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Metal-coordinated distibene and dibismuthene dications – isoelectronic analogues of butadiene dications†

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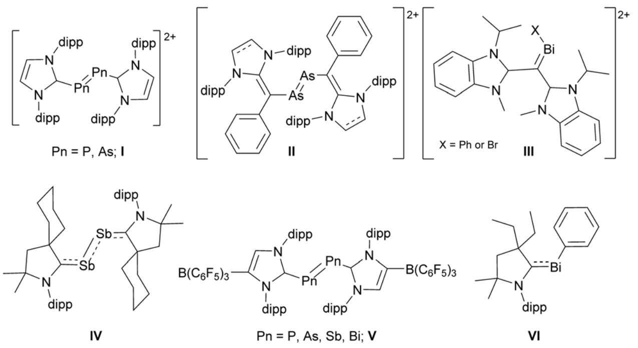
We report the synthesis and solid-state structures of DMAP-coordinated ([L(DMAP)GaPn]$_2$[OTf]$_2$; Pn = Sb 3, Bi 4) and base-free dipnictene dications ([LGaPn]$_2$[BArF$_x$]$_2$, Pn = Sb: x = 24, 5a; 20, 5b; Bi: x = 24, 6a; 20, 6b). Quantum chemical calculations indicate that the dications 5^{2+} and 6^{2+} represent isoelectronic analogues of the butadiene dication.

With the structural characterisation of the first room temperature-stable diphosphene [Mes*P]$_2$ (Mes* = 2,4,6-t-Bu$_3$-C$_6$H$_2$)[1] and disilene [Mes$_2$Si]$_2$ (Mes = 2,4,6-Me$_3$-C$_6$H$_2$)[2] in the early 1980s, the synthesis of multi-bonded compounds of heavy p-block elements became a rapidly developing field of research.[3] Neutral dipnictenes[4] have been kinetically stabilised using sterically demanding aryl,[5] amide,[6,7] boryle,[7,8] ferrocenyl,[9] and phosphanide ligands,[10] whereas electropositive L(X)M units (L = HC[C(Me)N(2,6-i-Pr$_2$C$_6$H$_3$)]$_2$, M = Al,[11] Ga[12–14]) have only recently been introduced as stabilising ligands.

Cationic dipnictenes recently received increasing interest.[15] Dipnictene dications were synthesised by oxidation of NHC- (**I**) and NHO-coordinated (**II**) dipnictenes (Scheme 1),[16–18] In contrast, distibene and dibismuthene cations stabilised by neutral carbenes are unknown,[19,20] although the neutral carbene-coordinated distibene **IV**[21] and dipnictene dications coordinated by anionic carbenes ((WCA-IDipp)$_2$E$_2$, E = P-Bi, **V**) have been reported.[22] In addition, carbene-coordinated bismuthinidenes (**III**, **VI**) were structurally characterised.[23] The reduced stability of carbene-coordinated low valent heavy pnictogen compounds most likely results from the decreasing (2p–np)π interactions (n = 5 (Sb), 6 (Bi)).[19,24,25] However, we demonstrated that L(X)Ga ligands stabilise Sb- and Bi-centred radicals and π-bonded compounds[26] including L(X)Ga-substituted cations and dipnictene radical anions.[27] We report here the synthesis of base-coordinated ([L(DMAP)GaPn]$_2$[OTf]$_2$ (Pn = Sb **3**, Bi **4**)) and base-free ([LGaPn]$_2$[BArF$_x$]$_2$ (x = 24, Pn = Sb **5a**, Bi **6a**; x = 20, Pn = Sb **5b**, Bi **6b**) dipnictene dications using triflate-coordinated dipnictenes [L(TfO)GaPn]$_2$ (Pn = Sb, Bi).

The synthesis of [L(TfO)GaBi]$_2$ (**2**) by reaction of LGa and Bi(OTf)$_3$ has been reported by Fischer *et al.*,[12] however, we only isolated mixtures of LGa(H)OTf (**7**),[28] Bi-centred radical [L(TfO)Ga]$_2$Bi$^\bullet$ (**8**) as was observed previously under similar reaction conditions for [L(X)Ga]$_2$Bi$^\bullet$ (X = Cl, I),[29] and dibismuthene **2**, which was isolated by fractional crystallization from 1,2-difluorobenzene. The analogous reaction of LGa and Sb(OTf)$_3$ gave [L(TfO)GaSb]$_2$ (**1**) in low yields (<20%), however, **1** was selectively formed in the reaction of MeOTf and [L(Me$_2$N)GaSb]$_2$. Room temperature ^{1}H NMR spectra of **1** and



Scheme 1 Structurally characterized carbene-coordinated dipnictene dications (**I**, **II**, **V**), carbene-coordinated **IV**, bismuth dication **III** and bismuthinidene **VI**.

