2:1 Complexes of Anilines with Tellurium Tetrachloride. Synthesis of Amino-Substituted Diphenyl Tellurides

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Complexes (2:1) prepared from anilines and tellurium tetrachloride were studied by ^{1}H, ^{13}C, ^{125}Te, and ^{15}N NMR spectroscopy and submitted to chemical degradation. It was found that N- and ortho-substituted anilines generally formed 2:1 complexes where a tellurium substituent was introduced para to the amine substituent (type I complexes). On reduction, these materials afforded mixtures of 4-amino-substituted diphenyl tellurides and diphenyl ditellurides which were readily converted to 4-amino-substituted diphenyl tellurides by Cu- or Pd-induced detelluration of the ditelluride component. Other anilines formed 2:1 complexes of the coordination type (type II complexes). In these materials, the anilines served as ligands to the electron-deficient tellurium atom. On reduction, the type II complexes afforded elemental tellurium and the corresponding anilines. When dissolved in dimethyl sulfoxide, both types of complexes were chemically modified. According to spectroscopic data, the anilines of the type II complexes were readily displaced by solvent molecules to form the corresponding DMSO complex. Type I complexes seemed to produce a mixture of compounds in rapid equilibrium with each other via proton and/or ligand exchange.

Introduction

Already in 1929, Morgan and Burgess discovered that 1 molar equiv of tellurium tetrachloride combined with 2 equiv of *N,N*-dimethylaniline to form a yellow solid complex.[1] When the compound was treated with boiling water, bis[4-(dimethylamino)phenyl]tellurium dichloride was formed. The structure of the 2:1 complex has not been investigated further and only one more synthetic transformation of the material, its conversion to [4-(dimethylamino)phenyl]tellurium trichloride, has been reported.[2] This transformation was also reported with 2:1 complexes prepared from other methyl-substituted anilines.[3]

In the following, we report the NMR (^{1}H, ^{13}C, ^{125}Te, and ^{15}N) properties of a large number of aniline/$TeCl_4$ complexes. On the basis of these studies, we also propose molecular structures of the compounds, although confirmatory X-ray structures are lacking due to the microcrystalline nature of the materials. A novel reductive transformation of the complexes was found to afford amino-substituted diphenyl tellurides.

Results

Complexes **1a**–**14a** (2:1) of anilines and $TeCl_4$ were prepared by addition of anilines to a $TeCl_4$ suspension in ether, followed by filtration of the crystalline product (Table I). The isolated yields are approximate because of varying amounts of crystal ether in the complexes. For example, the ^{1}H NMR spectrum of complex **3a** indicated the composition (aniline)$_2$TeCl$_4$·Et$_2$O of the material. Unfortunately, we were unable to recrystallize (vide infra) any of the complexes and satisfactory elemental analyses could not be obtained for the crude precipitated products used for the NMR and degradation studies.

Table I. 2:1 Complexes Prepared from Anilines and $TeCl_4$

complex	amine	yield (%)	complex type
1a	*N,N*-dimethylaniline	95	I
2a	*N*-methylaniline	66	I
3a	aniline	86[a]	I
4a	*o*-toluidine	90	I
5a	*m*-toluidine	96	II
6a	2,6-dimethylaniline	98	I
7a	2-ethoxyaniline	91	I
8a	2-(trifluoromethyl)aniline	43	I
9a	2-(methoxycarbonyl)aniline	78	I
10a	diphenylamine	74	I
11a	*p*-toluidine	98	II
12a	3,5-dimethylaniline	92	II
13a	3-nitroaniline	79	II
14a	2,4,6-tribromoaniline	88	II

[a] Based on the composition (aniline)$_2$TeCl$_4$·Et$_2$O, as indicated by ^{1}H and ^{13}C NMR spectra.

Sodium disulfite reduction of complexes **1a**–**10a** resulted in the formation of mixtures of diaryl ditellurides and diaryl tellurides (Scheme I). These were converted to pure diaryl tellurides by detelluration of the ditelluride component using activated copper[4] or palladium on carbon (Table II). On reduction, complex **5a**, obtained from 3-methylaniline and $TeCl_4$, afforded a mixture of the symmetric telluride **5b** and the unsymmetric telluride **5c**. When complexes **11a**–**14a** were reduced under similar conditions, elemental tellurium was precipitated and the respective anilines recovered in high yields (81–88%) (Scheme II).

