# Direct reactions of tellurium tetrahalides with chelating nitrogen ligands. Trapping of $TeI_2$ by a 1,2-bis(arylimino)acenaphthene (aryl-BIAN) ligand and C–H activation of an α,α′-diiminopyridine (DIMPY) ligand

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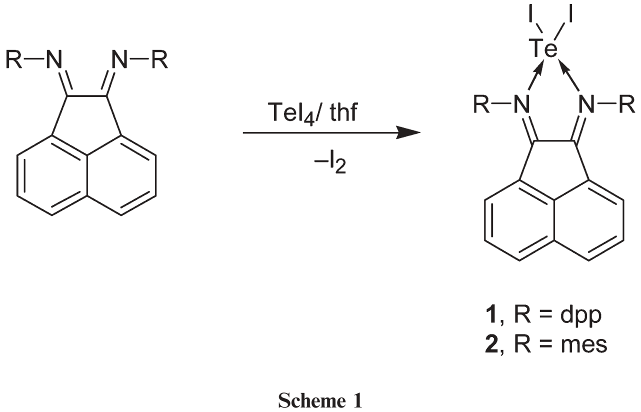
**The reaction of $TeI_4$ with the 2,6-diisopropylphenyl-substituted 1,2-bis(arylimino)acenaphthene ligand dpp-BIAN results in two-electron reduction of tellurium and formation of the complex (dpp-BIAN)$TeI_2$, while treatment of $TeCl_4$ with the α,α′-diiminopyridine ligand dpp-DIMPY causes C–H activation of an imino methyl group.**

It has been known for some time that synthetic access to cationic phosphorus(I) and arsenic(I) compounds can be gained by $SnCl_2$ reduction of pnicogen trihalides in the presence of chelating bis(phosphines)[1,2] or two monodentate phosphines.[3,4] More recently, it has been disclosed that such compounds can be prepared by the direct redox reactions of a bis(phosphine) with $EI_3$ (E = P, As)[5] or analogously *via* the reaction of $PCl_3$ with *N*-heterocyclic carbenes.[6] Our work in this area is focused on the use of chelating nitrogen ligands for trapping the $P^+$ and $As^+$ cations that result from either $SnCl_2$ reductive chemistry or direct redox routes. Interestingly, and in contrast to previous work, it was demonstrated that the product of the interaction of the 2,6-diisopropylphenyl-substituted 1,2-bis(arylimino)acenaphthene (dpp-BIAN) ligand with $PI_3$ is, in fact, the phosphorus(III) salt [(dpp-BIAN)P]$I_3$ due to the facile back transfer of two electrons from phosphorus into the LUMO of this ligand.[7] On the other hand, treatment of the α,α′-diiminopyridine ligand dpp-DIMPY with $AsI_3$ resulted in [dpp-DIMPYAs]$_2$[$As_2I_8$], X-ray crystallographic examination of which indicated that the arsenic cation retains the +1 oxidation state.[8] With the foregoing results in mind, we were prompted to explore the direct reactions of tellurium tetrahalides with aryl-BIAN and aryl-DIMPY ligands.

In view of the ability of the dpp-BIAN ligand to effect two-electron reduction of $EI_3$ (E = P, As),[7] it was reasoned that the analogous reaction of this ligand with $TeI_4$ would result in chelated $TeI_2$ or $TeI^+$ species. Given that $TeI_2$ does not exist in the solid state[9] (but is stable in the vapor phase[10]), the aryl-BIAN reduction route, if it resulted in (dpp-BIAN)$TeI_2$, could prove to be a mild and potentially useful source of $TeI_2$ complexes.[11] However, it was not clear *a priori* whether back-transfer of two electrons into the dpp-BIAN ligand would occur thereby producing a Te(IV) derivative.

