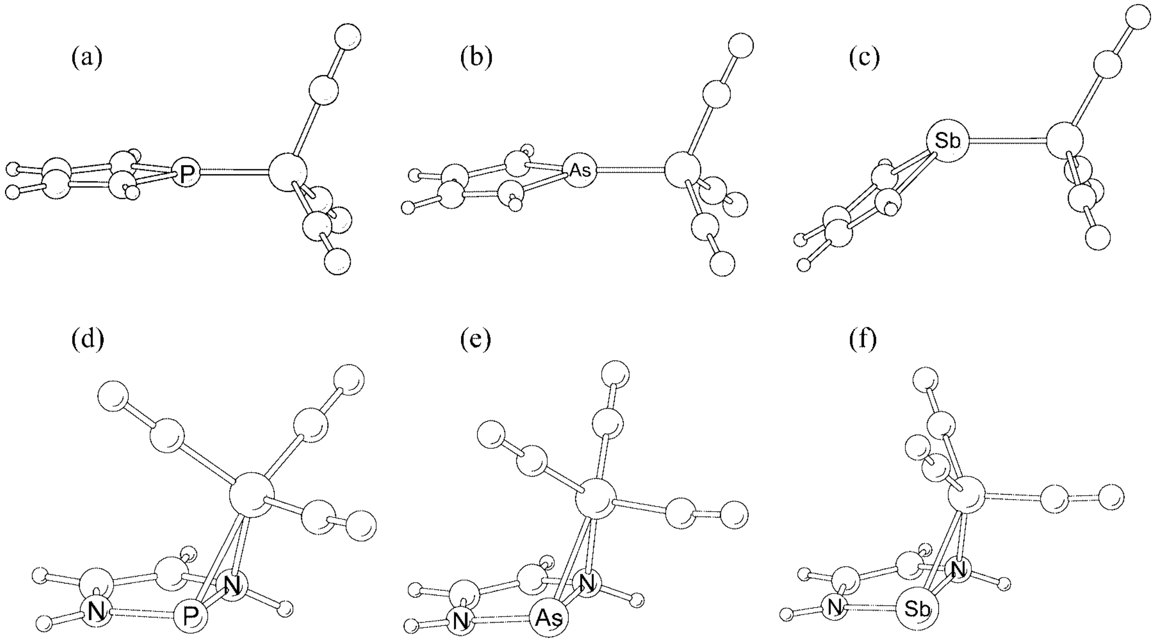


Fig. 4 Representation of the computed molecular structures of the tricarbonyl complexes **4c** (a), **8c** (b), and **14c** (c) and the η^2-complexes **4′c** (d), **8′c** (e), and **14′c** (f). Selected bond lengths and angles are listed in Table 2.

Table 2 Computed bond distances (in Å) and angles (in °) for the cationic ligands **2c**, **6c**, **12c**, the tetracarbonyl complexes **3c, 7c**, **10c,** and the tricarbonyl complexes **4c/4′c**, **8c/8′c,** and **11c/11′c**. The numbering scheme for all compounds is identical to the one used in Figures 1 and 2.

	2c	**3c**	**4c**	**4′c**	**6c**	**7c**	**8c**	**8′c**	**12c**	**13c**	**14c**	**14′c**
E	P	P	P	P	As	As	As	As	Sb	Sb	Sb	Sb
Symm.	C_{2v}	C_1	C_s	C_1	C_{2v}	C_s	C_s	C_1	C_{2v}	C_s	C_s	C_1
Co-E		2.885	2.008	2.255		2.885	2.142	2.359		2.960	2.376	2.524
Co-C_{eq}		1.788 1.775 1.771	1.778 1.781	1.769 1.775 1.793		1.791 1.776	1.774 1.780	1.764 1.777 1.787		1.791 1.780	1.761 1.796	1.756 1.790 1.801
Co-C_{ax}		1.792				1.788				1.788		
E-N	1.685	1.708	1.704	1.777 1.737	1.817	1.840	1.835	1.912 1.873	2.028	2.037	2.052	2.140 2.078
N-C	1.375	1.398	1.394	1.426 1.391	1.364	1.397	1.387	1.421 1.387	1.358	1.399	1.378	1.418 1.378
C-C	1.378	1.359	1.361	1.354	1.385	1.360	1.366	1.357	1.392	1.361	1.375	1.363
Σ_{ang}(E)		302.1	359.8	279.4		299.4	359.0	249.1		290.9	331.9	231.5

Table 3 Natural populations of electrons on the $Co(CO)_x$ moieties and selected Wiberg Bond Indexes (WBI) for the cationic ligands **2c**, **6c**, **12c**, the tetracarbonyl complexes **3c, 7c**, **10c,** and the tricarbonyl complexes **4c/4′c**, **8c/8′c,** and **11c/11′c**.