Since the complexes are soluble only in highly polar solvents, ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 and ^{125}Te NMR spectra in DMSO-d_6 and DMF solutions (Table III). Attempts to use D_2O as solvent resulted in rapid decomposition of the complexes. If the ^{125}Te NMR

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[1] Morgan, G. T.; Burgess, H. *J. Chem. Soc.* **1929**, 1103.

[2] Gupta, A. K.; Khandelwal, B. L.; Raina, K. *J. Inorg. Nucl. Chem.* **1977**, *39*, 162.

[3] Berry, F. J.; Gupta, A. K.; Khandelwal, B. L.; Raina, K. *J. Organomet. Chem.* **1979**, *172*, 445.

[4] Sadekov, I. D.; Bushkov, A. Yu.; Minkin, V. I. *Zh. Obshch. Khim.* **1973**, *43*, 815.

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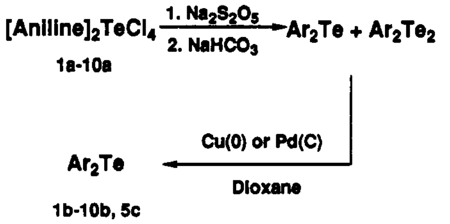
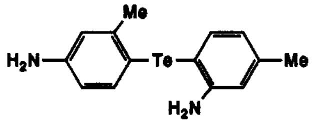
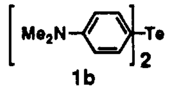
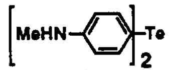
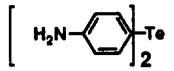
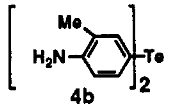
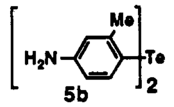
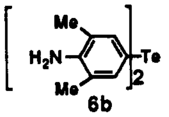
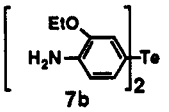
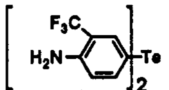
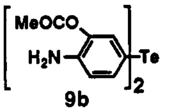
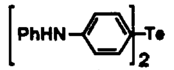
Scheme I





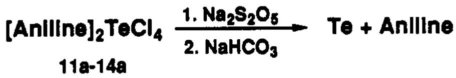
5c

Table II. Diaryl Tellurides Prepared from Reduction of Complexes 1a–10a

complex	diaryl telluride	yield (%)[a]
1a	 **1b**	60
2a	 **2b**	64
3a	 **3b**	58
4a	 **4b**	58
5a	 **5b** + **5c**	10 + 14
6a	 **6b**	52
7a	 **7b**	38
8a	 **8b**	72
9a	 **9b**	8
10a	 **10b**	52

[a] Isolated yield. It is assumed that all tellurides are formed via ditellurides. This means that only 50% of the tellurium in a complex appears in the diaryl telluride.

Scheme II



$$\underset{\mathbf{11a\text{-}14a}}{[\text{Aniline}]_2\text{TeCl}_4} \xrightarrow[\text{2. NaHCO}_3]{\text{1. Na}_2\text{S}_2\text{O}_5} \text{Te} + \text{Aniline}$$

Table III. ^{125}Te NMR Spectra of Complexes 1a–14a, 18, and 22

complex	shift (DMSO)[a]	ratio[b]	shift (DMF)[a]
1a	1275 (1531)		1253
2a	1281, 1530	8:1	
3a	1278		1258
4a	1246, 1531	4:1	
5a	1531		1495 (1174)
6a	1284		
7a	1279 (1531)		
8a	1250		
9a	1256, 1531	1:2	
10a	1254, 1262	1:4	
11a	1532		
12a	1532		1495
13a	1531		
14a	1530		1495 (1174)
18	1245		
22	1530		

[a] Shifts are reported in ppm relative to an external reference of neat Me$_2$Te. Small peaks are indicated by parentheses. [b] Approximate ratios of integrals were calculated only when two peaks were of comparable size.

Table IV. Proton-Decoupled ^{15}N NMR Spectra in DMSO

compd	shift[a]
PhNH$_2$ (0.2 M)	−321.0
PhNH$_3^+$, Cl$^-$ (0.1 M)	−326.4
3a (0.1 M)	−315.5, −328.4
3-MeC$_6$H$_4$NH$_2$ (0.2 M)	−321.5
5a (0.1 M)	−326.2 (−312.6)
3,5-Me$_2$C$_6$H$_3$NH$_2$ (0.2 M)	−322.2
12a (0.1 M)	−327.6

[a] Shifts are reported in ppm relative to neat MeNO$_2$. Small peaks are indicated by parentheses.

spectra contained two peaks of comparable size (integral ratio <10:1), it was attempted to estimate the molar ratio by comparison of the integrals. Due to low signal to noise ratio, these results are not very accurate. Proton-decoupled ^{15}N NMR spectra in DMSO-d_6 for some complexes and aniline derivatives are presented in Table IV.