Treatment of a suspension of $TeI_4$ in thf with an equimolar solution of dpp-BIAN resulted, after work-up, in a 93% yield of dark blue-green solid **1** (Scheme 1). The LRMS spectrum of **1**[12] exhibits a peak at *m*/*z* = 501 in the positive mode which corresponds to the free dpp-BIAN ligand. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra for **1**[12] show only slight differences from those of the free dpp-BIAN ligand. In order to secure a more complete characterization, it was necessary to perform a single-crystal X-ray diffraction study.[13] Compound **1** crystallizes in the monoclinic space group $P2_1/n$ and there are no unusually close intermolecular contacts. Individual molecules of **1** (Fig. 1) feature a $TeI_2$ moiety bonded to both nitrogen atoms of the dpp-BIAN ligand. As pointed out above, one of the points of interest in the structure of **1** is whether, akin to [(dpp-BIAN)P]$^+$, two electrons would be transferred from Te into the LUMO of the dpp-BIAN ligand. However, examination of the metrical parameters for the Te(1)–N(1)–C(1)–C(12)–N(2) ring indicate that intramolecular electron transfer does not take place and that tellurium is in the +2 oxidation state. Thus the C–N bond distances, which average 1.284(8) Å, fall in the carbon–nitrogen double bond range while the C(1)–C(12) bond distance of 1.501(8) Å is indicative of a bond order of one. Accordingly, N(1) and N(2) form donor–acceptor bonds to the $TeI_2$ fragment. Inferentially, these bonds are weak because the average N → Te bond distance of 2.398(5) Å is considerably longer than that in *e.g.* the bis(ketiminato)complex $(Ph_2C{=}N)_2TeCl_2$ (av. 2.026(3) Å)[14] We attribute our inability to record $^{125}Te$ NMR spectra for **1** and **2** to the weakness of these bonds and consequent facile exchange processes. Within experimental error, the two iodine atoms lie in the same plane as the $C_2N_2Te$ ring, thus allowing a *trans* arrangement of the lone pair



Scheme 1

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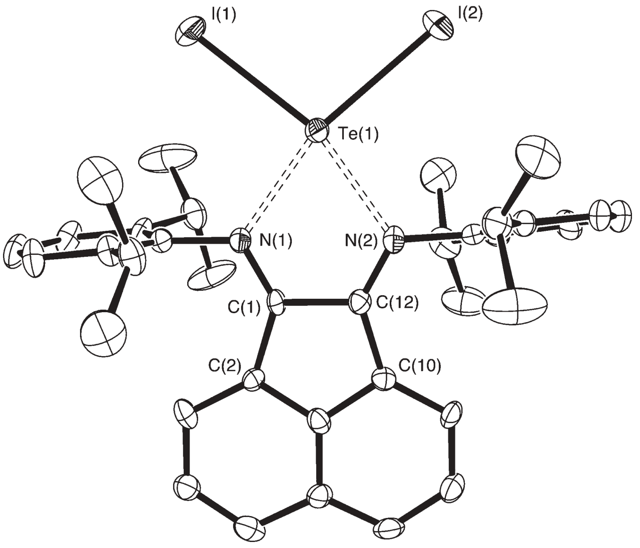


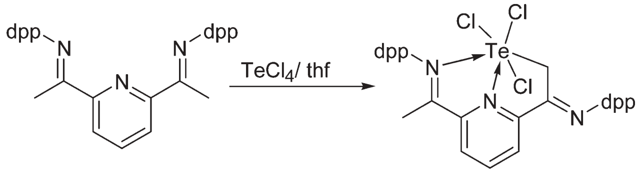
**Fig. 1** View of **1** showing the atom numbering scheme and thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) with the corresponding values for **2** shown in brackets: Te(1)–I(1) 2.8686(9), [2.8836(11)], Te(1)–I(2) 2.8687(10) [2.8897(8)], Te(1)–N(1) 2.403(5) [2.363(3)], Te(1)–N(2) 2.393(5) [2.384(4)], N(1)–C(1) 1.291(8) [1.287(5)], C(1)–C(12) 1.501(8) [1.507(6)], C(12)–N(2) 1.277(8) [1.290(5)], I(1)–Te(1)–I(2) 100.92(3) [102.12(2)], N(1)–Te(1)–N(2) 70.17(17) [71.09(13)], Te(1)–N(1)–C(1) 115.0(4) [115.7(3)], N(1)–C(1)–C(12) 119.7(5) [119.2(4)], C(1)–C(12)–N(2) 118.9(6) [118.9(4)], C(12)–N(2)–Te(1) 116.3(4) [115.0(3)].

electrons on Te. The N(1)–Te(1)–N(2) bond angle of 70.17(17)° is considerably more acute then the ideal octahedral value due to the relative rigidity of the dpp-BIAN skeleton. As a consequence, the I(1)–Te(1)–I(2) bond angle (100.92(3)°) is more obtuse than the ideal value. Based solely on spectroscopic evidence, the reaction of $TeCl_4$ with dpp-BIAN appears to result in 1 : 1 complex formation rather than a redox process.

