One-Pot Synthesis of Pyridyltellurium Derivatives from a Reaction with Isopropylmagnesium Chloride and X-ray Crystal Structures of Various Pyridyl Ditellurides

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Dedicated to the memory of Prof. R. C. Paul (1919−2002)

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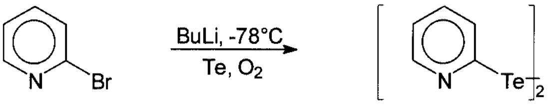
A one-pot synthesis of various symmetrical and unsymmetrical 2-pyridyl-, 2-bromo-5-pyridyl-, and 2,5-dibromo-3-pyridyltellurium compounds has been carried out, at room temperature, by selective single bromine-magnesium exchange of 2-bromo-, 2,5-dibromo- and 2,3,5-tribromopyridine, respectively, with isopropylmagnesium chloride. This exchange reaction gives the corresponding pyridylmagnesium chlorides, which, upon insertion of elemental tellurium (activated), give the pyridyltelluromagnesium chlorides, and, subsequently, the corresponding dipyridyl ditellurides upon aerial oxidation. The pyridyltelluromagnesium chlorides give unsymmetrical pyridyltellurium derivatives in good yield upon treatment with alkyl halides. The X-ray crystal structures of bis(2-pyridyl) ditelluride, bis(2,5-dibromo-6-methyl-3-pyridyl) ditelluride and bis(2,5-dibromo-3-pyridyl) ditelluride are discussed.

Introduction

Organic synthesis using tellurium-based methodologies has recently become increasingly important.[1,2] Compared to alkyl- and aryltellurium compounds,[3,4] the use of pyridyltellurium derivatives in organic synthesis has been relatively less studied. This may primarily be due to the lack of a convenient and efficient synthesis of these compounds. Most recently developed methods for the syntheses of dipyridyl ditellurides involve either deprotonation of BF_3-complexed pyridine[5] or bromine-lithium exchange[6] of 2-bromopyridine with BuLi at −78 °C followed by tellurium insertion and subsequent aerial oxidation. The low temperature invariably required in these preparations restricts its utility in large-scale preparations (Scheme 1).



Scheme 1. Preparation of dipyridyl ditellurides at low temperature

Owing to the instability of the lithiated pyridine the reaction has to be carried out at low temperature in order to avoid its decomposition. The corresponding pyridylmagnesium halides are comparatively stable even at higher temperatures (>25 °C). However, pyridylmagnesium halides are extremely difficult to generate directly from the corresponding halides and magnesium.[7−10] Meunier et al.[11] have reported a magnesium-halogen exchange reaction that generates pyridylmagnesium halides, although the successful quenching of pyridylmagnesium halides with electrophiles was achieved only recently.[12−14] In continuation of our ongoing project on the chemistry of pyridyltellurium compounds,[15−18] we decided to examine the reactivity of pyridylmagnesium halides for the synthesis of pyridyltellurium derivatives. Colonna et al. have also reported the synthesis of dipyridyl ditelluride in very low yield by employing magnesium-halogen exchange of 2-bromopyridine with ethylmagnesium bromide, although the results were later found to be non-reproducible.[19]

Result and Discussion

We found that elemental tellurium adds smoothly to 2-pyridylmagnesium chloride (**1a**), generated in situ by the bromine-magnesium exchange reaction between 2-bromopyridine and *i*PrMgCl in THF, at room temperature, to afford a species chemically equivalent to 2-pyridyltelluromag-

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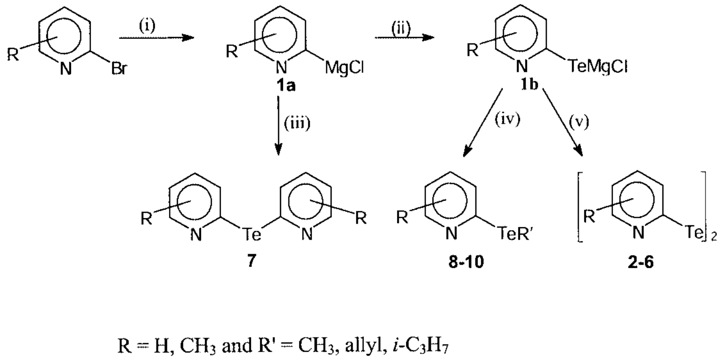


Scheme 2. Reagents and conditions: (i) *i*PrMgCl (1.2 equiv.), THF, room temp.; (ii) Te, 15 min; (iii) R-Py_2Te_2; (iv) R′X (X = Br, I), (v) H_2O, O_2

nesium chloride (**1b**). Its aerial oxidation gave dipyridyl ditelluride in moderate to excellent yields. Reaction of **1b** with a number of electrophiles gives unsymmetrical 2-alkyltelluropyridines in good yields (Scheme 2).

This protocol was extended to the selective synthesis of various symmetrical 3,3′-dipyridyl and 5,5′-dipyridyl ditellurides. We found that when *i*PrMgCl reacts with 2,5-dibromopyridine, a single bromine-magnesium exchange takes place at C-5 of the pyridine ring, which is attributed to the fact that electrophilic attack at C-5 is more favorable than atC-2. The bromine-magnesium exchange with 2,3,5-tribromopyridine occurs at C-3 due to the *ortho* activating effect of the bromine present at C-2. Further bromine-magnesium exchange was not possible even after the addition of a twofold excess of *i*PrMgCl, as shown in Scheme 3. The present methodology was also successfully extended to a variety of methyl-substituted 2-bromopyridines. The scope and efficiencies are summarized in the Exp. Sect.

