

Transmetallation reaction of Schiff-base-type arylmercury compounds with 4-ethoxyphenyltellurium(IV) trichloride and the crystal structure of (4-ethoxyphenyl)[(2-benzylideneamino-5-methyl)phenyl]tellurium(IV) dichloride

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Abstract

A series of new asymmetric diaryltellurium dichlorides were synthesized by the transmetallation reaction of Schiff-base-type arylmercury compounds with 4-ethoxyphenyltellurium trichloride. All the asymmetric diaryltellurium dichlorides prepared were characterized by elemental analysis, IR, ^1H nuclear magnetic resonance and mass spectroscopy. The crystal structure of (4-ethoxyphenyl)[(2-benzylideneamino-5-methyl)phenyl]tellurium dichloride shows that the coordination on tellurium can be considered as essentially pseudo-octahedral, with lone pair electrons occupying the fourth equatorial site. The Te–N distance of 2.905(2) Å is shorter than the sum of the van der Waals radii of Te and N (about 3.7 Å), indicating the substantial secondary intramolecular coordination between Te and N. The N → Te intramolecular coordination holds the Schiff base moiety in near-planar geometry.

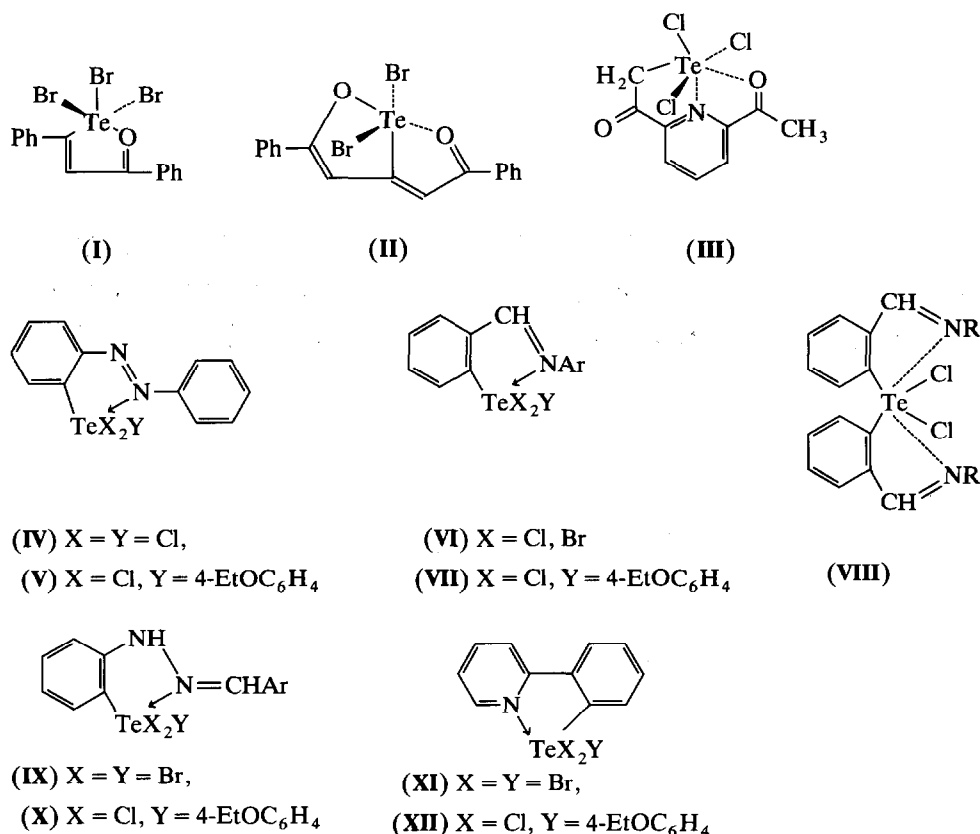
Key words: Mercury; Tellurium; Aryl; Transmetallation; Intramolecular coordination

1. Introduction

The main advantage of organomercury compounds as transmetallating reagents over the classical organolithium and Grignard reagents has been described in the literature [1]. They have been widely used in the synthesis of those containing *ortho* coordinating groups through transmetallation reactions. With the increasing interest in the effects of intramolecular coordination on organotellurium compounds, a number of Te^{IV} compounds bearing a carbonyl (I–III) [2–4], azo (IV and V) [5,6] or azomethine (VI–XII) [7–9] group have been synthesized and characterized to possess an intramolecular O → Te or N → Te coordination bond.