We have also prepared and structurally characterized the analogous complex [(mes-BIAN)$TeI_2$] (**2**) using the same synthetic protocol. The structure of **2** is very similar to that of **1** and pertinent metrical parameters are indicated in brackets in the caption to Fig. 1. It is, however, noteworthy that **2** is much more labile than **1**, particularly in solution, which highlights the stabilizing influence of the bulky dpp substituents.

Slow addition of a thf solution of $TeCl_4$ to an equimolar solution of dpp-DIMPY in the same solvent at 25 °C resulted, after work-up, in a 74% yield of yellow, solid **3** (Scheme 2). Taken collectively, the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra for **3**[12] indicate that upon coordination the plane of symmetry of the free ligand has been eliminated. Thus, *e.g.* four *i*-Pr methyl resonances are detected for **3** rather than two for the free ligand. Moreover, it is clear that an imine methyl group has been converted into a methylene group. The $CI^+$ LRMS for **3**[12] was not particularly informative; however, in the negative mode, a peak at *m*/*z* 235 was evident and attributable to $[TeCl_3]^-$. The fact that the $^{125}Te\{^{1}H\}$ NMR chemical shift for **3** ($\delta$ 1314.7 ppm) is very close to that for $Ph_2P(NSiMe_3)_2TeCl_3$ ($\delta$ = 1317.3 ppm)[15] was suggestive of the presence of a $Cl_3TeN_2$ moiety. Further structural information was obtained from a single-crystal X-ray diffraction study.[13] The solid state of **3** consists of individual molecules and there are no unusually short intermolecular contacts (Fig. 2). The molecular structure of **3** comprises a $TeCl_3$ moiety that is σ-bonded to a $CH_2$ group at C(9) and linked by N → Te donor–acceptor bonds to the pyridine nitrogen and one of the imino nitrogens. Note, however, that the N → Te bond distance for the pyridine nitrogen (2.321(3) Å) is considerably shorter than for the imino nitrogen (2.732(3) Å).[16] That no redox reaction has taken place is clear from the fact that the C(2)–N(1) bond retains its double bond character as evidenced by the observation that this bond distance (1.272(5) Å) is identical to that of the uncoordinated imino bond C(8)–N(3) within experimental error (1.276(5) Å). The $TeCl_3$ moiety is essentially T-shaped, but tends towards a shallow trigonal pyramid due to the stereochemically-active tellurium lone pair. While the mechanism of the reaction of $TeCl_4$ with dpp-DIMPY is not yet clear, it is apparent that C–H activation of the C(9) methyl group has taken place.[17] The DIMPY ligand class has been employed extensively for the development of unprecedented Ziegler–Natta catalysts.[18] However, a search of the Cambridge Structural Database revealed that the mode of coordination of the DIMPY ligand in **3** is unprecedented.

Finally, we wish to point out recent work by Ragogna *et al.*[19] which demonstrated that the reaction of $SeCl_4$ with the *tert*-butyl-substituted diazabutadiene ligand results in cleavage of one of the *t*-Bu–N bonds and formation of the 1,2,5-selenadiazolium cation. It is already clear that the interaction of chalcogen halides with nitrogen ligands promises a rich harvest of unusual reactions.