Discussion

The results from the reductions of complexes **1a–14a** indicate that TeCl$_4$ forms two types of 1:2 complexes with anilines: one where a tellurium substituent has been introduced into the aromatic ring of the aniline (type I complexes **1a–4a**, **6a–10a**) and another type where the aniline is intact (type II complexes **5a**, **11a–14a**). This interpretation is also corroborated by ^{125}Te NMR data. Type I complexes resonate in the 1250–1300 ppm region, whereas type II complexes resonate close to 1530 ppm. The ^{1}H NMR spectra of compounds **1a–3a** indicated the presence of two different aromatic units in the complexes, one of them 1,4-disubstituted. Eight peaks in the aromatic region of the corresponding ^{13}C spectra, four for each aromatic unit, further supported the above interpretation. A DEPT spectrum (where only hydrogen-substituted carbons are visible) of complex **3a** contained three signals less than the corresponding ^{13}C NMR spectrum, and the ^{15}N NMR spectrum showed two peaks of comparable size (Table IV). TeCl$_4$ is an electrophilic reagent, and it is not surprising to find that it readily introduces a tellurium substituent into the para position of an activated aromatic compound. For example, anisole[5] and phenol[6] are known

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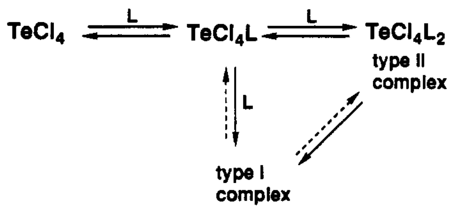
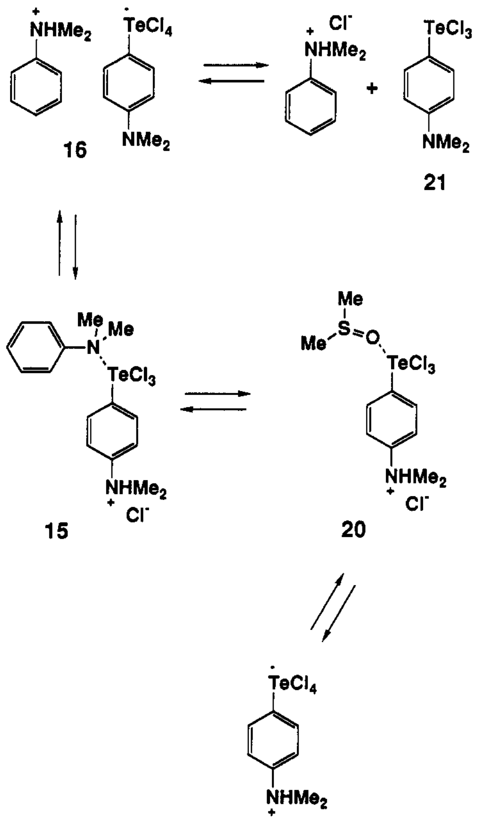
(5) Morgan, G. T.; Kellett, R. E. *J. Chem. Soc.* **1926**, 1080.

Scheme III



Scheme IV



to produce aryltellurium trichlorides on treatment with tellurium tetrachloride.

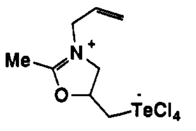
The two types of complexes may be formed as indicated in Scheme III. We propose that the type II complexes are coordination complexes of $TeCl_4$ with two anilines. The type I complexes may either originate from the type II complexes or via a rearrangement (in analogy with the Hofmann–Martius reaction[7]) of a 1:1 complex of tellurium tetrachloride with the aniline.

On the basis of the spectroscopic and degradation data, two possible structures of the type I complexes were initially considered (Scheme IV; *N,N*-dimethylaniline used as a representative aniline). One of them was an aryltellurium trichloride **15** with an *N,N*-dimethylaniline molecule coordinated or loosely bound to the electron-deficient tellurium substituent. The other structure was the aryltetrachlorotellurate **16**. This type of pentacoordinated tellurium compound is well-known. Petragnani and co-workers[8] prepared phosphonium, tropylium, and telluronium aryltetrahalotellurates from aryltellurium trihalides, and Bergman and Sidén[9] have confirmed the zwitterionic structure of oxazoline derivative **17** by X-ray crystallography.

