J|A|C|S
COMMUNICATIONS

Capture of Phosphorus(I) and Arsenic(I) Moieties by a 1,2-Bis(arylimino)acenaphthene (Aryl-BIAN) Ligand. A Case of Intramolecular Charge Transfer

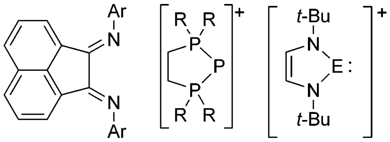
Gregor Reeske, Clint R. Hoberg, Nicholas J. Hill, and Alan H. Cowley*

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165

Received January 2, 2006; E-mail: cowley@mail.utexas.edu

The presence of an extensive π-system and two Lewis basic sites enables the 1,2-bis(arylimino)acenaphthene (aryl-BIAN) class of ligands (**1**, Chart 1) to function as both electron and proton sponges. This desirable combination of properties has resulted in the widespread use of aryl-BIAN-supported transition metal derivatives as versatile catalysts for a variety of important reactions.[1] However, considerably less information is available regarding aryl-BIAN complexes of the main group elements.[2] To date, this ligand class has not been used in the context of group 15 chemistry.

Chart 1



1 **2** **4** (E = P) **5** (E = As)

It has been known for several years that the reduction of PCl$_3$ with SnCl$_2$ in the presence of chelating bis(phosphines) results in the formation of cyclic triphosphenium ions (**2**, Chart 1).[3] Use of a similar protocol with AsCl$_3$ permits the isolation of an arsenic analogue of **2** with a six-membered C$_3$P$_2$As ring.[4] Subsequently, several other cyclic triphosphenium cations featuring a variety of ring sizes and types have been reported.[5] Although the mechanism of formation of these cations has not been established, it is reasonable to assume that the SnCl$_2$ reduction of ECl$_3$ (E = P, As) results initially in "ECl" and SnCl$_4$[6] and that the former is trapped by the chelating bis(phosphine) prior to or concomitant with abstraction of Cl$^-$ by SnCl$_4$. In more recent work, it has been discovered that **2** (R = Ph) can be isolated as the iodide salt from the redox reaction of PI$_3$ with bis(diphenylphosphinoethane).[7] Acyclic cations of the types [R$_3$PPPR$_3$]$^+$ and [R$_3$PAsPR$_3$]$^+$ are also known[8,9] as are some N-heterocyclic carbene (NHC) analogues.[10] Typically, the ^{31}P chemical shifts of the central phosphorus atom of cyclic triphosphenium cations fall in the range of δ −210 to −270.[5] Moreover, in the case of **2** (R = Ph), this atom is sufficiently basic to undergo protonation,[11] hence these salts are best regarded as adducts of phosphorus(I), namely, the predominant canonical form is $D^+ \rightarrow P^- \leftarrow D^+$ (D = phosphine, NHC).

Given the foregoing, we became interested in exploring the consequences of trapping the putative ECl molecules with ligands other than phosphines and carbenes. Treatment of an equimolar mixture of PCl$_3$ and SnCl$_2$ with dpp-BIAN (**1**; Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) in THF solution at ambient temperature resulted, after workup, in a 66% yield of a dark green salt of composition [(dpp-BIAN)P][SnCl$_5$·THF] (**3**). The most obvious feature of the NMR spectral data for **3** is the ^{31}P chemical shift of δ +232.5, which falls in the region observed for phosphenium cations.[12] Further insight was gained from a single-crystal X-ray diffraction study of **3** (Figure 1).[13]