**3**

**Scheme 2**

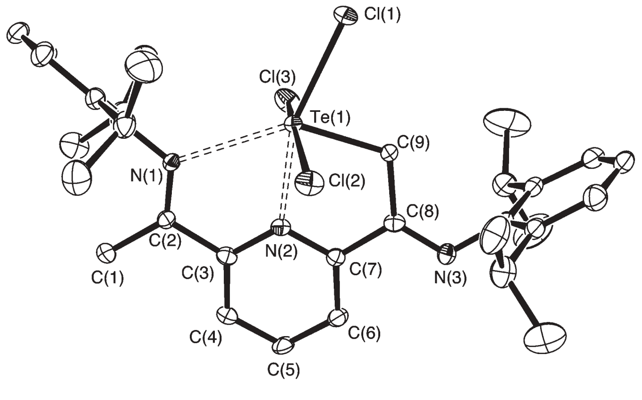


**Fig. 2** View of **3** showing the atom numbering scheme and thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Te(1)–Cl(1) 2.5255(11), Te(1)–Cl(2) 2.5440(12), Te(1)–Cl(3) 2.5418(12), Te(1)–N(1) 2.732(3), Te(1)–N(2) 2.321(3), Te(1)–C(9) 2.126(4), N(1)–C(2) 1.272(5), C(2)–C(3) 1.508(5), C(7)–C(8) 1.482(5), C(8)–N(3) 1.276(5), C(8)–C(9) 1.498(5), Cl(1)–Te(1)–Cl(2) 98.65(3), Cl(1)–Te(1)–Cl(3) 93.61(4), Cl(2)–Te(1)–Cl(3) 163.68(4), N(1)–Te(1)–N(2) 63.56(10), N(1)–Te(1)–C(9) 140.52(12), N(1)–C(2)–C(3) 117.4(3), Te(1)–C(9)–C(8) 112.4(3), C(7)–C(8)–C(9) 117.6(3).

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12 **1**: A solution of dpp-BIAN (0.2 g, 0.4 mmol) in thf (30 mL) was added dropwise to a suspension of $TeI_4$ (0.254 g, 0.4 mmol) in thf (50 mL) at 25 °C over a period of 0.5 h. The dark blue reaction mixture was stirred for 12 h, following which it was filtered through Celite®. Removal of all the solvent and volatiles under reduced pressure afforded 0.328 g (93%) of dark green-blue solid **1**. Single crystals of **1** were obtained by slow evaporation of a 5 : 1 $CH_2Cl_2$–*n*-hexane or thf–*n*-hexane solution under an argon atmosphere. Mp 233–236 °C. Analysis: found for $C_{36}H_{40}I_2N_2Te\cdot 2CH_2Cl_2$: C 43.91, H 4.52, N 2.69; calc. C 43.86, H 4.53, N 2.69. $^1H$ NMR (300.14 MHz, $CD_2Cl_2$) $\delta$: 0.96 [d, $^3J(^1H\text{-}^1H)$ = 6.9 Hz, 12 H, $CH_3$], 1.46 [d, $^1J(^1H\text{-}^1H)$ = 6.6 Hz, 12 H, $CH_3$], 3.04 [m, 4 H, CH], 6.75 [d, $^3J(^1H\text{-}^1H)$ = 6.9 Hz, 2 H, H(3)], 7.46–7.48 [m, 6 H, H(arom.)-dpp], 7.52–7.57 [m, 2 H, H(4)], 8.20 [d, $^3J(^1H\text{-}^1H)$ = 8.4 Hz, 2 H, H(5)]. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_2Cl_2$) $\delta$: 24.09, 24.16, 29.76 [*i*-Pr], 124.94, 126.52, 127.33, 128.57, 129.06, 131.00, 132.49, 138.69, 141.11, 143.22, 163.81 [C(arom.)]. LRMS ($CI^+$ *m*/*z*) (%): 501 (53%, dpp-BIAN), 457 (100%, dpp-BIAN − *i*-Pr). **2**: This compound, which is significantly less stable in solution than **1**, was prepared by treatment of mes-BIAN (0.2 g, 0.48 mmol) with $TeI_4$ (0.305 g, 0.48 mmol) following the procedure described above for **1**. The yield of deep blue single crystals of **2** was 0.05 g (13%). Mp 252–254 °C. Analysis: found for $C_{30}H_{28}I_2N_2Te$: C 45.26, H 3.53, N 3.46; calc. C 45.15, H 3.54, N 3.51. $^1H$ NMR (300.14 MHz, $CD_2Cl_2$) $\delta$: 2.21 [s, 12 H, $CH_3$], 2.46 [s, 6 H, $CH_3$], 6.85 [d, $^3J(^1H\text{-}^1H)$ = 7.2 Hz, 2 H, H(3)], 7.11 [s, 4 H, H(arom.)-mes], 7.55 [m, 2 H, H(4)], 8.13 [d, $^3J(^1H\text{-}^1H)$ = 8.4 Hz, 2 H, H(5)]. LRMS ($CI^+$ *m*/*z*) (%): 417 (40%, mes-BIAN), 401 (100%, mes-BIAN − $CH_3$). **3**: A solution of dpp-DIMPY (0.2 g, 0.415 mmol) in thf (50 mL) was added slowly to a solution of $TeCl_4$ (0.112 g, 0.415 mmol) in thf (40 mL) at ambient temperature. After the reaction mixture had been stirred for 12 h it was filtered trough Celite® and all volatiles were removed under reduced pressure to afford 0.230 g, (74%) of yellow solid **3**. Single crystals of **3** were obtained by recrystallization from thf–*n*-hexane under an argon atmosphere. Mp 230–232 °C. Analysis for $C_{33}H_{42}Cl_2N_3Te\cdot$thf: found C 56.21, H 6.33, N 5.25; calc. C 56.48, H 6.41, N 5.34. $^1H$ NMR (300.14 MHz, $CD_2Cl_2$) $\delta$: 1.06 [d, $^3J(^1H\text{-}^1H)$ = 6.9 Hz, 6 H, dpp-$CH_3$], 1.07 [d, $^3J(^1H\text{-}^1H)$ = 6.6 Hz, 6 H, dpp-$CH_3$], 1.17 [d, $^3J(^1H\text{-}^1H)$ = 7.5 Hz, 6 H, dpp-$CH_3$], 1.19 [d, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 6 H, dpp-$CH_3$], 1,76 [m, 4 H, thf], 2.29 [s, 3 H, $CH_3$], 2.72 [m, 2 H, dpp-CH], 2.83 [m, 2 H, dpp-CH], 3.62 [m, 4 H, thf], 4.17 [s, 2 H, $CH_2$], 7.15–7.20 [m, 6 H, H(arom.)-dpp], 8.25 [dd, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, $^4J(^1H\text{-}^1H)$ = 0.9 Hz, 1 H, H(arom.)-py], 8.43 [t, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 1 H, H(arom.)-py], 8.76 [dd, $^3J(^1H\text{-}^1H)$ = 8.1 Hz, $^4J(^1H\text{-}^1H)$ = 0.9 Hz, 1 H, H(arom.)-py]. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_2Cl_2$) $\delta$: 18.83, 22.48, 23.57, 23.97, 24.78, 25.69 [thf] 28.32, 28.61,57.85, 67.85 [thf], 123.78, 124.12, 125.63, 126.05, 126.18, 128.29, 134.93, 137.45, 141.53, 143.31, 144.76, 148.80, 153.19, 159.59, 162.71. $^{125}Te\{^1H\}$ NMR (157.70 MHz, $CD_2Cl_2$) $\delta$: 1314.7. LRMS ($CI^+$ *m*/*z*) (%): 482 (100%, DIMPY), 466 (DIMPY − $CH_3$). LRMS ($CI^-$ *m*/*z*) (%): 235 (100%, $TeCl_3^-$).