	2c	**3c**	**4c**	**4′c**	**6c**	**7c**	**8c**	**8′c**	**12c**	**13c**	**14c**	**14′c**
q($Co(CO)_x$)		−0.49	−0.50	−0.28		−0.47	−0.52	−0.30		−0.47	−0.58	−0.29
WBI(E-Co)		0.24	0.67	0.49		0.24	0.60	0.47		0.25	0.52	0.43
WBI(E-N)	1.06	0.92	0.88	0.82 0.83	0.97	0.83	0.80	0.75 0.75	0.85	0.73	0.69	0.65 0.65
WBI(N-C)	1.21	1.11	1.12	1.04 1.13	1.26	1.12	1.15	1.05 1.15	1.31	1.13	1.20	1.07 1.20
WBI(C-C)	1.55	1.70	1.68	1.73	1.49	1.69	1.65	1.71	1.44	1.69	1.58	1.67

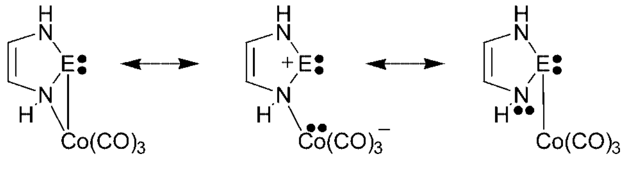
WBI(Co-N): 4′c: 0.18, 8′c: 0.19, 14′c 0.25

ateness of calculations referring to isolated molecules in the gas phase to model E−X bond polarization by intermolecular interactions in condensed phases; both effects have considerable influence on P−Cl distances in 2-chloro-1,3,2-diazaphospholenes [19]. The failure to reproduce an ion pair structure (which had been inferred in the case of **3a**) for **3c** may again be attributable to the overestimation of the electrostatic attraction between differently charged species in gas phase calculations.

The complexes **3c**, **7c**, **13c** (Fig. 3) display all very similar molecular structures whose shapes resemble that of the cobalta-diazaarsolene **7b**. Even though the Co−E distances are much longer than normal single bonds and, surprisingly, fail to reflect the change in the size of E, the results of NBO population analyses (Tab. 3) suggest a marked charge equalization between the $[Co(CO)_4]^-$ and $[E(NH)_2(CH)_2]^+$ fragments. All these features are best explained by the presence of a covalent Co−E interaction with low bond order which results (as judged by the Wiberg Bond Index, WBI) from population of the σ*(Co−E) orbital as a consequence of hyperconjugative interaction with the adjacent nitrogen-centered lone-pairs. Both the trends in computed bond lengths in the EN_2C_2 rings and the electron population reveal a higher degree of π-bond localization than in the cations **2c**, **6c**, **12c**. On the whole, all data further substantiate the description of the highly polarized Co−E bond in terms of bond/no-bond resonance between the canonical structures **7′** − **7‴** (scheme 3).

The tricarbonyl complexes **4c**, **8c**, and **14c** (Fig. 4) contain planar heterocyclic ligands and cobalt atoms with tetrahedral and pnicogen atoms with planar (**4c**, **8c**) or pyramidal (**14c**) coordination spheres that are connected by rather short Co−E bonds. The values of bond lengths and Wiberg Bond Indices are in accord with a similar bonding situation as in Fischer-type carbene-complexes, which is characterized by a superposition of E→M charge transfer (σ-bonding contribution) and M→E back-donation (π-bonding contribution) to yield formal double bonds. As in diazaphospholene-complexes [17], M→E back-donation attenuates π-interactions across the E−N bonds and supports the formation of a butadiene-dianion analogous 4π-system in the N_2C_2 part of the heterocycle.

