Journal of Organometallic Chemistry, 397 (1990) 153–159
Elsevier Sequoia S.A., Lausanne
JOM 21099

Cyclotellurated derivatives of 2-(3-thienyl)pyridine

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(Received April 19th, 1990)

Abstract

Cyclometallated tellurium complexes of the monoanionic ligand 2-(3-thienyl)pyridine have been synthesised via organolithium compounds. Reaction of RLi (where R = 3-(2-py)-2-C_4H_2S) with elemental tellurium followed by oxidative workup afforded a novel ditelluride of the formula R_2Te_2. Reactions of ditelluride with bromine and thionyl chloride gave the corresponding aryltellurium tribromide and trichloride. Reduction of the trichloride with a stoichiometric amount of hydrazine hydrate gave the organyltellurium(II) chloride. The derivatives have been characterized by ^1H NMR, ^{13}C NMR, UV/Vis and MS techniques.

Introduction

Nitrogen-containing heteroaromatic compounds such as pyridine, quinoline, phenylimidazole and phenylthiazole can give cyclometallated compounds having five membered ring structure with nitrogen coordinated to the metal [1]. Recently, there has been a growing interest in organotellurium intramolecular-coordination compounds containing a nitrogen donor ligand. Direct telluration of azobenzene [2], Schiff bases [3], hydrazones [4] and heteroaromatics [5] has been reported. Very recently, tellurated derivatives of substituted pyridines have been reported by McWhinnie et al. [6] whose main objective was the synthesis of bidentate or multidentate ligands containing a "hard" donor atom such as nitrogen in addition to tellurium. Novel tritellurides of the type R_2Te_3, where R = 2-(2-pyridyl)phenyl or 2-(quinolin-2-yl)phenyl [7], have attracted considerable interest for the synthesis of such compounds.

Among the substituted pyridines, 2-(3-thienyl)pyridine (**1**) is known to give five membered ring compounds, and *ortho*metallated derivatives of palladium, rhodium and ruthenium have been reported [8]. Recently tetraorganotin compounds containing 2-(3-thienyl)pyridine have been extensively studied by Kumar Das and coworkers [9–11].

0022-328X/90/$03.50

Recently we succeeded in obtaining novel aryltellurenyl halides and hybrid bidentate ligands of the type, R′TeX and R′TeR″ (where R′ = *N*,*N*′-dimethylbenzylamine and R″ = CH_3, C_2H_5, and n-C_4H_9) [12]. We describe here the synthesis of a range of organotellurium derivatives containing the 2-(3-thienyl)pyridine ligand.

Experimental

All reactions were carried out under oxygen-free argon. n-BuLi (15% hexane, EMERK), 2-(3-thienyl)pyridine (Aldrich) and tellurium powder (Fluka) were reagent grade quality. The solvents were purified and dried by standard methods.

*Synthesis of bis[3-(pyridyl)-2-thienyl-*C,N*]ditelluride*

To a stirred solution of 2-(3-thienyl)pyridine (0.42 mL, 3.1 mmol) in dry ether (20 mL) under argon n-butyllithium (2.1 mL, 3.5 mmol) was added dropwise at room temperature. The resulting brown solution was stirred for a further 2 h, then elemental tellurium (0.39 g, 3.1 mmol) was added rapidly under a strong stream of argon. After 2 h stirring a light yellow suspension of the lithium arenetellurolate, [3-(2-py)-C_4H_2S]TeLi, was obtained. This was poured into a beaker containing water (100 mL) and left overnight to allow completion of oxidation. The organic layer was separated and the aqueous layer extracted several times with dichloromethane, and the combined extracts were dried over anhydrous sodium sulphate. Filtration followed by evaporation left a residue, which was recrystallised from a mixture of chloroform and hexane to give the ditelluride.

*Synthesis of [3-(2-pyridyl)-2-thienyl-*C,N*]tellurium(IV) tribromide*

A solution of the ditelluride (0.7 g, 1.2 mmol) in a mixture of chloroform (25 mL) and hexane (15 mL) was treated with a solution of bromine (0.2 mL, 4.23 mmol) in chloroform. The yellowish orange [3-(2-py)-2-C_4H_2S]$TeBr_3$ precipitated out immediately. It was washed with hexane and dried. The yield was 68%.