Table V. ^1H NMR Shifts of the 1,4-Disubstituted Unit in Complex 1a, on Addition of $PhN^+HMe_2Cl^-$

added $PhNHMe_2{}^+Cl^-$ (molar equiv)	δ (ppm)[a]
0.00	8.20, 6.81
0.07	8.21, 6.83
0.34	8.24, 6.91
0.76	8.27, 6.99

[a] In DMSO-d_6.



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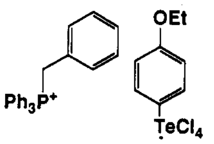
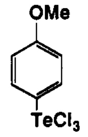
^{125}Te NMR shifts of complexes **1a**–**10a** (1246–1284 ppm, except for complex **5a**) are in accord with the one we obtained for aryltetrachlorotellurate **18**[8] (1245 ppm).



18



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However, aryltellurium trichlorides also resonate in the same region, as exemplified by 4-methoxyphenyl trichloride **19** (1246 ppm).[10] As judged by a comparison of ^1H and ^{15}N NMR spectra (Table IV) of anilinium chloride and aniline, neither of these compounds seems to be present in a DMSO-d_6 solution of complex **3a**. However, on addition of increasing amounts of *N,N*-dimethylanilinium chloride to a solution of complex **1a**, the chemical shifts of the protons in the 1,4-disubstituted aromatic nucleus were significantly and gradually altered (Table V). This suggests that a rapid dynamic equilibrium is established in a DMSO-d_6 solution of complex **1a**, involving structures interrelated by ligand and/or proton shifts, as suggested in Scheme IV. Attempts to observe the different structures of complex **1a** by cooling a 0.1 M DMF solution to −50 °C resulted only in a broadening of the peak in the ^{125}Te NMR spectrum. Recrystallization of complex **1a** from mixtures of DMSO, diethyl ether, and chlorinated solvents resulted in the isolation (40% yield) of a yellow crystalline material which showed ^1H NMR characteristics and analytical data in accord with an aryltellurium trichloride structure **20**. In this compound, the hydrogen chloride formed in the electrophilic substitution reaction is intercepted by the dimethylamino group para to tellurium and the *N,N*-dimethylaniline ligand is displaced by a solvent molecule (Scheme IV). The isolation of compound **20** clearly indicates that the solid-state and solution structures of complex **1a** are different. At present we have no suggestions as to the solid-state structure. Unfortunately, the microcrystalline nature of the materials makes them unsuitable for X-ray analysis.

Attempts were also carried out to independently synthesize some of the compounds proposed in Scheme IV. Thus, it was planned to reproduce the spectrum of complex

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(6) Reichel, L.; Kirschbaum, E. *Liebigs Ann. Chem.* **1936**, *523*, 211.

(7) See Ogata, Y.; Tabuchi, H.; Yoshida, K. *Tetrahedron* **1964**, *20*, 2717 and references cited therein.

(8) Petragnani, N.; Castellanos, L. T.; Wynne, K. J.; Maxwell, W. *J. Organomet. Chem.* **1973**, *55*, 295.

(9) Bergman, J.; Sidén, J.; Maartman-Moe, K. *Tetrahedron* **1984**, *40*, 1607.

(10) Chadha, R. K.; Miller, J. M. *Can. J. Chem.* **1982**, *60*, 2256.

1a by mixing the aryltellurium trichloride **21** with *N,N*-dimethylanilinium chloride in DMSO-d_6. However, compound **21** in our hands could not be obtained using the procedures described by Gupta and co-workers.[2] Chlorination of bis[4-(dimethylamino)phenyl] ditelluride[11] gave more promising results, but the material obtained seemed to be rapidly hydrolyzed by the small amounts of water present in dried DMSO-d_6.

The formulation of complexes **11a**–**14a** is in accord with the reduction results. Other similar 1:2 complexes of tellurium tetrachloride with DMSO,[12] acetonitrile,[13] and pyridine[14,15] were previously described. Attempted recrystallization of complexes **13a** and **14a** resulted in isolation of the yellow complex TeCl$_4$·2DMSO (**22**). The ^{125}Te NMR data for the type II complexes **11a**–**14a** (Table III) clearly show that these materials in DMSO-d_6 solution are undergoing ligand exchange to give complex **22** (^{125}Te NMR shift at 1530 ppm). In DMF solution, a small peak, in addition to the DMF complex peak at 1495 ppm (Table III), appeared in the ^{125}Te NMR spectra of compounds **5a** and **14a**.