The complexes **4′c**, **8′c**, **14′c** (Fig. 4) feature metal atoms that are bound to three carbonyls and one η^2-bound heterocyclic ligand in a Ψ-tetrahedral arrangement. The coordination of the pnicogen atom E is pyramidal and the Co−E bonds are 6 to 12 % longer than in the carbene-like isomers **4c**, **8c**, **14c**, but still much shorter than in the tetracarbonyl complexes. Evaluation of structural data and NBO results (Tab. 3) suggests a decrease in E−N and N−C bond orders and an increase in C=C bond order with respect to **4c**, **8c**, **14c** which implies a further π-bond localization; the observation of identical WBI values for uncoordinated and metal-bridged E−N bonds suggests that the larger bond lengths of the latter reflect mainly rehybridization at the nitrogen atom and not a lower π-bond order. In summary, the η^2-complexes can be described as metallacyclic structures with polar Co−N and Co−E bonds that may be rationalized in terms of resonance between the canonical structures shown in scheme 5.



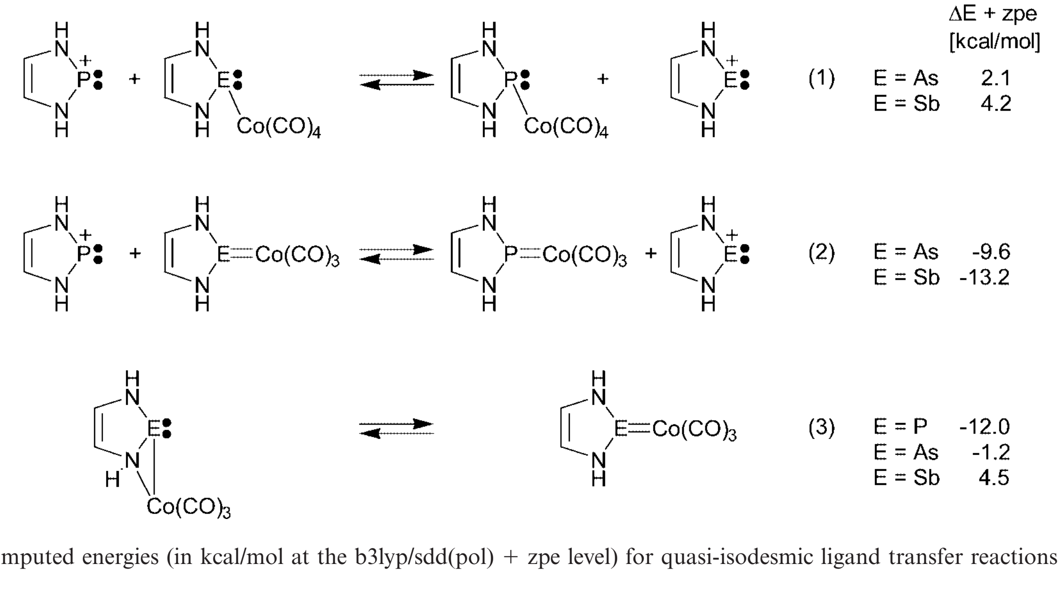
Scheme 5

Insight into the energetic relation between the different types of complexes is feasible from inspection of the computed energies for the quasi-isodesmic reactions displayed in Scheme 6. Comparison of the energies of reactions (1) and (2) involving formal transfer of $Co(CO)_n$ units between different cationic ligands suggests that the tetracarbonyl complexes (**3c**, **7c**, **13c**) become slightly more stable and the tricarbonyl complexes (**4c**, **8c**, **14c**) less stable when the atomic number of E increases. The first trend parallels previous findings of 1,3,2-diazaarsolenium and -diazastibolenium ions being better chloride acceptors than analogous diazaphospholenium ions and reflects presumably a greater Lewis-acidity with increasing size and polarizability of the cationic center [15, 16]. The lower stability of carbene-like complexes with As- and Sb-centered ligands (**8c**, **14c**) may be seen in the context of a growing reluctance of these elements to undergo isovalent orbital hybridization which is illustrated in a rising degree of s-character for the lone-pair at the pnicogen atom that is observed upon going from **3c**, **4′c** (E = P) to **7c**, **8′c** (E = As) and **13c**, **14′c** (E = Sb). As this effect disfavors formation of trigonal-planar frameworks of σ-bonds, it provides obviously a strong driving force for the pyramidal coordination of the Sb-atom in **14c** and the stabilization of the η^2-complexes **8′c**, **14′c** relative to the carbene-like isomers **8c**, **14c**, respectively (reaction (3), scheme 6).