*Synthesis of [3-(2-pyridyl)-2-thienyl-*C,N*]tellurium(IV) trichloride*

This compound was made by reaction of the ditelluride (0.6 g, 1.04 mmol) with a slight excess of thionyl chloride in a mixture of chloroform (25 mL) and ether (15 mL) at 0 °C. The light yellow precipitate of [3-(2-ph)-2-C_4H_2S]$TeCl_3$ was recrystallised from ethanol to give the pure product; yield 66%.

*Synthesis of [3-(2-pyridyl)-2-thienyl-*C,N*]tellurium(II) chloride*

To a solution of [3-(2-py)-2-C_4H_2S]$TeCl_3$ (0.25 g, 0.63 mmol) in methanol (25 mL), hydrazine hydrate in methanol was added dropwise until the solution became clear. The precipitated tellurium was removed by filtration. The filtrate was concentrated and the the residue recrystallised from chloroform to give the pure aryltellurenyl chloride in 61% yield.

*Synthesis of (methyl)[3-(2-pyridyl)-2-thienyl-*C,N*]tellurium(IV) dibromide*

A cream-coloured suspension of the lithium arenetellurolate, [3-(2-py)-2-C_4H_2S]TeLi was prepared from 2-(3-thienyl)pyridine (0.42 mL, 3.1 mmol), n-butyllithium (2.1 mL, 3.5 mmol), and tellurium (0.39 g, 3.1 mmol). Iodomethane (0.19

mL, 3.1 mmol) was added from a syringe, and after 1 h stirring at room temperature the mixture was added to water. The organic layer was separated and the aqueous layer extracted several times with ether. The combined extracts were dried over anhydrous sodium sulphate, then evaporated to leave a yellowish-brown oil which was treated with bromine to give the diorganyltellurium dibromide. Yield 58%.

Physical measurements

Elemental analyses for C, H and N were carried out with Carlo Erba elemental analysis model 1106. NMR spectra were recorded with a JEOL FX100 instrument. The mass spectra were recorded at 70 eV. The UV/Vis solution spectrum was recorded with a Shimadzu UV-260 spectrophotometer.

Results and discussion

The lithiated 2-(3-thienyl)pyridine was readily obtained by treatment of the thienylpyridine with n-butyllithium in ether [9]. Reaction of 2 equivalents of RLi (where $R = 3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S$) with R'_2TeCl_2 (where $R' = p\text{-}CH_3OC_6H_4$) was attempted with a view to preparing the novel tetraorganotellurium compound $R_2TeR'_2$ but work-up only recovered R'_2TeCl_2.

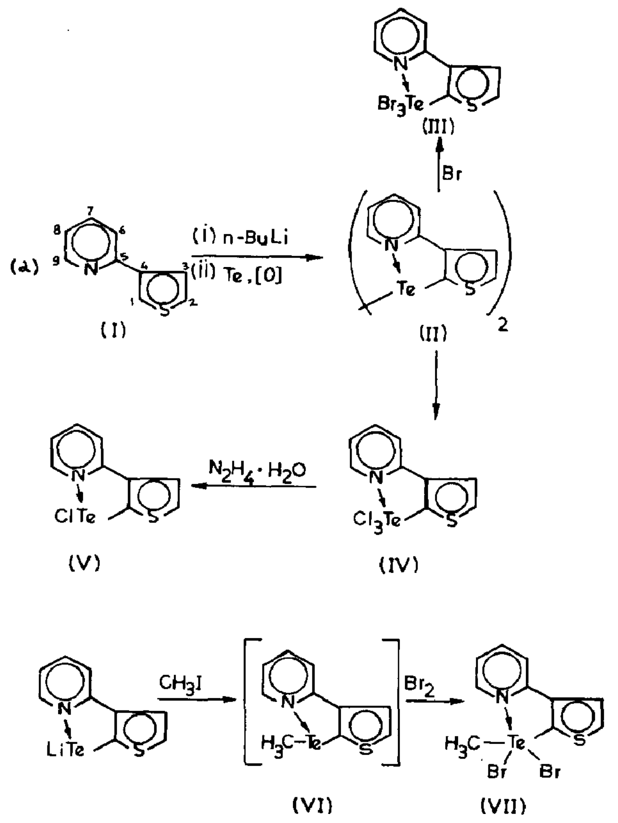
However, telluration of RLi was achieved by reaction with elemental tellurium. When finely ground elemental tellurium was added to the solution of RLi, the metal was consumed within 2 h to give a light-yellow suspension of the novel lithium arenetellurolate, $[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeLi$. Similar heteroatom-facilitated lithiations of thiophene and benzothiophene, followed by telluration, have been reported by Cava et al. [5b] McWhinnie et al. [5c] obtained a 2-tellurated derivative of thiophene via a mercurated intermediate.