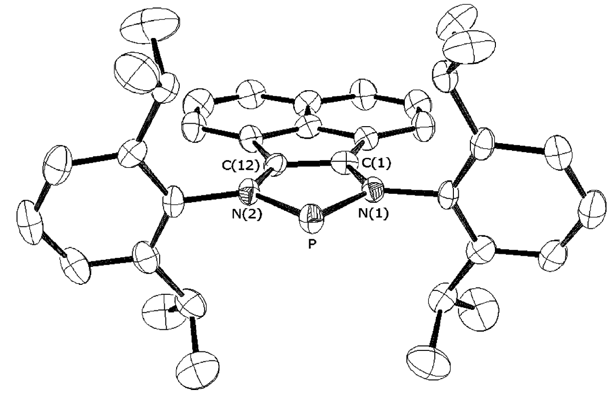


Figure 1. ORTEP view of the [(dpp-BIAN)P]$^+$ cation of **3** showing the atom numbering scheme. Selected bond distances [Å] and angles [°] with corresponding values for **6** in parentheses: P−N(1) 1.694(4) [1.700(4)], P−N(2) 1.689(4) [1.685(5)], N(1)−C(1) 1.351(5) [1.354(7)], N(2)−C(12) 1.366(5) [1.361(7)], C(1)−C(12) 1.395(5) [1.380(8)], N(1)−P−N(2) 90.23(17) [89.75(2)], P−N(1)−C(1) 113.1(3) [113.2(4)], N(1)−C(1)−C(12) 112.3(4) [111.8(5)], C(1)−C(12)−N(2) 110.9(4) [111.7(5)], C(12)−N(2)−P 113.4(3) [113.5(4)].

The most noteworthy structural features concern the C−C and C−N bond distances within the planar PN$_2$C$_2$ ring. Specifically, the C(1)−C(12) bond distance (1.395(5) Å) is considerably shorter than the corresponding distance in the uncoordinated dpp-BIAN ligand (1.527 Å)[14] and indicative of double bond character. Moreover, the C−N bond distances in **3** (av. 1.385(5) Å) are longer than those in free dpp-BIAN (1.272 Å)[14] and commensurate with a bond order of approximately one. Overall, the metrical parameters for the PN$_2$C$_2$ ring are very similar to those found for cyclic phosphenium cation **4** (Chart 1).[15] Moreover, the structure of the dpp-BIAN ligand in **3** also bears a close resemblance to that of the complex [(dtb-BIAN)Mg(THF)$_2$] which was prepared via the reaction of activated Mg metal with the neutral dtb-BIAN ligand (**1**; Ar = 2,5-di-*tert*-butylphenyl).[16] Thus, akin to Mg metal, the "PCl" molecule functions as a two-electron reductant toward the aryl-BIAN ligand. Accordingly, and in contrast to **2** and related triphosphenium cations, the dicoordinate phosphorus atom of **3** is in the +3 rather than the +1 oxidation state. The fact that internal redox takes place in the case of **3** but not **2** is attributable to the presence of a low-lying LUMO in the neutral dpp-BIAN ligand and the aromaticity of the resulting [(dpp-BIAN)]$^{2-}$ anion. The [SnCl$_5$·THF]$^-$ counteranion is essentially octahedral and the closest P$^+$···Cl contacts are to Cl(1) (3.374(5) Å) and Cl(2) (3.328(5) Å).

We have also investigated the ambient temperature reaction of equimolar quantities of dpp-BIAN and PI$_3$ in CH$_2$Cl$_2$ solution in

10.1021/ja058459m CCC: $33.50

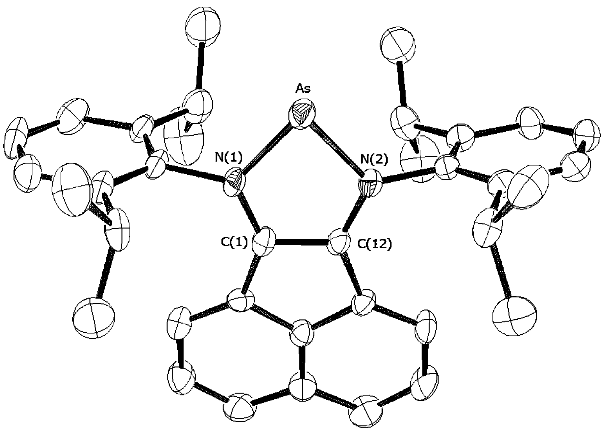


Figure 2. ORTEP view of the [(dpp-BIAN)As]$^+$ cation of **7** showing the atom numbering scheme. Selected bond distances [Å] and angles [°]: As−N(1) 1.839(3), As−N(2) 1.857(4), N(1)−C(1) 1.348(5), N(2)−C(12) 1.348(5), C(1)−C(12) 1.399(6), N(1)−As−N(2) 84.89(15), As−N(1)−C(1) 114.7(3), N(1)−C(1)−C(12) 112.6(4), C(1)−C(12)−N(2) 115.3(4), C(12)−N(2)−As 112.5(3).