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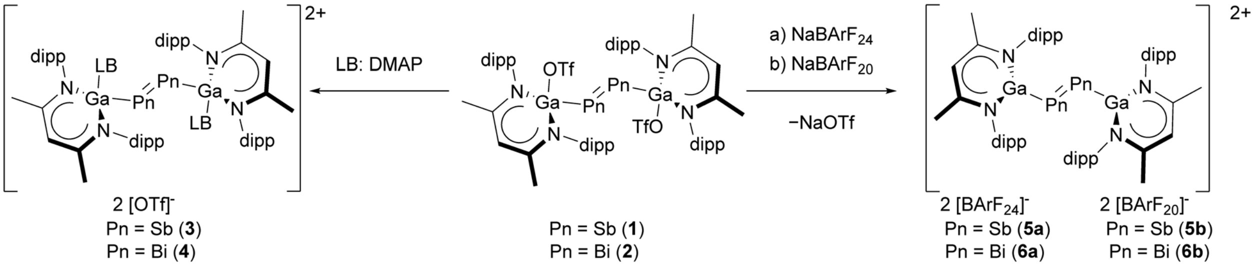

Scheme 2 Synthesis of DMAP-coordinated and base-free dipnictene dications **3**–**6**.

2 in CD_2Cl_2 showed broad resonances (Fig. S1 and S8, ESI†), indicating (partial) dissociation of the OTf group in solution. In contrast, sharp singlets for the γ-H atoms and the Me groups of the ligand backbone (ArNCCH_3) as well as two septets and four doublets for the *i*-Pr groups were observed at temperatures below −20 °C (Fig. S39 and S40, ESI†) and in less polar solvents such as C_6D_6 (Fig. S4, ESI†).[12] The reaction of 4-dimethylaminopyridine (DMAP) with **1** and **2** gave $[L(DMAP)GaPn]_2[OTf]_2$ (Pn = Sb **3**, Bi **4**) containing DMAP-coordinated dipnictene dications (Scheme 2).

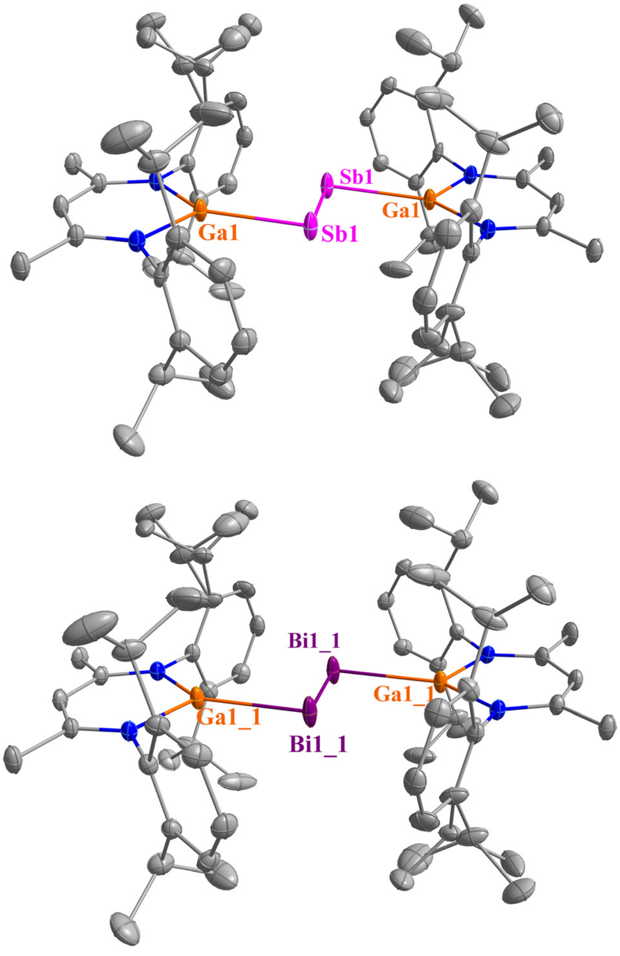

Fig. 1 Molecular structures of the dipnictene dications in **5b** and **6b** in the crystals. The H-atoms and $[BArF_{20}]$ anions are omitted for clarity; displacement ellipsoids are drawn at the 50% probability level.

The OTf groups in radical **8** can be substituted analogously, but the product decomposed and only few crystals of $[L(DMAP)Ga]_2Bi[OTf]$ (**9**) were isolated and analysed (sc-XRD, Fig. S53, ESI†).