Although the implication of the energies of reaction (3) − that P- and As-centered cations (**2c**, **6c**) form preferably $Co(CO)_3$-complexes with carbene-like structures and the Sb-centered cation **10c** η^2-complexes − is in accord with the observed constitution of **4a,b** and **8b**, generalization of this prediction is prevented by the present unfeasibility to assess the impact of steric and electronic factors associated with the presence of bulkier substituents at the nitrogen atoms. Still, the presence of a sizeable energy difference between the isomeric species **4c** and **4′c** in combination with the abundance of known carbene-like phosphenium complexes [1, 2] suggests that the formation of η^2-phosphenium complexes may not be likely. This situation may be different for 1,3,2-diazaarsolenium ions where the preference for a certain coordination mode is less obvious and the existence of species as the complex **11** [13] suggests that the order of relative energies may be adjustable by careful tuning of steric and electronic requirements of substituents. The same arguments hold for the Sb-centered cations where it is conceivable that the energetic preference by some 4 kcal/mol in favor of the η^2-complex can be overcome by steric blocking of the nitrogen donor sites by bulky substituents.

Conclusions

It was shown that 1,3,2-diazaarsolene derivatives react with $Tl[Co(CO)_4]$ in the same way as the analogous phosphorus compounds to form complexes of formulae $[Co(ER_2)(CO)_4]$ and $[Co(ER_2)(CO)_3]$, respectively. A similar reactivity was also inferred for 1,3,2-diazastibolenes although the products were not isolable and their constitution remains uncertain. In spite of these general analogies, a close inspection of structure and bonding in the products formed reveals differences that reflect the changing bonding preferences of



Scheme 6 Computed energies (in kcal/mol at the b3lyp/sdd(pol) + zpe level) for quasi-isodesmic ligand transfer reactions.

the individual elements. The complexes [Co(ER$_2$)(CO)$_4$] exist as ion pairs for E = P and as covalent metalla-arsines for E = As; the Co−As bond may be represented as "inverse" M→L donor-acceptor bond, leading to a similar bonding description as in 2-chloro-1,3,2-diazaphospholenes or -diazaarsolenes and highlighting the importance of ligand electrophilicity as driving force for complex formation. The trend in Co−E interactions parallels previous findings of diazaarsolenium ions being better chloride acceptors than diazaphospholenium ions and is attributed to a growing Lewis-acidity with increasing size and polarizability of the ligand atom.

The tricarbonyl complexes [R$_2$E=Co(CO)$_3$] (E = P, As) can be described as carbene-like species with a formal double bond arising from superposition of E→M charge transfer (σ-bonding contribution) and M→E back-donation (π-bonding contribution). Computational studies disclose that η^2(EN)-coordination of the EN$_2$C$_2$ heterocycle provides an alternative bonding mode to the formation of a carbene-like structure which is less favorable for phosphorus containing rings but close in energy for arsenic and energetically even more favorable for antimony derivatives. The decreasing preference for the carbene-like coordination mode correlates with the reluctance of the heavier pnicogen elements to adopt a trigonal planar coordination geometry and is thus essentially attributable to the decreasing propensity for isovalent orbital hybridization and the presence of a lone-pair with an increasing degree of s-character.

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Experimental Section

General Remarks: All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra: Bruker Avance 400 (^{1}H: 400.13 MHz, ^{13}C: 100.6 MHz, ^{31}P 161.9 MHz, ^{59}Co 94.95 MHz) in thf-D$_8$ at 30 °C; chemical shifts referenced to ext. TMS (^{1}H, ^{13}C), 85 % H$_3$PO$_4$ (Ξ = 40.480747 MHz, ^{31}P) 0.56 M K$_3$Co(CN)$_6$ (Ξ = 23.727074 MHz, ^{59}Co); positive signs of chemical shifts denote shifts to lower frequencies, coupling constants are given as absolute values. MS: Kratos Concept 1H, Xe-FAB, m-NBA matrix. IR spectra: Nicolet FT-IR Magna 550 or Perkin-Elmer Paragon, NaCl cells. Elemental analysis: Perkin-Elmer 2400CHSN/O Analyser. Melting points were determined in sealed capillaries.