the absence of a reducing agent. ^{31}P NMR spectroscopic assay of the resulting dark brown reaction mixture revealed the exclusive presence of a sharp singlet at δ +234.5. That virtually quantitative formation of [(dpp-BIAN)P][I_3] (**6**) had occurred was confirmed on the basis of ^{1}H and ^{13}C NMR spectroscopic data along with an X-ray diffraction study of a single crystal grown from THF solution.[13] Comparison of the metrical parameters for the phosphenium cations of **3** and **6** reveals that they are identical within experimental error. The closest contact between P^+ and I_3^- is 3.883(6) Å. Although we have no mechanistic information, it is plausible that the interaction of dpp-BIAN with PI_3 results in the initial formation of I_2 and "[(dpp-BIAN)PI]", from which I^- is abstracted by I_2. As in the case of **3**, subsequent or concomitant intramolecular charge transfer affords the final product, **6**.

The arsenium salt [(dpp-BIAN)As][$SnCl_5$·THF] (**7**) has been prepared by a similar procedure to that employed for the synthesis of **3**. The green crystalline product was examined by single-crystal X-ray diffraction (Figure 2).[13] The AsN_2C_2 ring is planar, and the average C−N and As−N bond distances are very similar to those in **5**[15] and subsequently reported[17] cyclic arsenium cations, thus supporting the view that arsenic is in the +3 oxidation state. The fact that the C(1)−C(12) bond distances in **3**, **6**, and **7** are ~0.06 Å longer than the corresponding distances in **4** and **5** is presumably due to the constraints of the somewhat rigid dpp-BIAN framework. Finally, we note that the [(dpp-BIAN)As]$^+$ cation is isoelectronic with [(dpp-BIAN)Ge].[18] As expected, the N−E−N bond angle and E−N bond distances are smaller for the arsenic cation than the germylene due to the fact that the ionic radius of As^{3+} is less than that of Ge^{2+}. As in the case of **3**, the shortest cation−anion contacts involve As$^+$···Cl(1) (3.298(5) Å) and As$^+$···Cl(2) (3.215(5) Å).

In summary, we have prepared the salts [(dpp-BIAN)P][$SnCl_5$·THF], [(dpp-BIAN)P][I_3], and [(dpp-BIAN)As][$SnCl_5$·THF] which represent the first examples of group 15 complexes supported by a BIAN ligand. On the basis of NMR and X-ray structural data, it is concluded that, in contrast to the corresponding bis(phosphine) complexes, the phosphorus or arsenic atoms in these cations adopt the +3 oxidation state.

Acknowledgment. We are grateful to the Petroleum Research Fund (Grant 38970-AC1) and the Robert A. Welch Foundation (Grant F-135) for support.