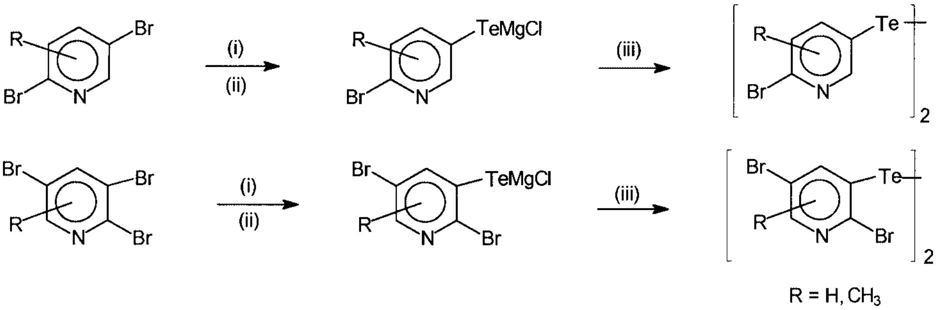
As a part of our ongoing study, we also compared the efficiency of the reaction by employing different Grignard reagents, such as ethylmagnesium bromide, *n*-propylmagnesium bromide, isopropylmagnesium chloride and butylmagnesium chloride. The results are given for the formation of bis(2-pyridyl) ditelluride in Table 1. These results show that a more sterically hindered Grignard reagent gives a better yield. This may be attributed to the fact that a more hindered Grignard reagent imparts stability to the pyridylmagnesium halide, thereby increasing the yield.

Table 1. Influence of the different Grignard reagents on the efficiency of the reaction

Grignard reagent	Compound	Solvent	Yield (%)
EtMgBr	Bis(2-pyridyl) ditelluride	THF	5
*i*PrMgCl	Bis(2-pyridyl) ditelluride	THF	80
*n*BuMgCl	Bis(2-pyridyl) ditelluride	THF	70
*n*PrMgBr	Bis(2-pyridyl) ditelluride	THF	27

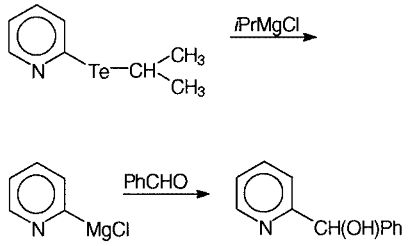
It is important to note that the use of an equimolar amount of bromopyridine and *i*PrMgCl resulted in a poor yield; however, a slight excess of *i*PrMgCl increased the yield considerably. We must emphasise that the conditions throughout the reaction have to be extremely dry as even traces of moisture can hinder the insertion of tellurium into the species **1a**.

Among the various applications of organotellurium compounds, transmetallation with organolithium or organocuprate reagents[20] is considered to be synthetically important. As a representative example, the transmetallation reaction of isopropyltelluropyridine with *i*PrMgCl was also carried out for C−C bond formation. Subsequent quenching with benzaldehyde in THF at room temperature gave phenyl(2-pyridyl)methanol in 65% yield, indicating a clean tellurium-magnesium exchange as shown in Scheme 4. This exchange is operationally simple and represents a consider-



Scheme 3. Reagents and conditions: (i) *i*PrMgCl, THF, room temp., 2 h; (ii) Te, 15 min; (iii) H_2O, O_2

able improvement over the reported method[21] in terms of the reaction conditions, ease and efficiency of the reaction on a molar scale.



Scheme 4. Transmetalation reaction of isopropyltelluropyridine with *i*PrMgCl

Table 2. Chemical-shift values (δ) of various symmetrical pyridyltellurium derivatives[a]

Compound	^{1}H (CH_3)	^{13}C (CH_3)	^{125}Te
Py_2Te_2	–	–	439
$(3\text{-}CH_3Py)_2Te_2$	2.449	24.679	473
$(4\text{-}CH_3Py)_2Te_2$	2.224	20.741	422
$(5\text{-}CH_3Py)_2Te_2$	2.286	17.807	436
$(3\text{-}CH_3\text{-}5\text{-}Br\text{-}Py)_2Te_2$	2.432	24.484	485
$(5\text{-}Br\text{-}Py)_2Te_2$	–	–	440
$(2,5\text{-}Br_2\text{-}Py)_2Te_2$	–	–	414
$(6\text{-}CH_3\text{-}2,5\text{-}Br_2\text{-}Py)_2Te_2$	2.609	23.881	407

^{125}Te chemical shift values could not be determined for unsymmetrical pyridyltellurium derivatives due their instability, particularly in solution.

^{125}Te NMR chemical shifts are listed in Table 2 and are found to be sensitive to the nature of the substituents present on the pyridine ring. The chemical shift for $(Br_2PyTe)_2$ is found at the most shielded position (δ = 407 ppm) and that for $(3\text{-}CH_3\text{-}5\text{-}BrPyTe)_2$ is found at the most deshielded position (δ = 485 ppm). For compounds **3** and **4**, in which a methyl group is substituted on the pyridine ring at the *meta* and *para* positions to the tellurium atom, respectively, the observed signals at δ = 422 and 436 ppm, respectively, indicate that the ^{125}Te resonance is influenced by polar effects due to shielding by an electron-donating group[22] i.e. the methyl group. Interestingly, when the methyl group is present *ortho* to tellurium on the ring, deshielding of the ^{125}Te resonance is observed (signals at δ = 473 and 485 ppm for compounds **2** and **7**, respectively). Conformational constraints and through-space interactions between the methyl group and tellurium are suggested as possible reasons for this observation. It is also noted that the ^{125}Te resonances for **8** and **9** are at δ = 407 and 414 ppm, respectively, which is attributed to intramolecular through-space interactions between the bromine and tellurium atoms. These interactions, being intramolecular, are also likely to be found in solution ppm. ^{125}Te NMR spectra of alkylpyridyltellurium compounds could not be recorded, as these compounds are exceedingly unstable in solution.

Solid-State Structures

Molecular Geometry and Crystal Structure of Bis(2-pyridyl) Ditelluride (1)

A single crystal of **1** was obtained by slow evaporation of a solution of **1** in diethyl ether and hexane. The molecular structure of **1** with the atom numbering scheme is given in Figure 1. Selected bond angles and bond lengths are given in Table 3. The molecule crystallizes in the triclinic $P\bar{1}$ space group with unit-cell dimensions a = 6.2870(4) Å, b = 8.4928(7) Å, c = 11.7370(12) Å and α = 109.101°, β = 99.717°, γ = 89.829(6)°. The molecular geometry of the pyridine rings is as expected in terms of bond angles and bond lengths. The two pyridine rings have an average C−C bond length of 1.37 Å and C−C−C bond angle of 119° (slightly distorted). The Te−Te bond length is significantly shorter (2.6759 Å) than the single covalent Te−Te bond length (2.74 Å) on the Pauling scale.[23] The Te(1)−C(1) [2.136(7) Å] and Te(2)−C(6) [2.144(6) Å] distances are also slightly longer than the some of the Pauling single-bond covalent radii for Te−C(sp^2) single bonds (2.11 Å), but are similar to the values found in bis(2-naphthyl) ditelluride[24] [2.135(6), 2.127(5) Å]. The C−E−E−C torsion angles are similar: 87.1° for E = S,[25] 84.3(2)° for E = Se[26] and 86.3(2)° for E = Te.