DFT calculations (B3LYP) were carried out with the Gaussian 98 program package [28] using the SDD basis set augmented by one set of polarisation functions on all heavy atoms. The basis set employs a D95V split-valence basis set for the lighter atoms, and Stuttgart/Dresden ECPs at As and Sb. Harmonic vibrational frequencies and zero-point vibrational energies (ZPE) were calculated at the same level. All structures reported here are minima on the potential energy surface (only positive eigenvalues of the Hessian matrix).

1,3-Di-tert.-butyl-1,3,2-diazaphospholenium tetracarbonyl cobaltate (3a). A solution of Tl[Co(CO)$_4$] (375 mg, 1.00 mmol) in CH$_2$Cl$_2$ (5 ml) was cooled to −78 °C and a solution of **1a** (235 mg, 1.00 mmol) in CH$_2$Cl$_2$ (10 ml) was added drop wise. A white precipitate formed immediately. The mixture was slowly warmed to ambient temperature and the product formed characterized by IR and NMR spectroscopy. ^{31}P{^{1}H} NMR: δ = 200.1. − ^{59}Co NMR: δ = −2979. − IR (NaCl, CH$_2$Cl$_2$): $\bar{\nu}$ = 1889 cm^{-1} (ν CO).

1,3-Di-tert.-butyl-1,3,2-diazaphospholenium tricarbonyl cobaltate (4a). Tl[Co(CO)$_4$] (750 mg, 2.00 mmol) and **1a** (470 mg, 2.00 mmol) were dissolved in toluene (20 ml). Evolution of CO was observed. The mixture was stirred for 2 h, the precipitate formed removed by filtration, and the solvents evaporated in vacuum. Recrystallization of the residue from MeCN (25 ml) at −25 °C afforded 532 mg (78 %) of **4a** as red crystals, mp.126 °C.
Anal. for C$_{13}$H$_{20}$CoN$_2$O$_3$P: calcd. C 45.63 H 5.89 N 8.19; found C 45.12 H 5.94 N 8.06 %.

^{1}H NMR (C$_6$D$_6$): δ = 6.35 (d, 2 H, $^3J_{PH}$ = 5.0 Hz, NCH), 1.40 (s, 18 H, CCH$_3$). − **^{13}C{^{1}H} NMR** (C$_6$D$_6$): δ = 211.3 (br), 120.0 (d, $^2J_{PC}$ = 4.2 Hz, PN**C**H), 60.2 (d, $^2J_{PC}$ = 7.9 Hz, N**C**CH$_3$), 31.0 (d, $^3J_{PC}$ = 5.5 Hz, NC**C**H$_3$). −**^{31}P{^{1}H} NMR** (C$_6$D$_6$): δ = 234.7 (br). − **IR** (KBr, nujol mull): $\bar{\nu}$ = 2015, 1948 cm^{-1} (ν CO).

1,3-Di-Mesityl-1,3,2-diazaphospholenium tricarbonyl cobaltate (4b). The reaction of Tl[Co(CO)$_4$] (750 mg, 2.00 mmol) and **1b** (720 mg, 2.00 mmol) was carried out as described above for **3a** to 860 mg (92 %) of **4b** as red crystals, mp.199 °C.
Anal. for C$_{23}$H$_{24}$CoN$_2$O$_3$P: calcd. C 59.24 H 5.19 N 6.01, found: C 58.93 H 5.20 N 6.01 %.

^{1}H NMR: δ = 6.74 (s, 4 H, m-CH), 5.92 (d, 2 H, $^3J_{PH}$ = 4.7 Hz, NCH), 2.10 (s, 12 H, *o*-CH$_3$), 2.05 (s, 6 H, *p*-CH$_3$).
^{13}C{^{1}H} NMR: δ = 208.9 (br), 139.1 (d, $^4J_{PC}$ = 1.9 Hz, *m*-C), 135.5 (d, $^3J_{PC}$ = 3.9 Hz, *o*-C), 133.6 (d, $^2J_{PC}$ = 7.0 Hz, *i*-C), 129.7 (d, $^5J_{PC}$ = 1.2 Hz, *p*-C), 124.2 (d, $^2J_{PC}$ = 3.8 Hz, PN**C**H), 21.0 (d, $^6J_{PC}$ = 0.7 Hz, *p*-CH$_3$), 17.8 (d, $^4J_{PC}$ = 1.1 Hz, *o*-CH$_3$).
^{31}P{^{1}H} NMR: δ = 233.0 (br). − **IR** (NaCl, CH$_3$CN): $\bar{\nu}$ = 2015, 1945 cm^{-1} (ν CO). − **MS** (EI, 70 eV, 380 K): m/e(%) = 466 (13) [M$^+$], 438 (1) [M$^+$−CO], 410 (39) [M$^+$−2 CO], 323 (100) [M$^+$−Co(CO)$_3$].