Although tellurium tetrahalides can function as electrophiles to react with, for example, aromatic ethers [10], compounds such as IV–XII are generally prepared by indirect methods. The reaction of tellurium tetrahalides or aryltellurium trichlorides with arylmercuric chlorides is one of the convenient methods for the preparation of organotellurium compounds. Singh and McWhinnie [7] claimed that they had synthesized the “*ortho*” tellurated Schiff bases VI and VII by the transmetallation reaction of the corresponding *ortho* mercured Schiff base with tellurium tetrabromide or 4-ethoxyphenyltellurium trichloride. Unfortunately, the structure of the mercured Schiff base reported by Singh and McWhinnie is incorrect according to our systematic study on the mercuration of Schiff bases of substituted benzylideneanilines [11]. In the mercured derivatives of Schiff bases, the mercury atom is

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attached to the *ortho* position of the *N*-phenyl ring rather than to that of the *C*-phenyl ring, and there exists an intramolecular N → Hg coordination via a four-membered ring. Therefore the structure of the “*ortho*” tellurated Schiff bases deduced from the “*ortho*” mercurated Schiff bases, reported by Singh and McWhinnie is not convincing. In the present work, we

report the synthesis of asymmetric diaryltellurium dichlorides by transmetallation reaction of Schiff-base-type arylmercury compounds with 4-ethoxyphenyltellurium trichloride and the X-ray crystal structure of one of the transmetallation products, (4-ethoxyphenyl) [(2-benzylideneamino-5-methyl) phenyl] tellurium dichloride.

TABLE 1. Syntheses and analytical data of 2a–2n

Compound	Colour	Yield (%)	m.p. (°C)	Anal. Found (calcd) (%)			MS: <i>m/z</i> (%)	
				C	H	N	M ⁺ – Cl	M ⁺ – 2Cl
2a	Pale yellow	87.6	212–213	51.11 (51.40)	3.96 (4.09)	2.35 (2.73)	480(52)	445(60)
2b	Pale yellow	92.0	219–221	51.17 (50.77)	4.36 (4.23)	2.67 (2.58)	510(45)	475(23)
2c	Pale yellow	82.8	191–193	50.45 (50.77)	4.27 (4.23)	2.64 (2.58)	510(52)	475(41)
2d	Pale yellow	83.0	207–209	50.47 (50.77)	4.00 (4.23)	2.88 (2.58)	510(24)	475(45)
2e	White	64.0	215–217	48.19 (48.17)	3.78 (3.65)	2.71 (2.55)	514(37)	479(51)
2f	White	70.0	190–192	47.75 (48.17)	3.33 (3.65)	2.37 (2.55)	514(20)	479(17)
2g	Pale yellow	86.7	175–177	48.12 (48.17)	3.63 (3.65)	2.55 (2.55)	514(32)	479(49)
2h	White	92.8	225–227	44.18 (44.56)	3.26 (3.38)	2.08 (2.36)	558(25)	525(63)
2i	White	76.0	215–217	45.06 (44.56)	3.19 (3.38)	2.27 (2.36)	558(19)	523(95)
2j	Yellow	98.5	250–252	47.27 (47.26)	3.62 (3.58)	5.28 (5.01)	525(29)	490(58)
2k	Yellow	76.1	237–239	47.11 (47.26)	4.04 (3.58)	5.29 (5.01)	525(20)	490(30)
2l	Pale yellow	60.0	210–212	47.09 (47.18)	3.37 (3.37)	2.67 (2.62)	500(20)	465(15)
2m	Yellow	70.2	224–226	43.38 (43.55)	3.12 (3.11)	2.69 (2.42)	544(8)	509(13)
2n	Yellow	65.0	223–225	49.37 (49.85)	3.64 (3.97)	2.41 (2.64)	496(18)	461(16)

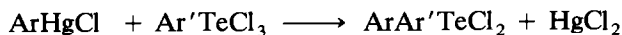
TABLE 2. IR and ¹H nuclear magnetic resonance spectral data of 2a–2n

