APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 1196–1201

Facile synthesis of pyridinium aryltetrachlorotellurates: crystal and molecular structure of $[C_5H_6N][RTeCl_4]$ (R = *m*-$O_2NC_6H_4$, *p*-NCC_6H_4)

Jens Beckmann*, Andrew Duthie and Cassandra Mitchell

Centre for Chiral and Molecular Technologies, Deakin University, Geelong 3217, Australia

Received 24 March 2005; Revised 22 April 2005; Accepted 1 July 2005

Arylation of $TeCl_4$ with arylboroxine–pyridine complexes $[(RBO)_3 \cdot C_5H_5N$, where R = *m*-$O_2NC_6H_4$ (1), *p*-$O_2NC_6H_4$ (2), *m*-NCC_6H_4 (3), *p*-NCC_6H_4 (4)] and advantageous moisture provided good yields of the pyridinium aryltetrachlorotellurates $[C_5H_6N][RTeCl_4]$ [R = *m*-$O_2NC_6H_4$ (5), *p*-$O_2NC_6H_4$ (6), *m*-NCC_6H_4 (7), *p*-NCC_6H_4 (8)]. Compounds 5 and 8 have been investigated by X-ray crystallography. Key features of both crystal structures are intermolecular secondary Te···Cl interactions between the aryltetrachlorotellurate anions and weak association of the cations and anions. Electrospray mass spectra of compound 5 reveal that the associative interactions also play a role in solution.

KEYWORDS: tellurium; X-ray crystallography; secondary bonding

INTRODUCTION

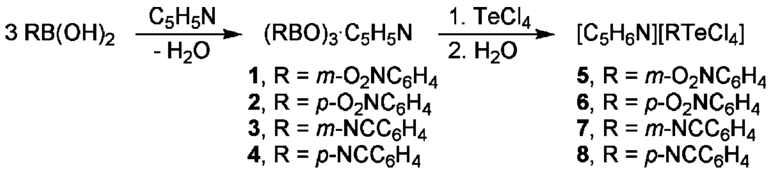
Attempts to prepare mono- and diaryltellurium chlorides from $TeCl_4$ by substitution reactions with arylmagnesium and organolithium compounds are usually unsuccessful due to competitive reduction processes and the formation of vast amounts of tellurium(II) compounds and organic by-products.[1] The arylation of $TeCl_4$ with arylmercury compounds, which is typically carried out in refluxing dioxane, is a well-established reaction for the preparation of mono- and diaryltellurium chlorides but the use of excessively toxic starting materials somewhat reduces the practicality of this method.[1] Alternative arylation reagents based on organometallic derivatives of silicon,[2] tin,[3] boron and aluminium[4] usually provide unsatisfactory results. However, recently Junk *et al.* reported the arylation of $TeCl_4$ with 'dried' arylboronic acids $[RB(OH)_2]$, which after reduction of the crude reaction mixtures with sodium bisulfite gave goods yields of diaryl ditellurides (RTeTeR) and diaryl tellurides (R_2Te).[5] Because complete drying of arylboronic acids and full conversion to water-free arylboroxines is essential to avoid hydrolytic losses of $TeCl_4$ and $RTeCl_3$ and inherently difficult to achieve in many cases, we have studied the applicability of the well-defined and water-free arylboroxine–pyridine complexes $(RBO)_3 \cdot C_5H_5N$[6] as arylation reagents in reactions with $TeCl_4$. Due to advantageous contact with moisture at the work-up stage, this reaction surprisingly afforded good yields of the pyridinium aryltetrachlorotellurates $[C_5H_6N][RTeCl_4]$.

RESULTS AND DISCUSSION

The condensation of three equivalents of arylboronic acids $[RB(OH)_2$, where R = *m*-$O_2NC_6H_4$, *p*-$O_2NC_6H_4$, *m*-NCC_6H_4, *p*-NCC_6H_4] occurred smoothly at room temperature in the presence of one equivalent of pyridine in acetone to give the new arylboroxine–pyridine complexes $(RBO)_3 \cdot C_5H_5N$ [R = *m*-$O_2NC_6H_4$ (**1**), *p*-$O_2NC_6H_4$ (**2**), *m*-NCC_6H_4 (**3**), *p*-NCC_6H_4 (**4**)] in yields of 48–98% as colourless solids (Scheme 1).[6] Compounds **1**–**4** were characterized by NMR spectroscopy and elemental analyses and the absence of water was checked by infrared (IR) spectroscopy. The reaction of compounds **1**–**4** with $TeCl_4$ in nitroethane was originally aimed at affording diaryltellurium dichlorides and was performed in a ratio of 2:3. However, in the presence of moisture at the work-up stage the pyridinium aryltetrachlorotellurates $[C_5H_6N][RTeCl_4]$ [R = *m*-$O_2NC_6H_4$ (**5**), *p*-$O_2NC_6H_4$ (**6**), *m*-NCC_6H_4 (**7**), *p*-NCC_6H_4 (**8**)] were isolated in yields of 63–81% as colourless solids. Compounds **5**–**8** were characterized by NMR spectroscopy and elemental analysis.