Aqueous oxidative work-up of RTeLi gave the new ditelluride [II] (Scheme 1). Compound II, m.p. 140 °C, was found to be stable at room temperature, but darkened on exposure to light for a few days. Its UV/Vis spectrum in methanol showed a broad band around 400 nm characteristic of Te–Te chromophore.

Treatment of the ditelluride with 3.3 equivalents of bromine in chloroform caused immediate cleavage of the Te–Te bond and formation of the corresponding aryltellurium(IV) tribromide (III) in 68% yield. Reaction of the ditelluride with a slight excess of thionyl chloride at 0 °C likewise afforded the aryltellurium(IV) trichloride (IV). Reduction of IV with stoichiometric amount of hydrazine hydrate yielded the novel organyltellurium(II) chloride (V) in good yield. The aryltellurenyl halide, m.p. 130 °C, was found to be remarkably stable. The stability can be attributed to the intramolecular coordination of the heterocyclic nitrogen to tellurium (vide infra).

The lithium arenetellurolate was used to synthesize the bidentate ligand, VI, containing 'hard' nitrogen and 'soft' tellurium donor atoms. Compound VI was obtained by treating the lithium arenetellurolate with one equivalent of iodomethane. The identity of the oily methyltelluro compound was confirmed by conversion into its dibromide, VII.

New *ortho*tellurated derivatives of 2-(3-thienyl)pyridine were identified by elemental analysis (Table 1) and mass spectrometry. The mass spectrum of compound VII showed no molecular ion, and the peak of highest mass was due to {[3-(2-py)-2-



Scheme 1

$C_4H_2S]TeBr_2\}$. Scheme 2 presents the fragmentation pattern, showing the main fragment ions.

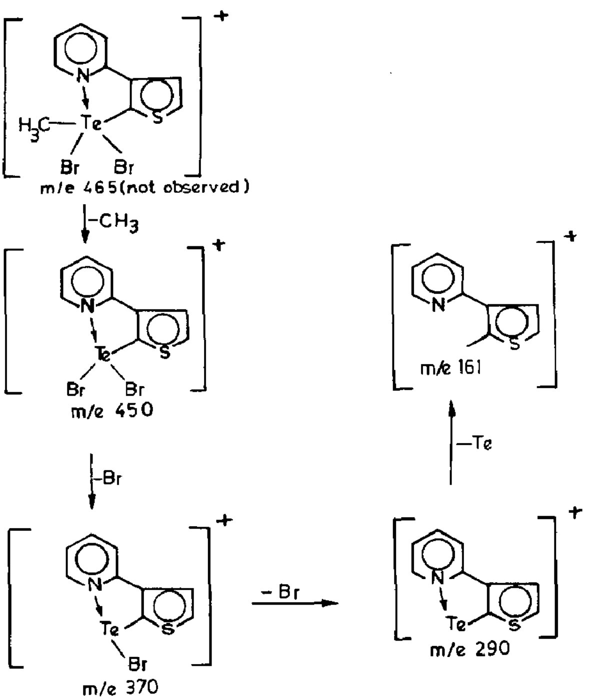
The ^1H chemical shifts of the tellurated derivatives are listed in Table 2. In the unsubstituted starting material the 2-pyridyl ring has a α-pyridyl hydrogen atom

Table 1

Analytical data for *ortho*tellurated derivatives of 2-(3-thienyl)pyridine

Compound	m.p. (°C)	Colour	Yield (%)	Anal. (Found (calcd.) (%))		
				C	H	N
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]_2Te_2$	140	brown	55	36.9 (37.5)	2.09 (2.09)	4.6 (4.86)
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeBr_3$	170 [a]	yellowish orange	68	21.0 (20.5)	1.3 (1.14)	2.7 (2.65)
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeCl_3$	200 [a]	pale yellow	66	28.3 (27.5)	1.6 (1.53)	3.6 (3.55)
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeCl$	130 [a]	yellow	61	33.2 (33.4)	2.0 (1.86)	4.7 (4.33)
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Te(CH_3)Br_2$	164 [a]	yellow	58	26.5 (26.0)	2.00 (1.95)	3.1 (3.02)

[a] Decomposes.