As judged by the ^{125}Te NMR data (Table III), many of the type I complexes (**2a**, **4a**, **7a**, and **9a**) seem to be contaminated by compounds which readily give complex **22** in DMSO-d_6 solution. The formation of this complex may result from ligand exchange of type II complexes, formed in addition to the type I complexes.

TeCl$_4$·2 DMSO

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Type I complexes do not generally form when the para position of the aniline is blocked (complexes **11a** and **14a**). This is also true with meta-substituted anilines (complexes **5a**, **12a**, and **13a**). However, reduction of complex **5a** afforded diaryl tellurides **5b** and **5c** in 10 and 14% yields, respectively. These compounds were conceivably formed in the reduction process. A small peak at −312.6 ppm in the ^{15}N NMR spectrum (Table IV) of complex **5a** may indicate the presence of a type I complex.

Surprisingly, the 2:1 complex **10a** of diphenylamine with TeCl$_4$ showed two peaks (1254 and 1262 ppm) in the low-shift region of the ^{125}Te NMR spectrum. However, on reduction, only the diaryl telluride **10b** could be isolated.

Few symmetrical amino-substituted diphenyl ditellurides/diphenyl tellurides have been described previously in the literature. Bis(4-aminophenyl) ditelluride was prepared in low yield from aniline and tellurium tetrachloride in a method related to ours.[16] We recently prepared bis[4-(dimethylamino)phenyl] ditelluride from 4-bromo-*N,N*-dimethylaniline via lithiation, tellurium insertion, and ferricyanide oxidation of the resulting lithium arenetellurolate.[11] The isomeric compound bis[3-(dimethylamino)phenyl] ditelluride was also reported.[16] Bis(2-aminophenyl) ditelluride was prepared by mercuration of azobenzene, transmetalation with TeCl$_4$, and sodium borohydride reduction.[17] Morgan and Burgess[1] obtained telluride **1b** on reduction of the corresponding *Te,Te*-dichloride, which in turn was prepared by treatment of complex **1a** in boiling water.

The procedure described in the present paper should be generally applicable to the preparation of diphenyl tellurides carrying amino groups in the para position. The amino groups may be substituted with alkyl and/or aryl groups, and ortho substituents of the amine are tolerable. Since no complexes were isolated from 2-hydroxyaniline or 2,6-dinitroaniline, the synthesis could not be generally applied to the preparation of hydroxy- or nitro-substituted derivatives. Although both *o*- and *m*-phenylenediamine afforded complexes with tellurium tetrachloride, reduction failed to produce any tetraaminated diphenyl tellurides.

Experimental Section

The anilines and tellurium tetrachloride were commercial products. Diethyl ether was predried over calcium chloride and stored over sodium wire. Analytical TLC plates and silica gel (230–400 mesh) were purchased from Merck. Melting points were determined using a Büchi 510 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with Bruker AC-F250 and AM 400 instruments. They were recorded in CDCl$_3$ or DMSO-d_6 solutions containing tetramethylsilane as the internal standard. ^{125}Te NMR spectra were obtained at 25 °C with the AM 400 instrument operating at 126.204 MHz with a spectral width of 71 kHz. The solutions were 0.05 M in DMSO-d_6 and 0.1 M in DMF (not deuterated). Chemical shifts are reported in ppm relative to an external reference of neat dimethyl telluride. ^{15}N NMR spectra were obtained with the same instrument operating at 40.550 MHz with varying spectral widths. The solutions were 0.1–0.2 M in DMSO-d_6. An external reference of 90% formamide in DMSO-d_6 (−268.4 ppm) was used, and shifts are reported relative to neat nitromethane. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany. Benzyltriphenylphosphonium (4-ethoxyphenyl)tetrachlorotellurate (**18**),[8] TeCl$_4$·2DMSO (**22**),[12] and activated copper[18] were prepared according to literature procedures.

Preparation of Complexes. General Procedure. TeCl$_4$ (3.39 g, 12.6 mmol) was finely ground under dry ether (40 mL) with a glass rod. The aniline (25.2 mmol), dissolved or suspended in dry ether (10 mL), was added dropwise with stirring. Trituration of the dark oil which formed usually caused rapid crystallization, but some complexes (**10a** and **13a**) required longer time, up to 1 week, to solidify. The resulting suspension was stirred for a few hours, filtered, washed with ether, and dried under reduced pressure. Complexes **8a** and **14a** were partly soluble in ether. Most of complex **14a** was obtained by evaporation of the ether phase and proved to be identical with the material isolated by filtration (^{1}H NMR). The yields of complexes **1a**–**14a** are presented in Table I. ^{1}H and ^{13}C NMR spectra, recorded in DMSO-d_6, are only reported for the complexes with a major peak in the ^{125}Te NMR spectrum (Table III).