---

*Correspondence to: Jens Beckmann, Institut für Chemie, Freie Universität Berlin, Fabeckstrasse 34–36, 14195 Berlin, Germany.
E-mail: beckmann@chemie.fu-berlin.de



Scheme 1.

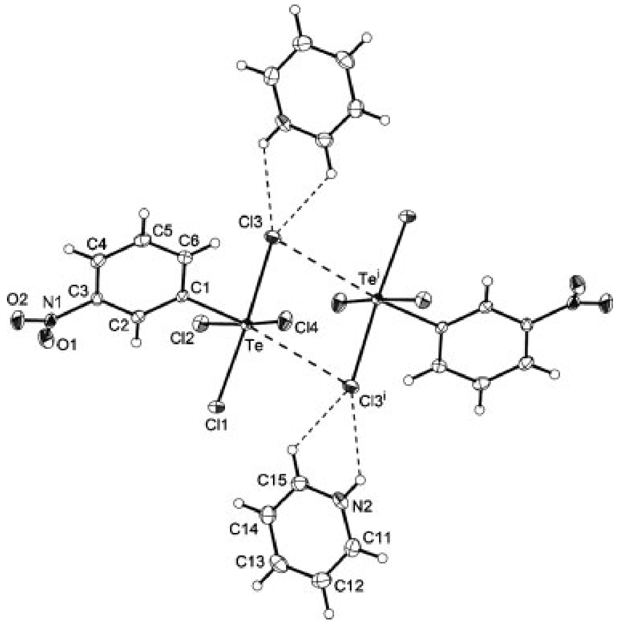


Figure 1. Molecular structure of $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (**5**) showing 50% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: i $= 1 - x, 1 - y, 1 - z$.

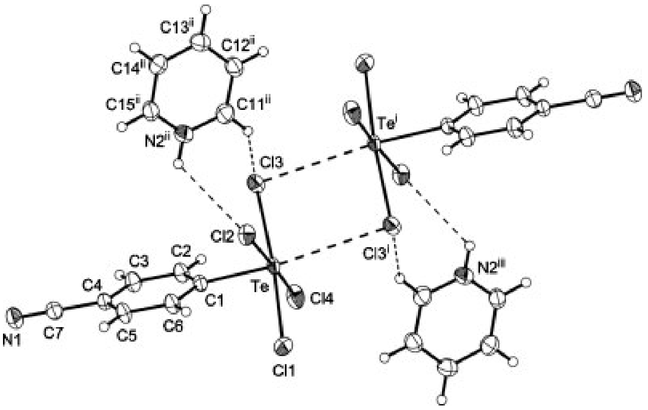


Figure 2. Molecular structure of $[C_5H_6N][p\text{-}NCC_6H_4TeCl_4]$ (**8**) showing 50% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: i $= -x, 1 - y, -z$; ii $= -1 + x, y, z$; iii $= 1 - x, 1 - y, 1 - z$.

The ^{125}Te NMR chemical shifts were observed in the small range of δ 1183–1193 ppm. Apparently the arylation of $TeCl_4$ occurs readily under the reaction conditions applied, but in the presence of pyridine, which can easily form pyridinium salts under protic conditions, the aryltellurium trichlorides are difficult to isolate. It is worth noting that the aryl groups applied, i.e. *m*- and *p*-$O_2NC_6H_4$ and *m*- and *p*-NCC_6H_4, are not amenable to Grignard-type reactions.