In contrast, reactions of **1** and **2** with Lewis base-free salts of weakly coordinating anions (WCAs), $NaBArF_{24}$ and $NaBArF_{20}$ ($BArF_{24} = B(3,5\text{-}(CF_3)_2C_6H_3)_4$, $BArF_{20} = B(C_6F_5)_4$), proceeded with elimination of NaOTf and formation of $[LGaPn]_2[BArF_{24}]_2$ (Pn = Sb **5a**; Bi **6a**) and $[LGaPn]_2[BArF_{20}]_2$ (Pn = Sb **5b**; Bi **6b**), respectively. Salts **3**–**6** are soluble in polar, non-coordinating solvents (*e.g.* CH_2Cl_2, 1,2-difluorobenzene) but insoluble in non-polar hydrocarbons (*e.g. n*-hexane, toluene, benzene) as well as fluorobenzene and bromobenzene (**5a**, **6a**).

The ^1H NMR spectra of DMAP-substituted dications **3** and **4** show singlets for the γ-H atoms and the Me groups and two septets and four doublets for the *i*-Pr groups. The rotation of the Ga-N_{DMAP} bonds in **3** and **4** is restricted, resulting in magnetically inequivalent aromatic protons of the DMAP ligand (Table S1, ESI†). In contrast, the base-free dications in **5** and **6** show only one septet and two doublets for the *i*-Pr groups, indicating trigonal-planar coordinated Ga centres or rapid inversion processes in the case of a pyramidal coordination sphere in solution. The γ-H resonances are shifted to lower field (Table S1, ESI†) due to an increased Lewis acidity of the Ga centres within the base-free dications of **5** and **6** compared to **1**–**4**. Electron density is therefore effectively pulled away from the ligand backbone and the dipnictene π system towards the Ga atoms. The coordination of an electropositive gallanediyl (LGa) ligand seems to be essential for the stabilisation of the dipnictene dications as was observed in the isolation of silylene-carbonyl complexes.[30] The π → π* transition in the dications **5a** and **6a** is red-shifted compared to their neutral counterparts (UV/Vis: 431 (**1**) to 471 (**5a**); 505 (**2**) to 542 (**6a**) nm; Fig. S41–S44, S66, ESI†), indicating electronic changes within the π system.[11b]

Single crystals of **1** and **2** (Fig. S45 and S46, ESI†) were obtained from saturated CH_2Cl_2 and fluorobenzene solutions upon storage at −30 °C, while those of **3**, **4**, **5a**, and **6a** (Fig. S47–S50, ESI†) were grown by slow diffusion of toluene or benzene into CH_2Cl_2 solutions of **3**, **4**, **5a**, and **6a**, respectively. The molecular units of **5a** and **6a** are disordered. Crystals of **5b** and **6b** were grown by layering their 1,2-difluorobenzene solutions with *n*-hexane (Fig. 1). Compounds **1** and **2** crystallise in the monoclinic space group $C2/c$, and those of **3**, **4**, **5b**, and **6b** in the triclinic space group $P\bar{1}$, respectively. The molecular units of all dipnictenes are located on a special position

Table 1 Selected experimental and calculated (PBE0-D3BJ/def2-TZVP level of theory) bond lengths [Å] and angles [°]

	Pn	$[L(TfO)GaPn]_2$ (Pn = Sb **1**, Bi **2**)	$[L(DMAP)GaPn]_2^{2+}$ (Pn = Sb **3**, Bi **4**)	$[LGaPn]_2^{2+}$ (Pn = Sb **5b**, Bi **6b**)
Pn–Pn	Sb	2.6395(4) (2.6262)	2.6433(5) (2.6389)	2.6530(3) (2.6523)
	Bi	2.8145(2) (2.7785)	2.8193(3) (2.7913)	2.8347(2) (2.8047)
Ga–Pn	Sb	2.5800(4) (2.5905/2.5777)	2.6067(4) (2.5942/2.6060)	2.5578(3) (2.5789/2.5856)
	Bi	2.6587(3) (2.6666/2.6626)	2.6873(3) (2.6707/2.6798)	2.6492(6) (2.6584/2.6585)
Ga–N_L	Sb	1.913(3) (1.923/1.934), 1.924(2) (1.942/1.936)	1.937(1) (1.941/1.938), 1.950(1) (1.945/1.945)	1.865(1) (1.879/1.882), 1.869(1) (1.883/1.883)
	Bi	1.925(2) 1.936/1.934, 1932(2) (1.945/1.943)	1.942(2), (1.946/1.947) 1.955(2) (1.951/1.951)	1.874(2) (1.889/1.888), 1.877(2) (1.889/1.888)

$N_L = N_{imine}$ of the β-diketiminate ligand.

with a centre of inversion at the midpoint between both pnictogens atoms.