Scheme 2

that gives rise to a multiplet at δ 8.56 ppm, and the remaining heteroaryl ring hydrogens resonate at 7.06–7.86 ppm.

The existence of an intramolecular interaction involving a N–Te coordination is evident from the significant downfield shift of the proton resonances in the tellurated compounds. In the trihalides (III, IV) the α-pyridyl hydrogen signal is shifted from 8.5 ppm to 9.2 ppm, the electronegative halogens contributing to a large downfield shift relative to other compounds. The other heteroaryl ring hydrogens undergo smaller downfield shifts, i.e. from 7.06–7.86 ppm to 7.45–8.89 ppm. In contrast, the electron-rich tellurium atoms cause shielding in the ditelluride, and the α-pyridyl hydrogen is only slightly shifted.

Table 2

^1H chemical shifts for the tellurated derivatives of 2-(3-thienyl)pyridine [a]

Compound	α-pyridyl hydrogen	Other heteroaryl ring hydrogens	Others
2-(3-thienyl)pyridine [b]	8.56–8.57 (m, 1H)	7.06–7.86 (m, 6H)	
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]_2Te_2$	8.72–8.73 (m, 1H)	7.27–8.59 (m, 6H)	
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeBr_3$	9.27–9.28 (m, 1H)	7.45–8.89 (m, 6H)	
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeCl_3$	9.2 (m, 1H)	7.59–8.78 (m, 6H)	
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeCl$	9.16–9.17 (m, 1H)	7.40–8.47 (m, 6H)	
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Te(CH_3)Br_2$	9.19–9.22 (m, 1H)	7.42–8.78 (m, 6H)	2.72 (s, 3H) $TeCH_3$

[a] Chemical shifts δ (ppm) relative to TMS; recorded in DMSO-d_6. [b] Recorded in $CDCl_3$.

Table 3

^{13}C chemical shifts ortho-tellurated derivatives of 2-(3-thienyl)pyridine [a,b]

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
2-(3-thienyl)pyridine	125.2	141.3	122.6	125.3	152.2	120.7	135.4	118.9	148.4
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]_2Te_2$	–	140.7	127.7	124.5	149.8	122.9	138.0	121.0	147.9
		(−0.6)	(5.1)	(−0.8)	(−2.4)	(2.2)	(2.6)	(2.1)	(−0.5)
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeBr_3$	132.7	143.3	130.0	125.4	150.1	124.9	141.8	122.9	146.7
	(7.5)	(2.0)	(7.4)	(0.1)	(−2.1)	(4.2)	(6.4)	(4.0)	(−1.7)
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeCl_3$	136.1	143.6	133.1	126.6	149.5	125.6	142.2	122.2	146.8
	(10.9)	(2.3)	(10.5)	(1.3)	(−2.7)	(4.9)	(6.8)	(3.3)	(−1.6)
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Te(CH_3)Br_2$	133.2	144.4	129.0	125.4	149.5	124.5	142.4	121.9	146.6
	(8.0)	(3.1)	(6.4)	(0.1)	(−2.7)	(3.8)	(7.0)	(3.0)	(−1.8)

[a] Chemical shifts δ (ppm) from TMS; recorded in DMSO-d_6. [b] Difference in shifts relative to 2-(3-thienyl)pyridine in parentheses.

The ^{13}C NMR spectra of the compounds were recorded in DMSO-d_6. Unlike the situation with the *ortho*-metallated derivatives of N,N-dimethylbenzylamine [12], the assignment of ^{13}C chemical shifts could not be facilitated by observing the cumulative effects of the built-in functional group and the tellurium-containing group. However, the values for the chemical shifts of tetraorganotin of 2-(3-thienyl)pyridine [11] provide a basis for comparison. The tentative assignments are given in Table 3. Since it was not possible to observe ^{125}Te–^{13}C coupling under the conditions used, the assignment of *ipso* carbons (C(1)) were made on the basis of the intensities of the peaks. The chemical shifts of the *ipso* carbons range from 132.7–136.1 ppm and the downfield shift is more pronounced in the case $[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]TeCl_3$.

As in the case of the ^{1}H NMR spectra the large downfield chemical shifts of the signals from the α-pyridyl carbons (C(5)) in the ^{13}C NMR spectra also reflect the intramolecular interaction involving a Te–N bond.

Acknowledgements

H.B.S. is grateful to CSIR, New Delhi and BRNS, Department of Atomic Energy for financial support.

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