Until very recently only a few compounds containing monoorganotetrahalotellurate anion had been investigated by X-ray crystallography. Early examples include $[Me_3Te][MeTeCl_4]$,[7] $Bu_4N[PhTeCl_3I]$[8] and $Et_2NH_2[p\text{-}PhOC_6H_4TeCl_4]$.[9] Very recently a number of fully characterized phenyltetrahalotellurates featuring different countercations $Q[PhTeX_4]$ ($Q = C_5H_6N$, 2-Br-C_5H_5N, $\{2\text{-Br-}C_5H_5N\}\{Co(NH_3)_4Cl_2\}$, PPN; X = Cl, Br, I) were published and compared with regard to the presence or absence of secondary Te···X interactions and N–H···X–Te hydrogen bonding of the cations and the anions.[10] The crystal and molecular structures of $[C_5H_6N][m\text{-}O_2CNC_6H_4TeCl_4]$ (**5**) and $[C_5H_6N][p\text{-}NCC_6H_4TeCl_4]$ (**8**) are shown in Figs 1 and 2, and selected crystal data and geometric parameters are collected in Tables 1 and 2, respectively. The geometry of the tellurium atoms of compounds **5** and **8** is distorted octahedral when considering the first coordination sphere and the lone pair of electrons. The respective primary Te–Cl (2.138(2)/2.141(1) Å) and average Te–Cl (2.510(1)/2.518(1) Å) bond lengths of compounds **5** and **8** are comparable with other aryltetrachlorotellurate anions.[10] Interestingly, neither the nitro group of compound **5** nor the cyano group of compound **3** is involved in coordination to the tellurium atoms. A common feature of both structures is that two centrosymmetrically related anions are associated via two secondary Te···Cl contacts of 3.538(1) and 3.488(1) Å for compounds **5** and **8**, respectively. The pyridinium cations are associated with the anions via weak C–H···Cl and N–H···Cl hydrogen bonds (for compound **5** or compound **8** there are a total of five contacts shorter than 2.95 Å; see Table 2), of which the N–H···Cl bonds are the shortest (N–H···Cl3 = 2.66 Å for compound **5**; N–H···Cl2 = 2.77 Å for compound **8**).

Electrospray mass spectrometry

In an effort to determine if the association of cations and anions also exists in solution, electrospray mass spectra of $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (**5**) were collected in MeCN. In the positive mode at a cone voltage of 20 V the ESMS spectrum shows mass clusters that were assigned unambiguously to the cationic ion pairs $\{[C_5H_6N]_{n+1}[m\text{-}O_2NC_6H_4TeCl_4]_n\}^+$ [$n = 1$

Table 1. Crystal data and structure refinement for $[C_5H_6N][m\text{-}O_2CNC_6H_4TeCl_4]$ (**5**) and $[C_5H_6N][p\text{-}NCC_6H_4TeCl_4]$ (**8**)

	5	8
Formula	$C_{11}H_{10}Cl_4N_2O_2Te$	$C_{12}H_{10}Cl_4N_2Te$
Formula weight (g mol^{-1})	471.61	451.62
Crystal system	Triclinic	Monoclinic
Crystal size (mm)	0.28 × 0.38 × 0.70	0.15 × 0.23 × 0.41
Space group	$P-1$	$P2_1/n$
a (Å)	8.955(1)	9.627(2)
b (Å)	9.957(1)	12.806(2)
c (Å)	10.386(1)	12.818(2)
α (°)	103.835(2)	90
β (°)	113.716(2)	96.738(3)
γ (°)	100.599(2)	90
V (Å^3)	781.4(2)	1569.4(5)
Z	2	4
D_{calcd} (mg m^{-3})	2.005	1.911
μ (mm^{-1})	2.588	2.563
$F(000)$	452	864
θ range (°)	2.2–27.0	2.3–30.5
No. of independent reflections	3387	4763
No. of reflections observed with ($I > 2\sigma(I)$)	3341	4389
No. refined parameters	181	172
GoF (F^2)	1.10	1.09
R_1 (F) ($I > 2\sigma(I)$)	0.026	0.016
wR_2 (F^2) (all data)	0.062	0.042
CCDC deposition no.	277 471	277 472

Table 2. Selected bond parameters [Å,°] for $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (**5**) and $[C_5H_6N][p\text{-}NCC_6H_4TeCl_4]$ (**8**)[a]

5		8	
Te–Cl1	2.472(1)	Te–Cl1	2.473(1)
Te–Cl2	2.506(1)	Te–Cl2	2.540(1)
Te–Cl3	2.558(1)	Te–Cl3	2.555(1)
Te–Cl4	2.504(1)	Te–Cl4	2.504(1)
Te···Cl3^{i}	3.538(1)	Te···Cl3^{v}	3.488(1)
Te–C1	2.138(2)	Te–C1	2.141(1)
Cl2···H5^{ii}	2.82	Cl2···H2A^{vi}	2.77
Cl2···H13^{iii}	2.87	Cl2···H15^{vii}	2.79
Cl3···H2A^{i}	2.66	Cl3···H11^{vi}	2.79
Cl3···H15^{i}	2.79	Cl3···H14^{viii}	2.86
Cl4···H12^{iv}	2.90	Cl4···H3^{ix}	2.92
Cl1–Te–Cl2	90.08(2)	Cl1–Te–Cl2	88.68(1)
Cl1–Te–Cl3	176.73(2)	Cl1–Te–Cl3	175.02(1)
Cl1–Te–Cl4	90.54(2)	Cl1–Te–Cl4	92.14(1)
Cl1–Te···Cl3^{i}	83.35(2)	Cl1–Te···Cl3^{v}	101.69(1)
Cl1–Te–C1	89.06(6)	Cl1–Te–C1	88.97(4)
Cl2–Te–Cl3	89.61(2)	Cl2–Te–Cl3	88.67(1)
Cl2–Te–Cl4	174.12(2)	Cl2–Te–Cl4	177.03(1)
Cl2–Te···Cl3^{i}	98.48(2)	Cl2–Te···Cl3^{v}	101.23(2)
Cl2–Te–C1	86.81(5)	Cl2–Te–C1	88.49(4)
Cl3–Te–Cl4	89.44(2)	Cl3–Te–Cl4	90.30(1)
Cl3–Te···Cl3^{i}	99.92(2)	Cl3–Te···Cl3^{v}	82.96(1)
Cl3–Te–C1	87.67(6)	Cl3–Te–C1	86.74(4)
Cl4–Te···Cl3^{i}	87.39(2)	Cl4–Te···Cl3^{v}	81.40(2)
Cl4–Te–C1	87.36(6)	Cl4–Te–C1	88.68(4)
Cl3^{i}···Te–C1	170.72(5)	Cl3^{v}···Te–C1	165.63(4)
Te–Cl3···Te^{i}	80.09(2)	Te–Cl3···Te^{i}	97.04(1)