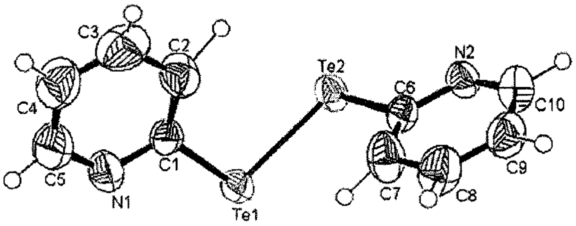


Figure 1. Perspective view of bis(2-pyridyl) ditelluride

Molecular Geometry and Crystal Structure of Bis(2,5-dibromo-3-pyridyl) Ditelluride (8)

Needle-shaped copper-colored crystals of compound **8** were obtained by slow evaporation of a solution in dichloromethane and hexane. The molecular structure of **8** with atom numbering scheme is given in Figure 2 (a). Selected bond angles and bond lengths are given in Table 4. The molecule crystallizes in the monoclinic space group $C2/c$ with cell dimensions a = 12.5073(15) Å, b = 9.4521(11) Å, c = 14.1713(13) Å and α = 90.00°, β = 111.707°, γ = 90.00°. The Te(1)−Te(2) bond length of this ditelluride [2.6830(15) Å] is significantly shorter than the sum of the Pauling single-bond covalent radii but is quite similar to the value found for compound **1**. The Te(1)−C(1) [2.127(13) Å] distance is also quite similar to the single C−Te bond in compound **1**. The Te(1)−N(1) distance (3.421 Å) is much higher than the sum of the covalent radii but is within the van der Waal distance of 3.61 Å[27] and therefore can be

Table 3. Bond lengths (Å) and angles (°) and torsion angles (°) for bis(2-pyridyl) ditelluride

Te(1)−C(1)	2.14(7)	C(1)−Te(1)−Te(2)	101.2(18)
Te(1)−Te(1)	2.68(6)	C(6)−Te(2)−Te(1)	100.6(17)
Te(2)−C(6)	2.14(6)	C(6)−N(2)−C(10)	116.9(6)
N(1)−C(1)	1.32(9)	N(1)−C(1)−C(2)	123.9(7)
N(1)−C(5)	1.33(11)	N(1)−C(1)−Te(1)	111.5(5)
N(2)−C(6)	1.33(9)	C(2)−C(1)−Te(1)	124.7(5)
N(2)−C(10)	1.37(10)	C(1)−C(2)−C(3)	117.3(8)
C(1)−C(2)	1.37(10)	C(1)−C(2)−H(2)	134.0(5)
C(2)−C(3)	1.40(13)	C(3)−C(2)−H(2)	105.0(5)
C(2)−H(2)	1.20(11)	C(4)−C(3)−C(2)	119.2(9)
C(3)−C(4)	1.34(15)	C(4)−C(3)−H(3)	127.0(5)
C(3)−H(3)	0.82(7)	C(2)−C(3)−H(3)	113.0(5)
C(4)−C(5)	1.38(14)	C(3)−C(4)−C(5)	119.2(9)
C(4)−H(4)	0.62(11)	C(3)−C(4)−H(4)	134.0(10)
C(5)−H(5)	1.06(8)	C(5)−C(4)−H(4)	107.0(10)
C(6)−C(7)	1.32(10)	N(1)−C(5)−C(4)	122.7(9)
C(7)−C(8)	1.37(12)	N(1)−C(5)−H(5)	114.0(5)
C(8)−C(9)	1.36(13)	N(2)−C(6)−C(7)	123.7(7)
C(8)−H(8)	0.97(8)	N(2)−C(6)−Te(2)	113.8(5)
C(9)−C(10)	1.38(12)	C(7)−C(6)−Te(2)	122.4(5)
C(9)−H(9)	0.92(6)	C(6)−C(7)−C(8)	119.0(7)
C(10)−H(10)	0.97(9)	C(6)−C(7)−H(7)	122.0(10)
C(1)−Te(1)−Te(2)−C(6)	86.30(2)	C(5)−N(1)−C(1)−C(2)	−2.0(12)
C(5)−N(1)−C(1)−Te(1)	178.50(8)	Te(2)−Te(1)−C(1)−N(1)	168.4(5)
Te(2)−Te(1)−C(1)−C(2)	−11.00(7)	N(1)−C(1)−C(2)−C(3)	2.0(13)
Te(1)−C(1)−C(2)−C(3)	−178.60(7)	C(1)−C(2)−C(3)−C(4)	−0.3(15)
Te(2)−C(6)−C(7)−C(8)	179.00(7)	C(10)−N(2)−C(6)−C(7)	1.5(11)
C(10)−N(2)−C(6)−Te(2)	178.80(5)	Te(1)−Te(2)−C(6)−N(2)	169.5(4)

Table 4. Bond lengths (Å) and angles (°) and torsion angles (°) for bis(2,5-dibromo-3-pyridyl) ditelluride[a]

Te(1)−C(1)[a]	2.13(13)	C(1)−Te(1)−Te(1)#1	100.1(3)
Te(1)−Te(1)#1	2.68(15)	C(2)−N(1)−C(3)	119.1(10)
Br(1)−C(2)	1.90(12)	C(5)−C(1)−C(2)	117.6(11)
Br(2)−C(4)	1.89(12)	C(5)−C(1)−Te(1)	123.6(8)
N(1)−C(2)	1.31(17)	C(2)−C(1)−Te(1)	118.8(9)
N(1)−C(3)	1.33(18)	N(1)−C(2)−C(1)	124.8(11)
C(1)−C(5)	1.39(16)	N(1)−C(2)−Br(1)	116.7(8)
C(1)−C(2)	1.40(16)	C(1)−C(2)−Br(1)	118.4(9)
C(3)−C(4)	1.39(16)	N(1)−C(3)−C(4)	120.6(11)
C(3)−H(3)	0.93	N(1)−C(3)−H(3)	119.7
C(4)−C(5)	1.42(16)	C(4)−C(3)−H(3)	119.7
C(5)−H(5)	0.93	C(3)−C(4)−Br(2)	119.2(9)
Te(1)#1−Te(1)−C(1)−C(5)	−11.90(9)	Te(1)#1−Te(1)−C(1)−C(2)	169.1(8)
C(3)−N(1)−C(2)−C(1)	0.00(18)	C(3)−N(1)−C(2)−Br(1)	176.9(8)
C(5)−C(1)−C(2)−N(1)	0.80(17)	Te(1)−C(1)−C(2)−N(1)	179.8(9)
Te(1)−C(1)−C(2)−Br(1)	3.00(12)	Te(1)−C(1)−C(5)−C(4)	−179.8(8)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + 3/2$.