1a: ^{1}H δ 8.21 (d, 2 H), 7.55–7.50 (m, 5 H), 7.37 (bs), 6.82 (d, 2 H), 3.14 (s, 6 H), 2.98 (s, 6 H); ^{13}C δ 150.5, 144.6, 138.1, 134.8, 129.9, 126.7, 119.0, 111.3, 44.6, 40.0.

2a: ^{1}H δ 8.6 (bs), 8.13 (d, 2 H), 7.64–7.30 (several peaks, 5 H), 6.63 (d, 2 H) 2.92 (s, 3 H), 2.73 (s, 3 H); ^{13}C δ 150.3, 139.6, 135.5, 135.0, 129.8, 126.7, 120.4, 111.0, 35.1, 29.8.

3a: ^{1}H δ 8.3 (bs), 8.10 (d, 2 H), 7.44 (m, 2 H), 7.31–7.24 (several peaks, 3 H), 6.66 (d, 2 H); ^{13}C δ 148.9, 138.0, 135.1, 134.1, 129.7, 126.4, 121.8, 113.3; DEPT δ 135.1, 129.7, 126.4, 121.8, 113.3 (methines or methyl groups). Methylenes (negative signals) were absent.

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[16] Junk, T. Ph.D. Thesis, Texas A&M University, 1988.

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[18] Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; Longman: London, 1957; p 192.

6a: ^{1}H δ 7.88 (s, 2 H), 7.3 (bs), 7.2–7.0 (m, 3 H), 2.29 (s, 6 H), 2.12 (s, 6 H); ^{13}C δ 145.3, 137.1, 133.3, 131.5, 129.7, 128.9, 125.9, 120.0, 18.1, 17.6.

7a: ^{1}H δ 8.0 (bs), 7.89 (d, 1 H), 7.77 (dd, 1 H), 7.30–7.10 (several peaks, 3 H), 6.96 (dt, 1 H), 6.71 (d, 1 H), 4.13 (q, 2 H), 4.02 (q, 2 H), 1.37 (t, 3 H), 1.35 (t, 3 H); ^{13}C δ 150.6, 144.0, 138.9, 138.0, 127.7, 127.4, 123.0, 122.3, 120.7, 118.1, 113.0, 112.6, 64.2, 63.8, 14.6, 14.5.

8a: ^{1}H δ 8.40 (d, 1 H), 8.23 (dd, 1 H), 7.32 (dd, 1 H), 7.28 (dt, 1 H), 6.86 (d, 1 H), 6.84 (dd, 1 H), 6.63 (dt, 1 H), 6.3 (bs).

11a: ^{1}H δ 9.7 (bs), 7.24 (d, 2 H), 7.18 (d, 2 H), 2.30 (s, 3 H); ^{13}C δ 136.6, 130.3, 130.0, 122.4, 20.5.

12a: ^{1}H δ 6.91 (t, 1 H), 6.84 (d, 2 H), 2.27 (s, 6 H); ^{13}C δ 138.9, 135.0, 127.0, 118.7, 20.8.

13a: ^{1}H δ 7.8 (bs), 7.62 (t, 1 H), 7.58 (dt, 1 H), 7.43 (t, 1 H), 7.20 (dt, 1 H); ^{13}C δ 148.6, 145.5, 130.3, 122.7, 113.4, 110.1.

14a: ^{1}H δ 7.63 (s, 2 H), 6.8 (bs); ^{13}C δ 142.6, 133.5, 107.9, 106.5.

Attempted Recrystallization of Complex 1a. Complex **1a** (0.55 g, 1.1 mmol) was dissolved in DMSO (5 mL). After filtration, dry ether (15 mL) and methylene chloride (5 mL) were added and the solution was left for 1 week at −20 °C. The precipitate which formed consisted of DMSO which dissolved when the temperature was allowed to rise. Chloroform (5 mL) was then added and the solution left overnight at −20 °C. Yellow crystals (0.20 g, 40%) of compound **20** were filtered off, dec >120 °C. ^{1}H NMR: δ 8.24 (d, 2 H), 6.92 (d, 2 H), 3.01 (s, 6 H), 2.54 (s, 6 H). Anal. Calcd for $C_{10}H_{17}Cl_4NOSTe$: C, 25.62; H, 3.66; N, 2.99; Cl, 30.25. Found: C, 26.72; H, 3.67; N, 2.90; Cl, 30.07.