[a] Symmetry operations: (i) $1-x,\ 1-y,\ 1-z$; (ii) $-1+x,\ y,\ z$; (iii) $1-x,\ 2-y,\ 2-z$; (iv) $1-x,\ 1-y,\ 2-z$; (v) $-x,\ 1-y,\ -z$; (vi) $-1+x,\ y,\ z$; (vii) $1-x,\ 1-y,\ 1-z$; (viii) $-0.5+x,\ 0.5-y,\ -0.5+z$; (ix) $1-x, 1-y, -z$.

(551.9 Da), 2 (1023.8 Da), 3 (1495.6 Da), 4 (1967.5 Da), 5 (2439.3 Da); Fig. 3]. Notably, the most intense mass cluster at 1023.8 Da incorporates the dimer $[m\text{-}O_2NC_6H_4TeCl_4]_2^{2-}$ found in the solid state structure of compound **5**. In the negative mode, spectra of compound **5** were collected at cone voltages of 20 and 50 V (Fig. 4 and Table 3). At 20 V the most intense peak at 391.8 Da is related to the anion $[m\text{-}O_2NC_6H_4TeCl_4]^-$. Higher mass clusters of lower intensity were assigned unambiguously to the dinuclear anions $[(m\text{-}O_2NC_6H_4TeCl_2)_2O + Cl]^-$ (692.7 Da), $[(m\text{-}O_2NC_6H_4TeCl_4)_2 + Na]^-$ (806.6 Da), $[(C_5H_6N)(m\text{-}O_2NC_6H_4TeCl_4)_2]^-$ (863.7 Da) and the tri- and tetranuclear anions $[(C_5H_6N)_{n-1}(m\text{-}O_2NC_6H_4TeCl_3)_3 + (n+1)Cl + Na]^-$ [$n = 1$ (1163.4 Da), 2 (1278.4 Da)], $[(C_5H_6N)_n(m\text{-}O_2NC_6H_4TeCl_3)_3 + (n+1)Cl]^-$ [$n = 1$ (1220.5 Da), 2 (1335.5 Da)], $[(C_5H_6N)_n(m\text{-}O_2NC_6H_4TeCl_3)_4 + (n+1)Cl]^-$ [$n = 1$ (1575.3 Da), 2 (1692.3 Da), 3 (1807.4 Da)] and $[(C_5H_6N)_n(m\text{-}O_2NC_6H_4TeCl_3)_4 + (n+2)Cl + Na]^-$ [$n = 1$ (1635.3 Da), 2 (1750.3 Da)]. At 50 V the prominent mass cluster at 391.8 Da belonging to the tellurium(IV) anion $[m\text{-}O_2NC_6H_4TeCl_4]^-$ is the second most intense cluster in the spectrum. Surprisingly, the most intense mass cluster was found at 321.9 Da and is related to the tellurium(II) anion $[m\text{-}O_2NC_6H_4TeCl_2]^-$, which can be rationalized as the product of a reductive elimination process with the formal loss of elemental chlorine under these conditions (Eqn (1)):

$$\overset{\text{IV}}{[m\text{-}O_2NC_6H_4TeCl_4]^-} \xrightarrow{\substack{\text{ESMS cond.,}\\ \text{pos. mode, 50V}}} \overset{\text{II}}{[m\text{-}O_2NC_6H_4TeCl_2]^-} + Cl_2 \tag{1}$$

Also observed was the new mass cluster at 234.8 Da, which is associated with the tellurium(II) anion $[TeCl_3]^-$, suggesting that partial cleavage of the m-nitrophenyl groups occurs. In the range 700–1800 Da the same mass clusters were observed at 20 and 50 V, albeit with slightly