considered as a weak interaction. The Te(1)−Br(1) distance (3.82 Å) is shorter than the sum of the van der Waal radii (4.06 Å). The Br(1)···Br(1) contacts (3.61 Å) are shorter than the Br(1)···Br(2) and Br(2)···Br(2) short contacts (3.948 Å and 3.960 Å, respectively). These observations clearly indicate that the molecules are bridged together by intermolecular secondary interactions. The crystal packing depicting these secondary interactions is shown in Figure 2 (b) and the distances are given in Table 5.

Table 5. Secondary interactions in bis(2,5-dibromo-3-pyridyl) ditelluride

Atoms	Interatomic distances	Symmetry transformations
Te1···Br2	3.821	$x, 1 - y$, z − 0.5
Br1···Br1	3.607	$2x, y, 1.5 - z$
Br1···Br2	3.948	$1.5 - x, 0.5 - y, 2 - z$
Br1···Br2	3.980	$x, 1 - y, z - 0.5$
Br2···Br2	3.960	$1.5 - x, 1.5 - y, 2 - z$

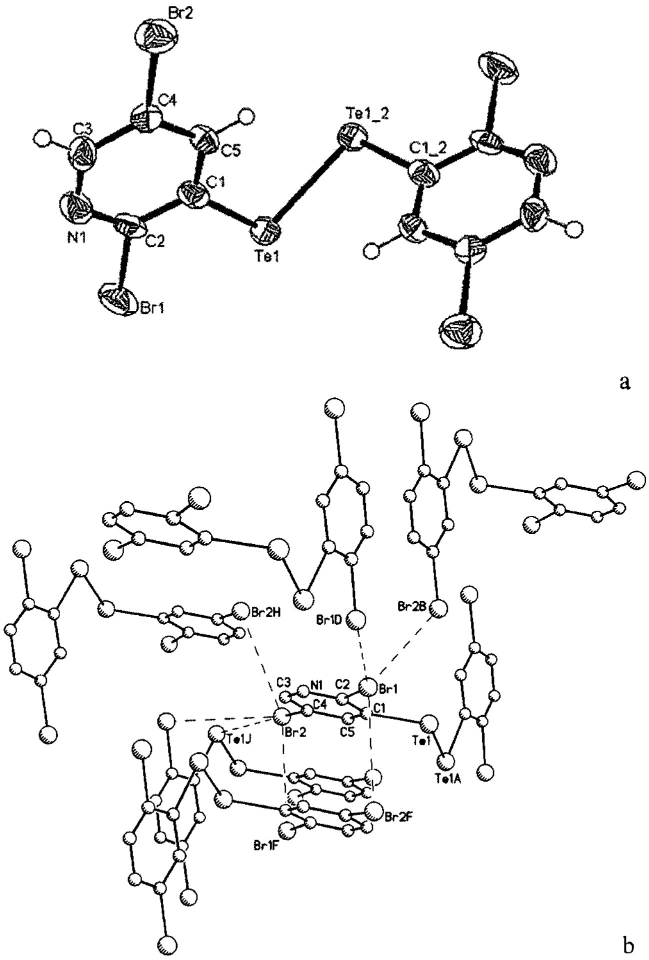


Figure 2. a) Perspective view of bis(2,5-dibromo-3-pyridyl) ditelluride; b) secondary interactions

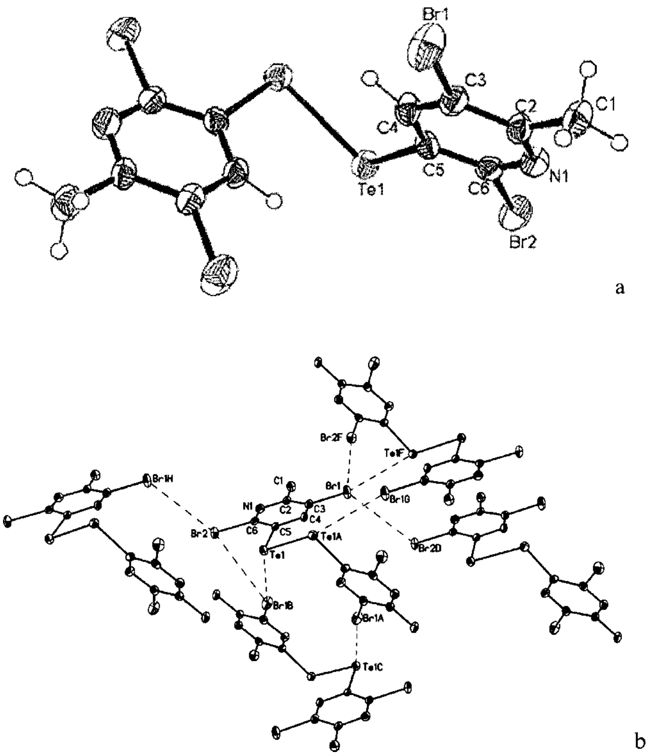


Figure 3. a) Perspective view of bis(2,5-dibromo-6-methyl-3-pyridyl) ditelluride; b) secondary interactions

Molecular Geometry and Crystal Structure of Bis(2,5-dibromo-6-methyl-3-pyridyl) Ditelluride (9)

Deep-red plates of **9** were obtained by slow evaporation of a solution in diethyl ether and hexane. The molecular

Table 6. Bond lengths (Å) and angles (°) and torsion angles (°) for bis(2,5-dibromo-6-methyl-3-pyridyl) ditelluride[a]