13 *Crystal data* for **1**: $C_{36}H_{40}I_2N_2Te$ (882.10), monoclinic, space group $P2_1/n$, $a$ = 11.663(2), $b$ = 16.601(3), $c$ = 20.231(4) Å, $\beta$ = 92.21(3)°, $V$ = 3914.2(12) Å$^3$, $Z$ = 4, $D_c$ = 1.497 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 2.360 mm$^{-1}$, $T$ = 153(2) K, 8948 independent reflections ($R_{int}$ = 0.0707), final $R$ indices (378 parameters) for 8948 independent reflections [$I < 2\sigma(I)$] are $R_1$ = 0.0609, w$R_2$ = 0.1545, GOF = 1.059. For **2**: $C_{30}H_{28}I_2NTe$ (797.94), monoclinic, space group $P2_1/n$, $a$ = 10.841(5), $b$ = 14.198(5), $c$ = 18.808(5) Å, $\beta$ = 91.621(5)°, $V$ = 2893.8(18) Å$^3$, $Z$ = 4, $D_c$ = 1.832 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 3.182 mm$^{-1}$, $T$ = 153(2) K, 6564 independent reflections ($R_{int}$ = 0.0454), final $R$ indices (322 parameters) for 6564 independent reflections [$I < 2\sigma(I)$] are $R_1$ = 0.0404, w$R_2$ = 0.0650, GOF = 1.006. For **3**: $C_{33}H_{42}Cl_3N_3Te$ (714.65), monoclinic, space group $P2_1/c$, $a$ = 14.910(3), $b$ = 14.050(3), $c$ = 21.163(4) Å, $\beta$ = 100.93(3)°, $V$ = 4353.1(15) Å$^3$, $Z$ = 4, $D_c$ = 1.090 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 0.888 mm$^{-1}$, $T$ = 153(2) K, 9933 independent reflections ($R_{int}$ = 0.0635), final $R$ indices (370 parameters) for 9933 independent reflections [$I < 2\sigma(I)$] are $R_1$ = 0.0503, w$R_2$ = 0.1115, GOF = 0.922. CCDC 614916 (**1**), CCDC 614917 (**2**), and CCDC 614918 (**3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610491f.

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