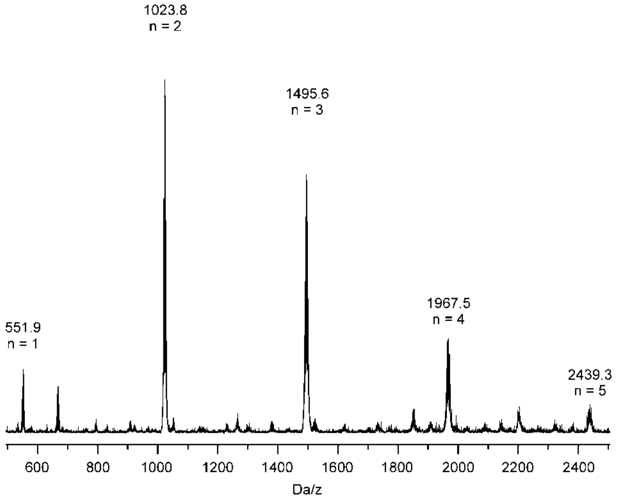


Figure 3. Electrospray mass spectrum (MeCN, positive mode, cone voltage 20 V) of $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (**5**) showing a series of mass clusters corresponding to $\{[C_5H_6N]_{n+1}[m\text{-}O_2NC_6H_4TeCl_4]_n\}^+$, where $n = 1$–5.

different intensities (Fig. 4). The presence of multinuclear cations and anions under ESMS conditions suggests that association via secondary Te···Cl bonding and C–H···Cl and N–H···Cl hydrogen bonding also plays an important role in solution.

Table 3. Peak assignments for the electrospray mass spectrum (MeCN, negative mode) of $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (**5**) at cone voltages of 20 and 50 V

		n		
		1	2	3
$[Te^{II}Cl_3]^-$	234.8			
$[RTe^{II}Cl_2]^-$	321.9			
$[(RTeCl_3)_n + Cl]^-$		391.8	748.6	1103.5
$\{(RTeCl_2)_2O + Cl\}^-$	692.7			
$\{[RTeCl_4]_2 + Na\}^-$	806.6			
$\{[C_5H_6N][RTeCl_4]_2\}^-$	863.7			
$\{[C_5H_6N]_{n-1}[RTeCl_3]_3 + (n + 1)Cl + Na\}^-$		1163.4	1278.4	
$\{[C_5H_6N]_n[RTeCl_3]_3 + (n + 1)Cl\}^-$		1220.5	1335.5	
$\{[C_5H_6N]_n[RTeCl_3]_4 + (n + 1)Cl\}^-$		1575.3	1692.3	1807.4
$\{[C_5H_6N]_n[RTeCl_3]_4 + (n + 2)Cl + Na\}^-$		1635.3	1750.3	