Te(1)−C(5)[a]	2.130(8)	C(5)−Te(1)−Te(1)#1	99.5(2)
Te(1)−Te(1)#1	2.69(11)	C(6)−N(1)−C(2)	119.1(7)
Br(1)−C(3)	1.89(9)	C(2)−C(1)−H(1A)	109.5
Br(2)−C(6)	1.91(9)	C(2)−C(1)−H(1B)	109.5
N(1)−C(6)	1.32(12)	H(1A)−C(1)−H(1B)	109.5
N(1)−C(2)	1.34(12)	C(2)−C(1)−H(1C)	109.5
C(1)−C(2)	1.50(12)	H(1A)−C(1)−H(1C)	109.5
C(1)−H(1A)	0.96	H(1B)−C(1)−H(1C)	109.5
C(1)−H(1B)	0.96	N(1)−C(2)−C(3)	119.6(8)
C(1)−H(1C)	0.96	N(1)−C(2)−C(1)	117.4(7)
C(2)−C(3)	1.39(11)	C(3)−C(2)−C(1)	123.0(8)
C(3)−C(4)	1.38(12)	C(4)−C(3)−Br(1)	118.6(6)
C(4)−C(5)	1.39(12)	C(3)−C(4)−H(10)	114.0(6)
C(4)−H(10)	0.98(11)	C(6)−C(5)−C(4)	116.1(8)
C(5)−C(6)	1.38(12)	C(6)−C(5)−Te(1)	121.1(6)
C(6)−N(1)−C(2)−C(3)	−1.10(12)	N(1)−C(2)−C(3)−C(4)	0.1(13)
C(1)−C(2)−C(3)−C(4)	177.50(8)	N(1)−C(2)−C(3)−Br(1)	−179.0(6)
C(3)−C(4)−C(5)−Te(1)	175.40(6)	Te(1)#1−Te(1)−C(5)−C(6)	−163.1(6)
Te(1)#1−Te(1)−C(5)−C(4)	19.60(7)	Te(1)−C(5)−C(6)−N(1)	−176.3(6)
Te(1)−C(5)−C(6)−Br(2)	3.40(9)	C(4)−C(5)−C(6)−Br(2)	−179.1(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, y, $-z + 3/2$.

structure of **9** with atom numbering scheme is given in Figure 3a. Selected bond angles and bond lengths are given in Table 6. The molecule crystallizes in the monoclinic space group $C2/c$ with cell dimensions a = 13.7342(15) Å, b = 12.1460(6) Å, c = 11.8950(10) Å and α = 90.00°, β = 116.663(8)°, γ = 90.66(8)°. The Te(1)−Te(2) bond length of this ditelluride [2.6847(11) Å] is only slightly longer than in molecule **8**, and the C(1)−Te(1) distance [2.130(8) Å] is also slightly longer than in **8**. The Te(1)−Br(1) distance [3.868 Å] is shorter than the sum of the van der Waal radii (4.06 Å) and therefore can be considered as a weak interaction. The various secondary interactions observed in the molecule are shown in Figure 3b and listed in Table 7.

Table 7. Secondary interactions in bis(2,5-dibromo-6-methyl-3-pyridyl) ditelluride

Atoms	Interatomic distances	Symmetry transformations
Te1···Br1	3.868	$x, -y, 0.5 + z$
Br1···Br2	3.937	$0.5 + x, 0.5 + y, z$
Br1···Br2	4.039	$x, -y, z - 0.5$

Conclusion

We have presented a mild and efficient protocol for hitherto difficult to synthesize pyridyltellurium compounds in moderate to excellent yields using readily available reagents, at room temperature, and studied their application in transmetallation reactions.

Experimental Section

All experiments were carried out under a dry, oxygen-free nitrogen atmosphere. All the reagents and solvents were purified and dried by standard techniques and deoxygenated by bubbling oxygen-free dry nitrogen gas through them prior to use. Infrared spectra were recorded between KBr pellets on a Perkin-Elmer Model 1430 ratio recording spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard — ^{125}Te NMR spectra are referenced to dimethyl telluride — on a Jeol 300 MHz spectrometer. The mass spectra were obtained on a VG 705 11 250J Mass spectrometer. Carbon, hydrogen and nitrogen were estimated microanalytically on a Perkin- Elmer 2400 CHN elemental analyzer. Bromopyridines were prepared from the corresponding 2-aminopyridines by literature methods.[28,29]

General Method for the Preparation of Symmetrical Dipyridyl Ditellurides: Bromopyridine (20 mmol) was added dropwise to a vigorously stirred mixture of isopropylmagnesium chloride (22 mmol) in THF. After stirring for 2 h at room temperature the mixture was cooled in an ice bath and elemental tellurium (20 mmol) was added. After all the tellurium had dissolved, the stirring was stopped and the reaction was diluted with acidified water. The mixture was then extracted with diethyl ether (4 × 100 mL) and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residue was purified by silica gel column chromatography with hexane/ethyl acetate (5:1) as eluent.

Bis(2-pyridyl) Ditelluride{[$(C_5H_4N)Te]_2$} (1): Yield: 2.8 g (70%). M.p. 48−50 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.98 (dt, $^{4}J_{H,H}$ = 2.0, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, *m* to N), 7.35 (dt, $^{4}J_{H,H}$ = 2.0, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, *p* to N), 7.94 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, *o* to Te), 8.42 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, *o* to N) ppm. ^{13}C NMR: δ = 121.57, 131.15, 135.3, 137.0, 149.9 ppm. ^{125}Te NMR: δ = 439 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2920, 1565, 1552, 1444, 1105, 1076, 1031, 983, 748, 660, 543, 458 cm^{-1}. $C_{10}H_8N_2Te_2$: calcd. C 29.26, H 1.95, N 6.82; found C 29.16, H 1.91, N 6.85.