Supporting Information Available: Experimental details, spectroscopic data, and X-ray crystallographic data for **3**, **6**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) van Laren, M. W.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3715. (b) van Belzen, R.; Hoffmann, H.; Elsevier, C. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1743. (c) Shirakawa, E.; Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 114.
(2) Schumann, H.; Hummert, M.; Lukoyanov, A. N.; Fedushkin, I. L. *Organometallics* **2005**, *24*, 3891 and references therein.
(3) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 63.
(4) Gamper, S. F.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 601.
(5) For summaries, see: (a) Boon, A. J.; Byers, H. L.; Dillon, K. B.; Goeta, A. E.; Longbottom, D. A. *Heteroat. Chem.* **2000**, *11*, 226. (b) Barnham, R. J.; Deng, R. M. K.; Dillon, K. B.; Goeta, A. E.; Howard, J. A. K.; Puschmann, H. *Heteroat. Chem.* **2001**, *12*, 501.
(6) (a) The formation of $\{PCl\}_n$ by reduction of PCl_3 with Li_2[*t*-BuNC(H)-C(H)Bu-*t*] has also been reported: Denk, M. K.; Gupta, S.; Ramachandran, R. *Tetrahedron Lett.* **1996**, *37*, 9025. (b) A similar reaction takes place with a stannylene reducing agent: Veith, M.; Volker, H.; Majoral, J. P.; Bertrand, G.; Manuel, G. *Tetrahedron Lett.* **1983**, *24*, 4219.
(7) Ellis, B. D.; Carlesimo, M.; Macdonald, C. L. B. *Chem. Commun.* **2003**, 1946. A similar reaction takes place with AsI_3 to give the analogous P−As−P cation.
(8) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226.
(9) Driess, M.; Ackermann, H.; Aust, J.; Merz, K.; von Wüllen, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 450.
(10) Ellis, B. D.; Dyker, C. A.; Decken, A.; Macdonald, C. L. B. *Chem. Commun.* **2005**, 1965.
(11) Lochschmidt, S.; Schmidpeter, A. *Z. Naturforsch.* **1985**, *40b*, 765.
(12) (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Sanchez, M.; Mazières, M. R.; Lamandé, L.; Wolf, R. In *Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry*; Regitz, M., Scherer, O., Eds.; Georg Thieme Verlag: Stuttgart, 1990; D1, p 129ff.
(13) All X-ray data sets were collected at 153 K on a Nonius-Kappa CCD diffractometer. Crystal data for **3**: $C_{40}H_{48}Cl_5N_2OPSn$, monoclinic, space group $P2_1/n$, $a = 13.189(5)$, $b = 22.335(5)$, $c = 14.637(5)$ Å, $\beta = 104.102(5)°$, $V = 4182(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.429$ g cm^{-3}, $2\theta_{max} = 52.00$, Mo Kα ($\lambda = 0.71073$ Å), total reflections collected = 15 498, unique reflections = 8180 ($R_{int} = 0.0562$), absorption coefficient $\mu = 1.002$ mm^{-1}, final R indices $R_1 = 0.0471$, w$R_2 = 0.0995$, GOF = 0.979. Crystal data for **6**: $C_{72}H_{80}I_6N_4P_2$, monoclinic, $P2_1/c$, $a = 17.625(4)$, $b = 15.265(3)$, $c = 17.014(3)$ Å, $\beta = 114.03(3)°$, $V = 4180.5(15)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.450$ g cm^{-3}, $2\theta_{max} = 54.96$, Mo Kα ($\lambda = 0.71073$ Å), total reflections collected = 17 430, unique reflections = 9546 ($R_{int} = 0.0437$), absorption coefficient $\mu = 2.304$ mm^{-1}, final R indices $R_1 = 0.0478$, w$R_2 = 0.1202$, GOF = 0.927. Crystal data for **7**: $C_{40}H_{48}AsCl_5N_2OSn$, monoclinic, $P2_1/n$, $a = 13.317(5)$, $b = 22.302(5)$, $c = 14.546(5)$ Å, $\beta = 103.936(5)°$, $V = 4193.5(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.495$ g cm^{-3}, $2\theta_{max} = 54.96$, Mo Kα ($\lambda = 0.71073$ Å), total reflections collected = 16 547, unique reflections = 9460 ($R_{int} = 0.0710$), absorption coefficient $\mu = 1.744$ mm^{-1}, final R indices $R_1 = 0.0512$, w$R_2 = 0.0831$, GOF = 0.985.
(14) (a) El-Ayaan, V.; Paulovicova, A.; Fukudya, Y. *J. Mol. Struct.* **2003**, *645*, 205. (b) Marsh, R. E. *Acta Crystallogr., Sect. B: Struct. Sci.* **2004**, *60*, 252.
(15) (a) Carmalt, C. J.; Lomelí, V.; McBurnett, B. G.; Cowley, A. H. *Chem. Commun.* **1997**, 2095. (b) Denk, M. K.; Gupta, S.; Lough, A. *J. Eur. J. Inorg. Chem.* **1999**, 41. (c) Gudat, D.; Haghverdi, A.; Hupfer, H.; Nieger, M. *Chem.—Eur. J.* **2000**, *6*, 3414.
(16) Fedushkin, I. L.; Chudakova, V. A.; Skatova, A. A.; Khvoinova, N. M.; Kurskii, Y. A.; Glukova, T. A.; Fukin, G. A.; Dechert, S.; Hummert, M.; Schumann, H *Z. Anorg. Allg. Chem.* **2004**, *630*, 501.
(17) Gans-Eichler, T.; Gudat, D.; Nieger, M. *Heteroat. Chem.* **2005**, *16*, 327.
(18) Fedushkin, I. L.; Skatova, A. M.; Chudakova, V. A.; Khvoinova, N. M.; Baurin, A. Y. *Organometallics* **2004**, *23*, 3714.

JA058459M