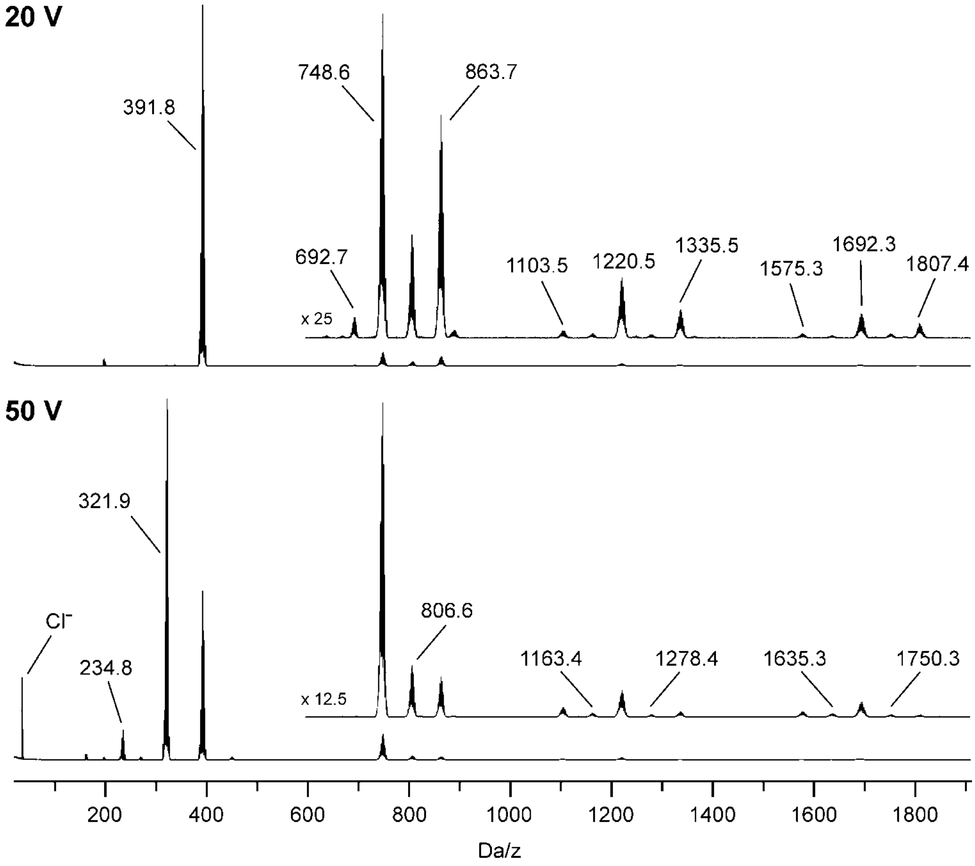


Figure 4. Electrospray mass spectrum (MeCN, negative mode) of $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (**5**) at cone voltages of 20 and 50 V. Refer to Table 3 for peak assignments.

EXPERIMENTAL

General

The arylboronic acid starting materials were purchased from Boron Molecular (Melbourne, Australia), whereas $TeCl_4$ was obtained from Aldrich. The ^1H, ^{13}C and ^{125}Te NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^1H, ^{13}C) and Me_2Te (^{125}Te). Microanalysis was carried out by CMAS, Belmont, Australia.

Synthesis of $(m\text{-}O_2NC_6H_4BO)_3\cdot C_5H_5N$ (1)

Pyridine (0.40, 5.00 mmol) was added to a solution of $m\text{-}O_2NC_6H_4B(OH)_2$ (2.50 g, 15.00 mmol) in acetone and stirred at room temperature for 15 min. The solvent was removed *in vacuo* and the residue crystallized from methanol. Collection of the precipitate by filtration and vacuum-drying gave the product as a white solid (1.44 g, 55% yield). m.p. 217–220 °C. ^1H NMR (270.17 MHz, CD_3OD): δ 7.43 (m, 3H), 7.50 (t, 2H), 7.92 (t, 1H), 7.95 (d, 3H), 8.09 (d, 3H), 8.43 (s, 3H), 8.61 (s, 2H); $^{13}C\{^1H\}$ NMR (67.94 MHz, CD_3OD): δ 125.08, 126.04, 128.81, 129.47, 138.2 (very broad), 140.13, 140.59, 147.64, 147.96, 148.85. Analysis calc. for $C_{23}H_{17}B_3N_4O_9$ (525.84): C 52.53, H 3.26, N 10.65; found: C 52.64, H 3.42, N 10.38%.

Synthesis of $(p\text{-}O_2NC_6H_4BO)_3\cdot C_5H_5N$ (2)

Pyridine (0.40, 5.00 mmol) was added to a solution of $p\text{-}O_2NC_6H_4B(OH)_2$ (2.50 g, 15.00 mmol) in acetone and stirred at room temperature for 15 min. The solvent was removed *in vacuo* and the residue crystallized from an acetone–hexane mixture. Collection of the precipitate by filtration and vacuum-drying gave the product as a light brown solid (1.26 g, 48% yield), m.p. 261–264 °C. ^1H NMR (270.17 MHz, CD_3OD): δ 7.51 (m, 2H), 7.82 (d, 6H), 7.93 (t, 1H), 8.06 (d, 6H), 8.59 (s, 2H); $^{13}C\{^1H\}$ NMR (67.94 MHz, CD_3OD): δ 122.92, 126.03, 135.48, 140.06, 144.2 (very broad), 148.19, 150.03. Analysis calc. for $C_{23}H_{17}B_3N_4O_9$ (525.84): C 52.53, H 3.26, N 10.65; found: C 52.46, H 3.61, N 10.26%.

Synthesis of $(m\text{-}NCC_6H_4BO)_3\cdot C_5H_5N$ (3)

Pyridine (0.40, 5.00 mmol) was added to a solution of $m\text{-}NCC_6H_4B(OH)_2$ (2.20 g, 15.00 mmol) in acetone and stirred at room temperature for 15 min. The solvent was removed *in vacuo* and the residue crystallized from a dichloromethane–hexane mixture. Collection of the precipitate by filtration and vacuum-drying gave the product as a white solid (1.94 g, 83% yield), m.p. 258–260 °C. ^1H NMR (270.17 MHz, CD_3OD): δ 7.38–7.52 (m, 5H), 7.65 (d, 3H), 7.86–8.00 (m, 7H), 8.56 (m, 2H); $^{13}C\{^1H\}$ NMR (67.94 MHz, CD_3OD): δ 112.42, 120.09, 125.84, 129.33, 133.92 (broad), 138.19, 139.03, 139.44, 148.82. Analysis calc. for $C_{26}H_{17}B_3N_4O_3$ (465.87): C 67.03, H 3.68, N 12.03; found: C 64.21, H 4.06, N 11.02%.