Bis(3-methyl-2-pyridyl) Ditelluride {[$(3\text{-}MeC_5H_3N)Te]_2$} (2): Yield: 3.5 g (70%). M.p. 120−125 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.4 (s, 6 H, CH_3), 7.05 (t, $^{3}J_{H,H}$ = 8.0 Hz, *m* to N), 7.47 (dd, $^{4}J_{H,H}$ = 2.3, $^{4}J_{H,H}$ = 8.0 Hz, 2 H, *p* to N), 8.24 (dd, $^{4}J_{H,H}$ = 2.3, $^{4}J_{H,H}$ = 8.0 Hz, 2 H, *o* to N) ppm. ^{13}C NMR: δ = 24.6, 122.46, 135.29, 138.33, 140.6, 148.3 ppm. ^{125}Te NMR: δ = 473 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2960, 1580, 1540, 1430, 1120, 1090, 1020, 1090, 1020, 840, 780, 660, 540 cm^{-1}. EI-MS: *m*/*z* (%) = 444 (7.33) [M]$^{+}$, 314 (14.51) [M − Te]$^{+}$, 183 (76.62) [M − Te_2H]$^{+}$, 92 (100) [M − CH_3PyTe_2]$^{+}$. $C_{12}H_{12}N_2Te_2$: calcd. C 32.43, H 2.70, N 6.30; found C 32.60, H 2.42, N 6.18.

Bis(4-methyl-2-pyridyl) Ditelluride {[$(4\text{-}MeC_5H_3N)Te]_2$} (3): Yield: 3.2 g (68%). M.p. 92−92 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.24 (s, 6 H, CH_3), 6.81 (d, $^{3}J_{H,H}$ = 4.8 Hz, 2 H, *m* to N), 7.82 (s, 2 H, *o* to Te), 8.25 (d, $^{3}J_{H,H}$ = 4.8 Hz, 2 H, *o* to N) ppm. ^{13}C NMR: δ = 20.7, 122.86, 131.68, 135.0, 148.27, 149.39 ppm. ^{125}Te NMR: δ = 422 ppm. IR (KBr): $\tilde{\nu}$ = 3025, 2963, 2908, 1573, 1546, 1261, 1097, 1020, 865, 685, 473 cm^{-1}. EI-MS: *m*/*z* (%) = 444 (1.8) [M]$^{+}$, 314 (41.15) [M − Te]$^{+}$, 183 (37.5) [M − Te_2]$^{+}$, 92 (100) [CH_3Py]$^{+}$. $C_{12}H_{12}N_2Te_2$: calcd. C 32.43, H 2.70, N 6.30; found C 32.74, H 2.13, N 6.92.

Bis(5-methyl-2-pyridyl) Ditelluride {[$(5\text{-}MeC_5H_3N)Te]_2$} (4): Yield: 3.5 g (70%). M.p. 110−112 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.28 (s, 6 H, CH_3), 7.18 (d, $^{3}J_{H,H}$ = 4.8 Hz, 2 H, *o* to Te), 7.91 (d, $^{3}J_{H,H}$ = 4.8 Hz, 2 H, *p* to N), 8.27 (s, 2 H, *o* to N) ppm. ^{13}C NMR: δ = 17.8, 131.0, 131.4, 134.9, 137.8, 150.2 ppm. ^{125}Te NMR: δ = 436 ppm. IR (KBr): $\tilde{\nu}$ = 3033, 2969, 2917, 1582, 1544, 1526, 1368, 1272, 1073, 983, 835, 694, 520 cm^{-1}. EI-MS: *m*/*z* (%) = 444 (8.2) [M]$^{+}$, 314 (12.1) [M − Te]$^{+}$, 183 (67.3) [M − Te_2H]$^{+}$, 92 (100) [M − CH_3PyTe_2]$^{+}$. $C_{12}H_{12}N_2Te_2$: calcd. C 32.43, H 2.70, N 6.30; found C 32.83, H 2.12, N 6.19.

Bis(6-methyl-2-pyridyl) Ditelluride {[$(6\text{-}MeC_5H_3N)Te]_2$} (5): Yield: 3.2 g (68%). M.p. 55−56 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.48 (s, 6 H, CH_3), 6.63 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, *m* to N), 7.19 (t, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, *p* to N), 7.63 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, *o* to Te) ppm. ^{13}C NMR: δ = 24.1, 121.1, 127.9, 134.6, 156.6, 156.6 ppm. IR (KBr): $\tilde{\nu}$ = 3033, 2969, 2917, 1582, 1544, 1526, 1368, 1272, 1073, 983, 835, 694, 520 cm^{-1}. EI-MS: *m*/*z* (%) = 444 (5.5) [M]$^{+}$, 314 (5.5) [M − Te]$^{+}$, 183 (30.9) [M − Te_2H]$^{+}$, 92 (100) [M − CH_3PyTe_2]$^{+}$. $C_{12}H_{12}N_2Te_2$: calcd. C 32.43, H 2.70, N 6.30; found C 32.21, H 2.52, N 6.18.

Bis(2-bromo-5-pyridyl) Ditelluride {[$(2\text{-}Br\text{-}5\text{-}C_5H_3N)Te]_2$} (6): Yield: 3.53 g (62%). M.p. 180 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.63 (d, $^{4}J_{H,H}$ = 2.0 Hz, 2 H, *m* to N), 7.86 (dd, $^{4}J_{H,H}$ = 2.0, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, *p* to N), 7.34 (d, $^{4}J_{H,H}$ = 8.0 Hz, 2 H, *o* to N) ppm. ^{13}C NMR: δ = 103.6, 129.2, 143.0, 148.0, 157.7 ppm. ^{125}Te NMR: δ = 440 ppm. EI-MS: *m*/*z* (%) = 574 (40.4) [M (^{130}Te)]$^{+}$, 442 (12.8) [$(BrPy)_2Te$]$^{+}$, 286 (61.7) [BrPyTeH]$^{+}$, 78 (100) [PyH]$^{+}$. $C_{10}H_6Br_2N_2Te_2$: calcd. C 21.12, H 1.05, N 4.92; found C 21.20, H 1.00, N 4.85.

Bis(2-bromo-3-methyl-5-pyridyl) Ditelluride {[$(2\text{-}Br\text{-}3\text{-}Me\text{-}5\text{-}C_5H_2N)Te]_2$} (7): Yield: 3.0 g (60%). M.p. 110−112 °C. ^{1}H NMR

(300 MHz, $CDCl_3$, 25 °C): $\delta = 2.43$ (s, 2 H, CH_3), 7.46 (d, $^4J_{H,H} = 2.0$ Hz, 2 H, *p* to N), 8.31 (d, $^4J_{H,H} = 2.0$ Hz, 2 H, *o* to N) ppm. ^{13}C NMR: $\delta = 24.4$, 120.5, 137.6, 137.9, 139.6, 149.1 ppm. ^{125}Te NMR: $\delta = 485$ ppm. EI-MS: *m/z* (%) = 602 (43.8) [M (^{130}Te)]$^+$, 570 (5.1) $[(BrPyTe)_2]^+$, 457 (15.2) $[(CH_3BrPy)_2Te]^+$, 444 (4.8) $[CH_3PyTe]_2{}^+$, 299 (20.5) $[CH_3BrPyTeH]^+$, 78 (100) $[PyH]^+$. $C_{12}H_{10}Br_2N_2Te_2$: calcd. C 24.08, H 2.00, N 4.68; found C 24.21, H 1.94, N 4.63.