Complex 1a and *N,N*-Dimethylanilinium Chloride. Complex **1a** (0.020 g) was dissolved in DMSO-d_6 (0.8 mL) in a 5-mm NMR tube. *N,N*-Dimethylanilinium chloride was then added in portions (0, 0.07, 0.27, and 0.42 molar equiv) and the ^{1}H NMR spectrum recorded after each addition. The chemical shifts of the 1,4-disubstituted unit are reported in Table V.

Preparation of Tellurides 1b–10b. Typical Procedure. To a stirred suspension of complex **1a** (2.95 g, 5.76 mmol) in methylene chloride (40 mL) was added $Na_2S_2O_5$ (2.19 g, 11.5 mmol) dissolved in water (40 mL). The red precipitate, which immediately formed, dissolved when solid sodium bicarbonate was added in small portions. Addition of sodium bicarbonate continued until the aqueous phase was neutralized (pH = 7–8). The phases were separated, and the aqueous phase was extracted with another portion of methylene chloride (25 mL). The mixture of *N,N*-dimethylaniline and bis[4-(dimethylamino)phenyl] telluride and ditelluride, obtained after drying ($MgSO_4$) and evaporation of the solvent, was dissolved in 1,4-dioxane (40 mL), and the solution was refluxed with activated copper (2.6 g) until the red color disappeared (ca. 15 min). Filtration, evaporation of the solvent, and flash chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) afforded 0.64 g (60%) of telluride **1b**. Melting points, NMR data, and elemental analyses of tellurides **1b**, **3b**, and **10b** were previously reported.[19] Physical, spectroscopic, and analytical data for other diphenyl tellurides are reported below. NMR spectra of all diphenyl tellurides were recorded in $CDCl_3$. For yields of tellurides **1b–10b** and **5c**, see Table II.

2b (semisolid): ^{1}H NMR δ 7.53 (d, 2 H), 6.45 (d, 2 H), 3.7 (bs, 1 H), 2.79 (s, 3 H). The material was analyzed after conversion to its corresponding *Te,Te*-dichloride as follows: To a stirred ice-cooled solution of telluride **2b** (0.090 g, 0.26 mmol) in dry methylene chloride (3 mL) was added sulfuryl chloride (0.036 g, 0.26 mmol) dissolved in methylene chloride (0.5 mL). Addition of hexanes (10 mL) to the resulting solution caused precipitation. After 2 h in the freezer (−20 °C), 0.095 g of bis[4-(methylamino)phenyl]tellurium dichloride was filtered off. The analytical sample was obtained after two recrystallizations from ethanol, dec > 140 °C. ^{1}H NMR (DMSO-d_6): δ 7.60 (d, 2 H), 6.62 (d, 2 H), 6.4 (bs, 1 H), 2.70 (s, 3 H). Anal. Calcd for $C_{14}H_{16}Cl_2N_2Te$: C, 40.93; H, 3.93. Found: C, 41.05; H, 3.79.

4b: mp 93–7 °C; ^{1}H NMR δ 7.44 (d, 1 H), 7.39 (dd, 1 H), 6.51 (d, 1 H), 3.6 (bs, 2 H), 2.09 (s, 3 H); ^{13}C δ 144.5, 140.6, 137.4, 123.5, 116.0, 101.6, 17.0. Anal. Calcd for $C_{14}H_{16}N_2Te$: C, 49.47; H, 4.74. Found: C, 49.39; H, 4.74.

In the reduction of complex **5a**, no copper or palladium treatment was necessary. Because of overlapping fractions, the separation of *m*-toluidine and tellurides **5b** and **5c** required four runs of flash chromatography (SiO_2, CH_2Cl_2/MeOH). **5b** (semisolid): ^{1}H NMR δ 7.31 (d, J_{ortho} = 8.1 Hz, 1 H), 6.62 (d, J_{meta} = 2.4 Hz, 1 H), 6.34 (dd, J_{ortho} = 8.1 Hz, J_{meta} = 2.5 Hz, 1 H), 3.6 (bs, 2 H), 2.34 (s, 3 H). Telluride **5b** was converted to bis(4-amino-2-methylphenyl)tellurium dichloride using the same procedure as for telluride **2b** (vide supra). The analytical sample was obtained after recrystallization from ethanol/methanol/methylene chloride, dec >135 °C. ^{1}H NMR (DMSO-d_6): δ 7.32 (d, 1 H), 6.59 (d, 1 H), 6.54 (dd, 1 H), 5.9 (bs, 2 H), 2.58 (s, 3 H). Anal. Calcd for $C_{14}H_{16}Cl_2N_2Te$: C, 40.93; H, 3.93. Found: C, 40.92; H, 4.00.