1,3-Di-Mesityl-1,3,2-diazaarsolenium tetracarbonyl cobaltate (7b). A solution of Tl[Co(CO)$_4$] (750 mg, 2.00 mmol) in MeCN (10 ml) was added drop wise to a solution of **5b** (800 mg, 2.00 mmol) in MeCN (10 ml). The precipitate formed was filtered off and the filtrate concentrated in vacuum. Storing the solution overnight at −30 °C gave a dark red crystalline precipitate which was collected by filtration to yield 400 mg (42 %) of **7b**, mp. 60 °C.
Anal. for C$_{23}$H$_{24}$AsCoN$_2$O$_3$: calcd. C 54.12 H 4.7 N 5.49, found: C 53.62 H 4.79 N 5.6 %.

^{1}H NMR (C$_6$D$_6$): δ = 6.73 (s, 4 H, m-CH), 6.31 (s, 2 H, NCH), 2.04 (s, 18 H, *o*/*p*-CH$_3$). − **^{13}C{^{1}H} NMR**: δ = 208.7 (br, CO), 139.1, 134.9, 135.9, 130.1 (*m*-CH), 127.2 (s, AsN**C**H), 21.0 (*p*-CH$_3$), 18.0 (*o*-CH$_3$). − **IR** (NaCl, CH$_3$CN): $\bar{\nu}$ = 2004, 1934, 1928 cm^{-1} (ν CO).

1,3-Di-Mesityl-1,3,2-diazaarsolenium tricarbonyl cobaltate (8b). A solution of **7b** in hexane was stored for several h at ambient temperature. All volatiles were evaporated and the residue dissolved in little MeCN. Storing the solution overnight at −30 °C gave a small amount of a red crystalline precipitate of **8b**, mp. 60-65 °C.

^{1}H NMR (CD$_2$Cl$_2$): δ = 7.40 (s, 2 H, NCH), 7.11 (s, 4 H, m-CH), 2.40 (s, 6 H, *p*-CH$_3$), 2.26 (s, 12 H, *o*-CH$_3$). − **^{13}C{^{1}H} NMR**: δ = 204 (br, CO), 139.2 (*i*-C), 135.6(*p*-C), 134.2 (*o*-C), 129.6 (*m*-CH), 130.0 (AsN**C**H), 20.7 (*p*-CH$_3$), 17.5 (*o*-CH$_3$). − **IR** (NaCl, hexane): $\bar{\nu}$ = 2023, 1964 cm^{-1} (ν CO).

Reaction of Tl[Co(CO)$_4$] with 9b. Tl[Co(CO)$_4$] (38 mg, 0.10 mmol) was added to a cooled (−78 °C) solution of **9b** (55 mg, 0.10 mmol) in d$_8$-toluene (1ml) or hexane (1 ml), respectively. The solution was first warmed to −40 °C until a red color was observed, and then further to ambient temperature. The red product formed decomposed slowly, and the color of the solution turned black. The transient product was characterized in the reaction mixture byNMR (in d_8-toluene) or IR spectroscopy (in hexane solution). Isolation of a stable product was not feasible. − **^{1}H NMR**: δ = 6.73 (s, 4 H, *m*-CH), 6.23 (s, 2 H, NCH), 2.16 (s, 12 H, *o*-CH_3), 2.36 (s, 6 H, *p*-CH_3). − **IR** (NaCl, hexane): $\tilde{\nu}$ = 2062 (s), 1977 (s), 2002 (w), 1942 (w) cm^{-1} (ν CO).