Bis(2,5-dibromo-3-pyridyl) Ditelluride{[(2,5-Br$_2$-3-C$_5$H$_2$N)Te]$_2$} (8): Yield: 4.32 g (60%). M.p. 185 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.05$ (d, $J_{H,H} = 2.0$ Hz, 2 H, p to N), 8.21 (d, $J_{H,H} = 2.0$ Hz, 2 H, o to N) ppm. ^{13}C NMR: $\delta = 113.0$, 122.3, 143.6, 148.2, 150.3 ppm. ^{125}Te NMR: $\delta = 414$ ppm. EI-MS: *m/z* (%) = 600 (27.5) $[(Br_2Py)_2Te]^+$, 520 (3.1) $[BrPyTeBr_2PyH]^+$, 440 (21.6) $[(BrPy)_2TeH]^+$, 366 (100) $[Br_2PyTeH]^+$. $C_{10}H_4Br_4N_2Te_2$: calcd. C 16.52, H 0.55, N 3.85; found C 16.38, H 0.51, N 3.79.

Bis(2,5-dibromo-6-methyl-3-pyridyl) Ditelluride {[(2,5-Br$_2$-6-Me-3-C$_5$HN)Te]$_2$} (9): Yield: 3.6 g (55%). M.p. 85−88 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.58$ (s, 6 H, CH_3), 7.48 (s, 2 H, p to N) ppm. ^{13}C NMR: $\delta = 22.7$, 120.1, 136.3, 138.8, 142.3, 150.3 ppm. ^{125}Te NMR: $\delta = 407$ ppm. EI-MS: *m/z* (%) = 630 (12.2) $[(CH_3Br_2Py)_2TeH]^+$, 600 (1.0) $[Br_2PyTe]^+$, 444 (3.8) $[CH_3PyTe]_2{}^+$, 380 (41.9) $[CH_3Br_2PyTeH]^+$, 207 (26.0) $[PyTeH^+]$, 78 (100) $[PyH]^+$. $C_{12}H_8Br_4N_2Te_2$: calcd. C 19.09, H 1.06, N 3.71; found C 18.95, H 1.09, N 3.78.

General Method for the Preparation of Unsymmetrical Pyridyl Tellurides and Dipyridyl Monotellurides: A solution of bromopyridine (20 mmol) in THF (20 mL) was treated with *i*PrMgCl (22 mmol) at room temperature. After two hours of stirring elemental tellurium (20 mmol) was added in parts. When all the tellurium had dissolved, the mixture was cooled in an ice bath and an equivalent amount of alkyl halide/bromopyridine was added. The reaction was monitored by TLC. When the spot corresponding to ditelluride had disappeared, the reaction mixture was washed with distilled water and extracted with dichloromethane. The product was purified by column chromatography using 1% ethyl acetate in hexane as eluent.

Bis(4-methyl-2-pyridyl) Telluride [(4-MeC$_5$H$_3$N)$_2$Te] (10): Viscous liquid. Yield: 40%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.27$ (s, 6 H, CH_3), 6.92 (d, $^3J_{H,H} = 4.8$ Hz, 2 H, *m* to N), 7.56 (s, 2 H, *o* to Te), 8.35 (d, $^3J_{H,H} = 4.8$ Hz, 2 H, *o* to N) ppm. ^{13}C NMR: $\delta = 20.85$, 124.05, 132.06, 135.70, 148.17, 150.23 ppm. ^{125}Te NMR: $\delta = 378$ ppm. EI-MS: *m/z* (%) = 314 (51.1) $[M - Te]^+$, 183 (43.5) $[M - Te_2]^+$, 92 (100) $[CH_3Py]^+$. IR (KBr): $\tilde{\nu} = 3023$, 2969, 2917, 1654, 1582, 1544, 1451, 1261, 1368, 694, 520, 473 cm^{-1}. $C_{12}H_{12}N_2Te$: calcd. C 46.21, H 3.85, N 8.98; found C 46.13, H 3.71, N 8.7.

(3-Methyl-2-telluropryridyl)methane [(3-MeC$_5$H$_3$N)TeCH$_3$] (11): Viscous liquid. Yield: 1.39 g (60%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.31$ (s, 3 H, py CH_3), 2.15 (s, 3 H,CH_3), 6.93 (dd, $J_{H,H} = 4.6$ Hz, 7.2 Hz, 1 H, *m* to N), 7.10 (d, $J_{H,H} = 7.2$ Hz, 1 H, *p* to N), 8.31 (d, $J_{H,H} = 4.6$ Hz, 1 H, *o* to N) ppm. ^{13}C NMR: $\delta =$ 153.08, 133.48, 121.72, 136.65, 147.69, 20.53, 10.52 ppm. EI-MS: *m/z* (%) = 237 (2.3) $[CH_3PyTeCH_3]^+$, 222 (4.8) $[CH_3PyTeH]^+$, 145 (21.3) $[CH_3TeH]^+$, 107 (53.7) $[CH_3PyCH_2]^+$, 92 [(100.0) $CH_3Py]^+$, 78 (71.0) $[PyH]^+$. C_7H_9NTe: calcd. C 36.20, H 3.87, N 6.03; found C 35.88, H 3.45, N 5.93.