5c (semisolid): ^{1}H NMR δ 7.59 (d, J_{ortho} = 7.7 Hz, 1 H), 7.18 (d, J_{ortho} = 8.1 Hz, 1 H), 6.61 (d, J_{meta} = 1.7 Hz, 1 H), 6.57 (d, J_{meta} = 2.6 Hz, 1 H), 6.42 (dd, J_{ortho} = 7.7 Hz, J_{meta} = 1.8 Hz, 1 H), 6.32 (dd, J_{ortho} = 8.2 Hz, J_{meta} = 2.6 Hz, 1 H), 4.2 (bs, 2 H), 3.6 (bs, 2 H), 2.32 (s, 3 H), 2.27 (s, 3 H); ^{125}Te ($CDCl_3$) δ 540. Anal. Calcd for $C_{14}H_{16}N_2Te$: C, 49.47; H, 4.74. Found: C, 49.38; H, 4.84.

6b: mp 152–3 °C: ^{1}H NMR δ 7.35 (s, 2 H), 3.6 (bs, 2 H), 2.11 (s, 6 H). Anal. Calcd for $C_{16}H_{20}N_2Te$: C, 52.23; H, 5.48. Found: C, 52.09; H, 5.44.

7b (semisolid): ^{1}H NMR δ 7.16–7.12 (m, 2 H), 6.56 (d, 1 H), 3.98 (q, 2 H), 3.8 (bs, 2 H), 1.39 (t, 3 H). Telluride **7b** was converted to bis(4-amino-3-ethoxyphenyl)tellurium dichloride using the same procedure as for telluride **2b** (vide supra). The analytical sample was obtained after crystallization from hexanes/methylene chloride, dec >120 °C. ^{1}H NMR (DMSO-d_6): δ 7.37 (d, J_{meta} = 1.7 Hz, 1 H), 7.26 (dd, J_{ortho} = 8.3 Hz, J_{meta} = 1.8 Hz, 1 H), 6.73 (d, J_{ortho} = 8.3 Hz, 1 H), 5.8 (bs, 2 H), 3.95 (q, 2 H), 1.33 (t, 3 H). Anal. Calcd for $C_{16}H_{20}Cl_2N_2O_2Te$: C, 40.81; H, 4.28. Found: C, 40.73; H, 4.25.

8b: mp 115–6 °C; ^{1}H NMR δ 7.80 (d, 1 H), 7.62 (dd, 1 H), 6.59 (d, 1 H), 4.2 (bs, 2 H). Anal. Calcd for $C_{14}H_{10}F_6N_2Te$: C, 37.55; H, 2.25. Found: C, 37.68; H, 2.37.

Complex 9a (2.79 g, 4.94 mmol) was reduced using the above procedure. After flash chromatography and copper treatment, a 1:1 mixture of ditelluride and telluride (0.165 g) was obtained. Reflux in 1,4-dioxane (15 mL) with Pd/C (0.53 g) for 1.5 h afforded 0.079 g (8%) of telluride **9b**. The analytical sample, mp 182–185 °C, was obtained after recrystallization from hexanes/methylene chloride. ^{1}H NMR: δ 8.29 (d, 1 H), 7.58 (dd, 1 h), 6.50 (d, 1 H), 5.8 (bs, 2 H), 3.85 (s, 3 H). Anal. Calcd for $C_{16}H_{16}N_2O_4Te$: C, 44.91; H, 3.77. Found: C, 44.67; H, 3.64.

Reduction of Complexes 11a–14a. The complexes were reduced according to the above procedure. After neutralization of the aqueous phase, filtration, and separation of the phases, TLC indicated no tellurium-containing species in the organic phase. Drying ($MgSO_4$) and evaporation of the solvent afforded the corresponding anilines (*p*-toluidine (yield not determined), 3,5-dimethylaniline (88%), 3-nitroaniline (81%), or 2,4,6-tribromoaniline (88%)).

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[19] Engman, L.; Persson, J.; Andersson, C. M.; Berglund, M. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1309.