Compound	IR (cm ⁻¹)	¹ H NMR: δ(ppm)
2a	3055w, 2980w, 2880w, 1622s, 1584s, 1568s, 1490s, 1475s, 1250vs, 1038m, 885w, 820s, 810s, 760m, 690m	9.10 (s, 1H, H-1); 8.18 (d, 2H, <i>J</i> = 9.0 Hz, H-10); 8.11–7.94 (m, 2H, H-3,5); 7.79 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.66–7.43 (m, 4H, H-2, 4, 6, 8); 7.25 (d, 2H, <i>J</i> = 4.0 Hz, H-11); 7.20 (s, 1H, H-9); 4.17 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.29 (s, 3H, Ar-CH ₃); 1.39 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2b	3060w, 2970w, 2910w, 2880w, 1621s, 1600s, 1582s, 1568s, 1510s, 1490s, 1475s, 1250vs, 1038s, 882m, 826s, 819m	8.99 (s, 1H, H-1); 8.15 (d, 2H, <i>J</i> = 9.0 Hz, H-10); 7.97 (d, 2H, <i>J</i> = 8.8 Hz, H-2, 6); 7.71 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.48 (d, 1H, <i>J</i> = 8.0 Hz, H-8); 7.24 (d, 2H, <i>J</i> = 9.1 Hz, H-11); 7.17 (s, 1H, H-9); 7.16 (d, 2H, <i>J</i> = 8.8 Hz, H-3, 5); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 3.87 (s, 3H, OCH ₃); 2.26 (s, 3H, ArCH ₃); 1.37 (t, 3H, <i>J</i> = 6.9 Hz, CH ₃)
2c	3060w, 2970w, 2920w, 2880w, 1621s, 1580s, 1485s, 1472s, 1250vs, 1040s, 896w, 866m, 826s, 819s, 795s, 682m	9.08 (s, 1H, H-1); 8.17 (d, 2H, <i>J</i> = 8.9 Hz, H-10); 7.78 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.64–7.42 (m, 4H, H-4, 5, 6, 9); 7.34–7.13 (m, 4H, H-2, 8, 11); 4.16 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 3.87 (s, 3H, OCH ₃); 2.29 (s, 3H, ArCH ₃); 1.39 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2d	3060w, 2975w, 2960w, 2910w, 2880w, 1614s, 1599s, 1582s, 1565m, 1490s, 1474s, 1460m, 1250vs, 1040s, 886m, 820s, 800s, 758s	9.22 (s, 1H, H-1); 8.14 (dd, 2H, <i>J</i> = 6.9 Hz, 2.1 Hz, H-10); 8.07 (dd, 1H, <i>J</i> = 7.8 Hz, 1.8 Hz, H-6); 7.71 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.61 (dt, 1H, <i>J</i> = 7.9 Hz, 1.8 Hz, H-4); 7.46 (dd, 1H, <i>J</i> = 8.4 Hz, 1.6 Hz, H-8); 7.24 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-11); 7.23 (t, 1H, <i>J</i> = 7.23 Hz, H-5); 7.18 (d, 1H, <i>J</i> = 1.4 Hz, H-9); 7.14 (d, 1H, <i>J</i> = 7.6 Hz, H-3); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 3.95 (s, 3H, OCH ₃); 2.27 (s, 3H, ArCH ₃); 1.37 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2e	3060w, 2975w, 2910w, 2890w, 1621s, 1582s, 1562m, 1490s, 1472m, 1248vs, 1040m, 882m, 828s, 819s	9.09 (s, 1H, H-1); 8.15 (dd, 2H, <i>J</i> = 6.9 Hz, 2.0 Hz, H-10); 8.02 (dd, 2H, <i>J</i> = 6.6 Hz, 1.8 Hz, H-2, 6); 7.76 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.70 (dd, 2H, <i>J</i> = 6.7 Hz, 1.8 Hz, H-3, 5); 7.49 (d, 1H, <i>J</i> = 8.3 Hz, H-8); 7.24 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-11); 7.19 (s, 1H, H-9); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.28 (s, 3H, ArCH ₃); 1.38 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2f	3050w, 2970w, 2910w, 2890w, 1620s, 1585s, 1562s, 1470s, 1250vs, 1180s, 1040s, 920m, 890m, 865m, 820s, 800s, 780s, 750s, 690s, 680s	9.11 (s, 1H, H-1); 8.16 (d, 2H, <i>J</i> = 8.8 Hz, H-10); 8.06 (s, 1H, H-2); 7.98 (d, 1H, <i>J</i> = 8.0 Hz, H-6); 7.77 (d, 1H, <i>J</i> = 8.0 Hz, H-4); 7.70 (d, 1H, <i>J</i> = 8.0 Hz, H-8); 7.66 (t, 1H, <i>J</i> = 8.0 Hz, H-5); 7.52 (d, 1H, <i>J</i> = 8.0 Hz, H-7); 7.25 (d, 2H, <i>J</i> = 8.8 Hz, H-11); 7.22 (s, 