Synthesis of $(p\text{-}NCC_6H_4BO)_3\cdot C_5H_5N$ (4)

Pyridine (0.40, 5.00 mmol) was added to a solution of $p\text{-}NCC_6H_4B(OH)_2$ (2.20 g, 15.00 mmol) in acetone and stirred at room temperature for 15 min. The solvent was removed *in vacuo* and the residue crystallized from a dichloromethane–hexane mixture. Collection of the precipitate by filtration and vacuum-drying gave the product as a white solid (2.29 g, 98% yield), m.p. 243–245 °C. ^1H NMR (270.17 MHz, CD_3OD): δ 7.47–7.55 (m, 2H), 7.61 (d, 6H), 7.80 (d, 6H), 7.94 (tt, 1H), 8.60 (m, 2H); $^{13}C\{^1H\}$ NMR (67.94 MHz, CD_3OD): δ 113.85, 119.85, 126.04, 131.92, 135.13, 140.02, 148.37. Analysis calc. for $C_{26}H_{17}B_3N_4O_3$ (465.87): C 67.03, H 3.68, N 12.03; found: C 66.70, H 3.84, N 11.67%.

Synthesis of $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (5)

A solution of $(m\text{-}O_2NC_6H_4BO)_3\cdot C_5H_5N$ (1.30 g, 2.47 mmol) and $TeCl_4$ (1.00 g, 3.71 mmol) in nitroethane (25 mL) was stirred at reflux for 1 h. After cooling, the solvent was removed *in vacuo* and dichloromethane–hexane (1 : 1, 10 ml) was added. Collection of the precipitate by filtration and air-drying gave the product as a white solid (1.29 g, 74% yield), m.p. 200–201 °C. ^1H NMR (299.98 MHz, d_6-DMSO): δ 7.81 (t, 1H), 8.07 (t, 2H), 8.30 (m, 1H), 8.59 (m, 1H), 8.86 (m, 1H), 8.93 (m, 2H), 9.31 (m, 1H); $^{13}C\{^1H\}$ NMR (75.44 MHz, d_6-DMSO): δ 124.78, 127.16, 128.28, 129.33, 139.43, 142.38, 146.11, 146.90, 155.73; $^{125}Te\{^1H\}$ NMR (94.74 MHz, d_6-DMSO): δ 1185.9. Analysis calc. for $C_{11}H_9Cl_4N_2O_2Te$ (470.61): C 28.07, H 1.93, N 5.95; found: C 28.21, H 2.29, N 6.16%.

Synthesis of $[C_5H_6N][p\text{-}O_2NC_6H_4TeCl_4]$ (6)

A solution of $(p\text{-}O_2NC_6H_4BO)_3\cdot C_5H_5N$ (1.30 g, 2.47 mmol) and $TeCl_4$ (1.00 g, 3.71 mmol) in nitroethane (25 ml) was stirred at reflux for 1 h. After cooling, the solvent was removed *in vacuo* and dichloromethane/hexane (1 : 1, 10 ml) was added. Collection of the precipitate by filtration and air-drying gave the product as a light brown solid (1.10 g, 63% yield), m.p. 194–196 °C. ^1H NMR (299.98 MHz, d_6-DMSO): δ 8.09 (t, 2H), 8.31 (d, 2H), 8.63 (m, 1H), 8.70 (d, 2H), 8.91 (d, 2H); $^{13}C\{^1H\}$ NMR (75.44 MHz, d_6-DMSO): δ 122.93, 127.54, 134.95, 141.95, 146.91, 147.97, 160.82; $^{125}Te\{^1H\}$ NMR (94.74 MHz, d_6-DMSO): δ 1183.0. Analysis calc. for $C_{11}H_9Cl_4N_2O_2Te$ (470.61): C 28.07, H 1.93, N 5.95; found: C 28.39, H 2.20, N 6.02%.

Synthesis of $[C_5H_6N][m\text{-}NCC_6H_4TeCl_4]$ (7)

A solution of $(m\text{-}NCC_6H_4BO)_3\cdot C_5H_5N$ (1.15 g, 2.47 mmol) and $TeCl_4$ (1.00 g, 3.71 mmol) in nitroethane (25 ml) was stirred at reflux for 1 h. After cooling, the solvent was removed *in vacuo* and dichloromethane (10 ml) was added. Collection of the precipitate by filtration and air-drying gave the product as a white solid (1.30 g, 78% yield), m.p. 223–225 °C. ^1H NMR (299.98 MHz, d_6-DMSO): δ 7.73 (t, 1H), 7.92 (m, 1H), 8.08 (m, 2H), 8.61 (m, 1H), 8.68–8.78 (m, 2H), 8.93 (d, 2H); $^{13}C\{^1H\}$ NMR (75.44 MHz, d_6-DMSO): δ 111.03, 118.32, 127.33, 129.26, 133.46, 136.77, 137.93, 142.08, 146.56, 155.20; $^{125}Te\{^1H\}$ NMR (94.74 MHz, d_6-DMSO): δ 1188.4. Analysis calc. for

$C_{12}H_9Cl_4N_2Te$ (450.63): C 31.98, H 2.01, N 6.22; found: C 32.00, H 2.05, N 6.28%.