The Pn–Pn bonds of **5b** (2.6530(3) Å) and **6b** (2.8347(2) Å) are slightly elongated compared to the neutral dipnictenes **1** (2.6395(4) Å) and **2** (2.8145(2) Å), while the Ga–Pn bonds are slightly shortened (2.5578(3) **5b**, 2.6492 (6) **6b**, 2.5800(4) **1**, 2.6587(3) **2** Å). In contrast, the Ga–Pn bond lengths in the DMAP-coordinated complexes (**3**, **4**) are elongated due to the increased coordination number at the Ga atom and the steric demand of the DMAP ligand (Table 1). The Ga atoms in both **5b** and **6b** are nearly planar as indicated by the root-mean-square deviation of the C_3N_2Ga atoms from the least-squares planes defined by those within the LGa ring, which decreased to only 0.01 Å for **5b** and 0.02 Å for **6b** compared to 0.177 Å (**1**) and 0.160 Å (**2**), respectively. Carbene-coordinated diarsenes and diphosphenes dications[16,18,31] showed significantly different C–Pn and Pn–Pn (Pn = P, As) bond lengths compared to their neutral counterparts, *i.e.*, the C–As bond lengths in NHO-coordinated diarsene dication **IV** are shortened by 0.1 Å while the As–As bond is elongated by 0.1 Å,[18] most likely caused by electronic changes in the conjugated ligand-Pn_2-system upon oxidation.

To gain further insight into the electronic structure of the molecules **1–6**, bond energy analyses,[32] quantum theory of atoms in molecules (QTAIM),[33] and interacting quantum atoms (IQA)[34] analyses were carried out (Fig. S54–S65, ESI†).

A comparison of the bond energy analyses for the homolytic and heterolytic cleavage of the Ga–Sb and Ga–Bi bonds shows that in all cases they are electron sharing bonds (Fig. S54 and S55, ESI†). The difference in the Ga–Pn and Pn–Pn bond lengths is small overall (Table 1), whereas the charges on the pnictogen atoms differ significantly. The base-free dications $\mathbf{5}^{2+}$ and $\mathbf{6}^{2+}$ have significantly higher positive charges on the pnictogen atoms (Fig. S64 and S65, ESI†) compared to the neutral compounds (**1**, **2**) and the DMAP-stabilised dications ($\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$), which have similar charges. In addition, the ellipticity at the bond critical points of the Pn–Pn double bonds is higher in dications $\mathbf{5}^{2+}$ and $\mathbf{6}^{2+}$, indicating an increase in the π bond character (Fig. S58 and S60, ESI†).

As mentioned above, dications **I** and **II** were synthesised by a two-step oxidation reaction of the corresponding neutral NHC-coordinated dipnictenes. Therefore, the corresponding neutral compounds **5** and **6** were calculated for comparison. The reduction of the dipnictene dications to the neutral analogues leads to an increase in both the ellipticity at the bond critical points and the bond order of the Ga–Pn bonds, while both the ellipticity and the bond order decrease for the Pn–Pn bonds (Fig. S58 and S60, ESI†), which is reflected in a decrease of the Ga–Pn and an increase of the Pn–Pn bond lengths by more than 0.1 Å. In addition, the IQA analyses show an increase in the covalent part of the total interatomic interaction energies for the Ga–Pn bond and a decrease for the Pn–Pn bond (Fig. S62 and S63, ESI†). The twofold reduction also leads to a greater increase in the electron density at the Pn atoms compared to the Ga atoms. In other words, the charge changes in oxidation and reduction essentially take place at the Pn centre.

Base-coordinated and base-free dipnictene dications were structurally characterised. Quantum chemical calculations and UV-vis spectroscopy studies reveal a weak π backbonding contribution from the Pn_2 unit to the LGa ligand. Due to the large size of the frontier orbitals, this interaction is much smaller than expected for similar systems composed of lighter elements. The neutral molecules **5** and **6** can be considered as isoelectronic analogues of butadiene and the cations $\mathbf{5}^{2+}$ and $\mathbf{6}^{2+}$ represent analogues of the butadiene dication.

M. W. performed the experiments, C. W. the single crystal X-ray diffraction, and G. H. the quantum chemical calculations. Y. S. and A. G. assisted with the single crystal X-ray diffraction experiments. The work was supervised by S. S. The manuscript was written with contributions from all authors. All authors approved the final version of the manuscript.

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Conflicts of interest

There are no conflicts to declare.

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