1H, H-9); 4.16 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.29 (s, 3H, ArCH ₃); 1.39 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2g	3060w, 2980w, 2910w, 2880w, 1614s, 1582s, 1568s, 1490s, 1478s, 1247vs, 1038s, 882m, 828s, 815s, 762s	9.25 (s, 1H, H-1); 8.22 (dd, 1H, <i>J</i> = 7.4 Hz, 1.6 Hz, H-6); 8.14 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-10); 7.82 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.67–7.57 (m, 3H, H-3, 4, 5); 7.50 (dd, 1H, <i>J</i> = 8.5 Hz, 1.6 Hz, H-8); 7.24 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-11); 7.21 (s, 1H, H-9); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.28 (s, 3H, ArCH ₃); 1.37 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2h	3060w, 2980w, 2910w, 2880w, 1621s, 1582s, 1560m, 1486s, 1470m, 1246s, 1040m, 800m, 822s, 819s	9.07 (s, 1H, H-1); 8.14 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-10); 7.94 (dd, 2H, <i>J</i> = 6.6 Hz, 1.8 Hz, H-2, 6); 7.84 (dd, 2H, <i>J</i> = 7.1 Hz, 1.9 Hz, H-3, 5); 7.76 (d, 1H, <i>J</i> = 8.1 Hz, H-7); 7.49 (dd, 1H, <i>J</i> = 8.3 Hz, 1.8 Hz, H-8); 7.24 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-11); 7.19 (s, 1H, H-9); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.27 (s, 3H, ArCH ₃); 1.37 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2i	3060w, 2980w, 2910w, 2880w, 1619s, 1582s, 1565s, 1550s, 1490s, 1472s, 1450m, 1250s, 1034s, 880m, 860m, 820s, 800s, 788s, 672m	9.08 (s, 1H, H-1); 8.18 (t, 1H, <i>J</i> = 1.7 Hz, H-2); 8.14 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-10); 8.00 (d, 1H, <i>J</i> = 7.7 Hz, H-4); 7.82 (dd, 1H, <i>J</i> = 7.1 Hz, 1.9 Hz, H-6); 7.75 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.58 (t, 1H, <i>J</i> = 7.8 Hz, H-5); 7.50 (d, 1H, <i>J</i> = 8.5 Hz, H-8); 7.24 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-11); 7.20 (s, 1H, H-9); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.28 (s, 3H, ArCH ₃); 1.38 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2j	3080w, 3050w, 2970w, 2910w, 2880w, 1622s, 1595s, 1580s, 1565s, 1518s, 1488s, 1470s, 1450m, 1340vs, 1250vs, 1040s, 880w, 850s, 835s, 815s, 800sh, 747m	9.25 (s, 1H, H-1); 8.47 (d, 2H, <i>J</i> = 8.7 Hz, H-2, 6); 8.24 (d, 2H, <i>J</i> = 8.8 Hz, H-3, 5); 8.16 (dd, 2H, <i>J</i> = 6.7 Hz, 1.9 Hz, H-10); 7.82 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.53 (d, 1H, <i>J</i> = 8.2 Hz, H-8); 7.25 (s, 1H, H-9); 7.22 (d, 2H, <i>J</i> = 6.8 Hz, H-11); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.29 (s, 3H, ArCH ₃); 1.38 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2k	3065w, 2975w, 2910w, 2870w, 2840w, 1626s, 1582s, 1563m, 1525vs, 1490s, 1472s, 1450m, 1348vs, 1250vs, 1039s, 882m, 866m, 830m, 820s, 798s, 735m, 680m	9.26 (s, 1H, H-1); 8.82 (t, 1H, <i>J</i> = 2.2 Hz, H-2); 8.43 (d, 1H, <i>J</i> = 7.7 Hz, H-6); 8.42 (d, 1H, <i>J</i> = 7.7 Hz, H-4); 8.15 (dd, 2H, <i>J</i> = 7.0 Hz, 2.1 Hz, H-10); 7.92 (t, 1H, <i>J</i> = 7.9 Hz, H-5); 7.79 (d, 1H, <i>J</i> = 8.2 Hz, H-7); 7.52 (d, 1H, <i>J</i> = 8.3 Hz, H-8); 7.24 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-11); 7.21 (s, 1H, H-9); 4.15 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 2.29 (s, 3H, ArCH ₃); 1.38 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)