Synthesis of $[C_5H_6N][p\text{-}NCC_6H_4TeCl_4]$ (8)

A solution of (p-$NCC_6H_4BO)_3 \cdot C_5H_5N$ (1.15 g, 2.47 mmol) and $TeCl_4$ (1.00 g, 3.71 mmol) in nitroethane (25 ml) was stirred at reflux for 1 h. After cooling, the solvent was removed *in vacuo* and dichloromethane (10 ml) was added. Collection of the precipitate by filtration and air-drying gave the product as a white solid (1.85 g, 81% yield), m.p. 236–238 °C.

^1H NMR (299.98 MHz, d_6-DMSO): δ 7.96 (m, 2H), 8.07 (m, 2H), 8.61 (m, 3H), 8.92 (m, 2H); $^{13}C\{^1H\}$ NMR (75.44 MHz, d_6-DMSO): δ 112.32, 118.24, 127.26, 131.69, 134.12, 142.15, 146.42, 159.13; $^{125}Te\{^1H\}$ NMR (94.74 MHz, d_6-DMSO): δ 1193.7. Analysis calc. for $C_{12}H_9Cl_4N_2Te$ (450.63): C 31.98, H 2.01, N 6.22; found: C 31.85, H 2.02, N 5.90%.

Crystallography

Single crystals of $[C_5H_6N][m\text{-}O_2NC_6H_4TeCl_4]$ (**5**) and $[C_5H_6N][p\text{-}NCC_6H_4TeCl_4]$ (**8**) suitable for X-ray crystallography were grown from the slow evaporation of their respective chloroform solutions. Intensity data were collected at 173 K on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS.[11] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[12] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model. Crystallographic parameters and details of the data collection and refinement are given in Table 1. Figures were created using DIAMOND.[13]

Acknowledgement

Mrs Irene Brüdgam (Freie Universität Berlin) is gratefully acknowledged for the X-ray data collection.

REFERENCES

1. (a) Sadekov ID, Bushkov AY, Minkin VI. *Russ. Chem. Rev.* 1979; **48**: 343; (b) Maksimenko AA, Zakharov AV, Sadekov ID. *Russ. Chem. Rev.* 2000; **69**: 861; (c) Maksimenko AA, Zakharov AV, Sadekov ID. *Sulf. Rep.* 2002; **23**: 125.
2. Sadekov ID, Maksimenko AA. *J. Gen. Chem. USSR* 1977; **47**: 1755.
3. Schumann H, Magerstaedt M. *J. Organomet. Chem.* 1982; **232**: 147.
4. Rainville DP, Zingaro RA. *J. Organomet. Chem.* 1980; **190**: 277.
5. Clark AR, Nair R, Fronczek FR, Junk T. *Tetrahedron Lett.* 2002; **43**: 1387.
6. (a) McKinley NF, O'Shea DF. *J. Organomet Chem.* 2004; **69**: 5087; (b) Beckmann J, Dakternieks D, Duthie A, Lim AEK. Tiekink ERT. *J. Organomet. Chem.* 2001; **633**: 149.
7. Einstein FWB, Trotter J, Williston CS. *J. Chem. Soc. A* 1967; 2018.
8. Alcock NW, Harrison WD. *J. Chem. Soc. Dalton Trans.* 1983; 2015.
9. Chadha RK, Drake JE, Khan MA. *Can. J. Chem.* 1984; **62**: 32.
10. (a) Schulz Lang E, Fernandes RM, Peppe C, Burrow RA, Vazquez-Lopez EM. *Z. Anorg. Allg. Chem.* 2003; **629**: 215; (b) Schulz Lang E, de Oliveira GM, Fernandes RM, Vazquez-Lopez EM. *Inorg. Chem. Commun.* 2003; **6**: 869; (c) Beckmann J, Duthie A, Moran S. *Appl. Organomet. Chem.* 2005; **19**: 690.
11. SMART, SAINT and SADABS. Siemens Analytical X-ray Instruments: Madison, Wisconsin USA, 1999.
12. Farrugia LJ. *J. Appl. Cryst.* 1999; **32**: 837.
13. DIAMOND V2.1d. Crystal Impact, K. Brandenburg and M. Berndt GbR, 2002; http://www.crystalimpact.de.