2-(3-Methyl-2-telluropyridyl)-2-methylethane [(3-MeC$_5$H$_3$N)-TeCH(CH$_3$)$_2$] (12): Viscous liquid. Yield: 1.56 g (60%). ^1H NMR

Table 8. Crystal and structure refinement data for **1**, **8** and **9**

	1	**8**	**9**
Empirical formula	$C_{10}H_8N_2Te_2$	$C_{10}H_4Br_4N_2Te_2$	$C_6H_4Br_2NTe$
Molecular mass	411.38	726.99	377.52
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, *C*2/*c*	monoclinic, *C*2/*c*
a (Å)	6.2870(4)	12.5073(15)	13.7340(15)
b (Å)	8.4920(7)	9.4521(11)	12.1460(6)
c (Å)	11.7370(12)	14.1713(15)	11.8950(10)
α (°)	109.101(8)	90.000	90.000(6)
β (°)	99.717(7)	111.707(10)	116.663(8)
γ (°)	89.829(6)	90.000	90.000(6)
V (A^3)	582.71(9)	1556.5(3)	1773.2(3)
Z, $D_{calcd.}$ (Mg/m^3)	2, 2.345	4, 3.102	8, 2.828
Absorption coefficient (mm^{-1})	4.970	14.000	12.294
F(000)	372	1288	1352
Crystal size (mm)	0.35 × 0.30 × 0.25	0.40 × 0.25 × 0.25	0.25 × 0.25 × 0.225
θ range for data collection (°)	1.86 to 24.93	2.78 to 24.97	2.35 to 24.92
Index ranges	$0 \le h \le 7$	$-14 \le h \le 0$	$0 \le h \le 16$
	$-9 \le k \le 10$	$-11 \le k \le 0$	$0 \le k \le 14$
	$-13 \le l \le 13$	$-15 \le l \le 16$	$-14 \le l \le 12$
Reflections collected/unique	1980/1980 [*R*(int.) = 0.0000]	1431/1365 [*R*(int.) = 0.1066]	1471/1471 [*R*(int.) = 0.0000]
Completeness to 2θ (%)	96.7	46.8	44.8
Absorption correction	Psi-scan	Psi-scan	Psi-scan
Max./min. transmission	1.000/0.907	1.000/0.863	1.000/0.895
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	1980/0/159	1365/0/83	1471/0/96
Goodness-of-fit on F^2	1.192	1.084	1.097
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0353$, $\omega R2 = 0.1015$	$R1 = 0.0567$, $\omega R2 = 0.1617$	$R1 = 0.0551$, $\omega R2 = 0.1409$
R indices (all data)	$R1 = 0.0361$, $\omega R2 = 0.1021$	$R1 = 0.0670$, $\omega R2 = 0.1692$	$R1 = 0.0586$, $\omega R2 = 0.1453$
Largest diff. peak and hole (e·Å^{-3})	1.213 and −1.403	1.664 and −2.908	2.904 and −1.276

(300 MHz, $CDCl_3$, 25 °C): δ = 1.58 (d, $J_{H,H}$ = 15.5 Hz, 6 H, $2CH_3$), 2.15 (s, 3 H, $pyCH_3$), 3.70 (m, $J_{H,H}$ = 15.5 Hz, 1 H, CH), 6.93 (dd, $J_{H,H}$ = 4.6 Hz, 7.2 Hz, 1 H, *m* to N), 7.10 (d, $J_{H,H}$ = 7.2 Hz, 1 H, *p* to N), 8.31 (d, $J_{H,H}$ = 4.6 Hz, 1 H, *o* to N) ppm. ^{13}C NMR: δ = 17.58, 26.63, 20.53, 153.08, 133.48, 121.72, 136.65, 147.69 ppm. EI-MS: *m/z* (%) = 265 (18.7) $[CH_3PyTeC_3H_7]^+$, 222 (55.3) $[CH_3PyTeH]^+$, 174 (11.5) $[C_3H_7TeH]^+$, 92 (100.0) $[CH_3Py]^+$, 78 (48.8) $[PyH]^+$. $C_9H_{13}NTe$: calcd. C 41.53, H 5.00, N 5.38; found C 41.05, H 4.89, N 5.04.

2-(3-Methyl-2-telluropyridyl)-1-propene [(3-MeC$_5$H$_3$N)Te(CH$_2$-CH=CH$_2$)] (13): Viscous liquid. Yield: 1.47 g (57%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.19 (s, 3 H, CH_3), 3.94 (d, $J_{H,H}$ = 7.8 Hz, 2 H, $TeCH_2$), 4.29 (d, $J_{H,H}$ = 9.9 Hz, 1 H, $=CH_2$), 5.07 (d, $J_{H,H}$ = 9.9 Hz, 1 H, $=CH_2$), 6.07(m, $J_{H,H}$ = 8.0, 1.7, 7.6 Hz, 1 H, CH), 6.93 (dd, $J_{H,H}$ = 4.6 Hz, 7.2 Hz, 1 H, *m* to N), 7.10 (d, $J_{H,H}$ = 7.2 Hz, 1 H, *p* to N), 8.31 (d, $J_{H,H}$ = 4.6 Hz, 1 H, *o* to N) ppm. ^{13}C NMR: δ = 12.28, 21.44, 136.71, 114.66, 120.30, 134.96, 137.01, 147.48, 148.13 ppm. EI-MS: *m/z* (%) = 263 (1.8) $[(CH_3PyTeC_3H_5]^+$, 237 (4.7) $[(CH_3PyTeCH_3]^+$, 222 (15.2) $[CH_3PyTeH]^+$, 171 (14.2) $[C_3H_5TeH]^+$, 92 (100.0) $[CH_3Py]^+$, 78 (53.0) $[PyH]^+$. IR (KBr): $\tilde{\nu}$ = 3067, 3043, 2977, 2929, 1662, 1571, 1451, 1346, 1277, 1148, 698, 539, 467 cm^{-1}. $C_9H_{11}NTe$: calcd. C 41.22, H 4.20, N 5.34; found C 40.17, H 4.16, N 5.39.

Crystal Structure Determination and Refinement: A crystal of **1**, **8** or **9** were mounted on an Enraf–Nonius CAD-4 diffractometer in Lindeman glass capillaries at 293(2) K. Final cell dimensions and reflection intensities were measured with graphite-monochromated Mo-K_α radiation in the ω-2θ scan mode. Anisotropic thermal parameters were used for heavier atoms Te and Br only. Carbon atoms were refined isotropically and hydrogen atoms were placed in calculated positions riding their respective bonded atoms. All other relevant information about the data collection and the refinement id presented in Table 8. The crystal structure was solved by direct methods and refined on F^2 using SHELX-97.[30]
CCDC-225524 (for **1**), -229371 (for **8**) and -220146 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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