Crystal structure determinations

4a: red crystals, $C_{13}H_{20}CoN_2O_3P$, M = 342.2, crystal size 0.20 x 0.15 x 0.10 mm, monoclinic, space group $P2_1/n$ (No. 14): a = 11.9463(4) Å, b = 8.9321(3) Å, c = 15.1454(7) Å, β = 91.783(2)°, V = 1615.3(1) Å^3, Z = 4, ρ(calcd) = 1.41 Mg m^{-3}, $F(000)$ = 712, μ = 1.17 mm^{-1}, 8490 reflexes (2 θ_{max} = 55°) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_α radiation (λ = 0.71073 Å), 3624 unique [R_{int} = 0.027] used for structure solution (Direct Methods, SHELXS-97 [30]) and refinement (full-matrix least-squares on F^2, SHELXL-97 [31]) with 181 parameters, no absorption correction, H-atoms with a riding model, $R1$ ($I > 2\sigma(I)$) = 0.023, $wR2$ = 0.059, largest diff. peak and hole 0.274 and −0.310 e Å^{-3}.

4b: red crystals, $C_{23}H_{24}CoN_2O_3P$, M = 466.3, crystal size 0.50 x 0.30 x 0.20 mm, monoclinic, space group $P2_1/c$ (No. 14): a = 19.9890(2) Å, b = 7.8653(1) Å, c = 15.1176(3) Å, β = 101.619(1)°, V = 2328.1(1) Å^3, Z = 4, ρ(calcd) = 1.33 Mg m^{-3}, $F(000)$ = 968, μ = 0.83 mm^{-1}, 36218 reflexes (2 θ_{max} = 55°) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_α radiation (λ = 0.71073 Å), 5281 unique [R_{int} = 0.059] used for structure solution (Direct Methods, SHELXS-97 [30]) and refinement (full-matrix least-squares on F^2, SHELXL-97 [31]) with 277 parameters, empirical absorption correction from multiple reflections, H-atoms with a riding model, $R1$ ($I > 2\sigma(I)$) = 0.030, $wR2$ = 0.081, largest diff. peak and hole 0.286 and −0.298 e Å^{-3}.

7b: red crystals, $C_{24}H_{24}AsCoN_2O_4$, M = 538.3, crystal size 0.30 x 0.20 x 0.10 mm, triclinic, space group $P\bar{1}$ (No. 2): a = 10.6396(3) Å, b = 10.7829(3) Å, c = 11.2066(4) Å, α = 112.236(2)°, β = 96.521(2)°, γ = 93.104(2)°, V = 1175.8(1) Å^3, Z = 2, ρ(calcd) = 1.52 Mg m^{-3}, $F(000)$ = 548, μ = 2.16 mm^{-1}, 22309 reflexes (2 θ_{max} = 55°) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_α radiation (λ = 0.71073 Å), 5252 unique [R_{int} = 0.074] used for structure solution (Direct Methods, SHELXS-97 [30]) and refinement (full-matrix least-squares on F^2, SHELXL-97 [31]) with 295 parameters, empirical absorption correction from multiple reflections, H-atoms with a riding model, $R1$ ($I > 2\sigma(I)$) = 0.032, $wR2$ = 0.063, largest diff. peak and hole 0.561 and −0.503 e Å^{-3}.

8b: red crystals, $C_{23}H_{24}AsCoN_2O_3$, M = 466.3, crystal size 0.10 x 0.13 x 0.34 mm, monoclinic, space group $P2_1/c$ (No. 14): a = 8.2259(9) Å, b = 15.0722(16) Å, c = 19.7199(19) Å, β = 101.76(1)°, V = 2393.6(4) Å^3, Z = 4, ρ(calcd) = 1.42 Mg m^{-3}, $F(000)$ = 1040, μ = 2.11 mm^{-1}, 11912 reflexes (2 θ_{max} = 50°) measured on a Nonius Kappa-CCD diffractometer at 223(2) K using MoKa radiation (λ = 0.71073 Å), 4175 unique [R_{int} = 0.079] used for structure solution (Direct Methods, SHELXS-97 [30]) and refinement (full-matrix least-squares on F^2, SHELXL-97 [31]) with 277 parameters, analytical absorption correction, H-atoms refined free, $R1$ ($I > 2\sigma(I)$) = 0.038, $wR2$ = 0.071, largest diff. peak and hole 0.472 and −0.841 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-258388 (**4a**), 258389 (**4b**), 258390 (**7b**), 258391 (**8b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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