2. Results and discussion

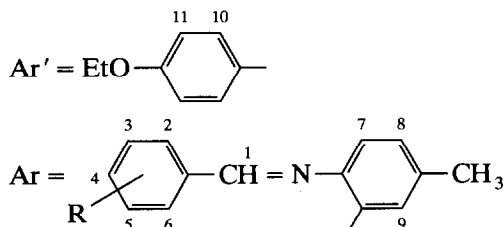
2.1. Transmetallation reaction

When **1a–1n** were heated to reflux in dry 1,4-dioxane with 4-ethoxyphenyl-tellurium trichloride (1:1) for 3 h, pale-yellow solutions were obtained:



1(a–n)

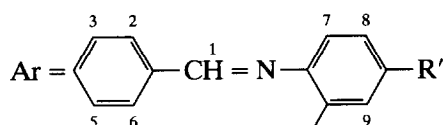
2(a–n)



R = H (**a**), *p*-MeO (**b**), *m*-MeO (**c**), *o*-MeO (**d**)

p-Cl (**e**), *m*-Cl (**f**), *o*-Cl (**g**), *p*-Br (**h**),

m-Br (**i**), *p*-NO₂ (**j**), *m*-NO₂ (**k**)



R' = Cl (**l**), Br (**m**), MeO (**n**)

Cooling the mixture gave crystals of HgCl₂ which were removed by filtration. The filtrate was evaporated to dryness *in vacuo*, the resulting solids were extracted with chloroform and the undissolved solids were filtered off. Concentration of the extract by vacuum distillation gave the corresponding transmetallation products **2a–2n** with 60–98.5% yields. The influence of the nature of substituents on the yields of the reaction is not very significant. The results of the reactions are shown in Table 1.

2.2. Spectral properties of transmetallation products

The IR spectral data of **2a–2n** (Table 2) showed absorption bands at about 3060 cm⁻¹, 1600–1450 cm⁻¹ and 1626–1614 cm⁻¹ which can be attributed to the $\nu(\text{Ar-H})$, $\nu(\text{C=C})$ and $\nu(\text{C=N})$ respectively. The absorption bands at 1250 and 1040 cm⁻¹ were due to $\nu(\text{Ar-O-C})$. Moreover, the corresponding $\delta(\text{Ar-H})$ bands appeared in the range of 900–650 cm⁻¹.

The assigned ¹H nuclear magnetic resonance (NMR) spectral data for **2a–2n** listed in Table 2 show that the different substituents at *C*-phenyl ring have no substantial effect on the chemical shifts of *N*-phenyl ring protons and ethoxyphenyl ring protons but influence the δ values of *C*-phenyl ring protons significantly. Moreover, the influence of the *para* or *meta* substituent at *C*-phenyl ring on the chemical shift of the methine proton (H-1) exhibits a linear correlation with the corresponding Hammett's substituent constants σ_p or σ_m :

$$\delta(\text{H-1}) = 9.03 + 0.26\sigma \quad n = 9, r = 0.942$$

The influence of the *ortho* substituent of *C*-phenyl ring on the chemical shift of the methine proton is very different from that of *para* or *meta* substituent. Both the electron-donating (*o*-OMe) and electron-withdrawing (*o*-Cl) groups cause a significant downfield shift of the methine proton relative to their *para* and *meta* isomers. This phenomenon is considered to be associated with the space interaction between the methine proton and the *ortho* substituent, which was also found in their corresponding mercurated derivatives [12].

Mass spectroscopy of the transmetallation products **2a–2n** indicates that no M⁺ was found under the experimental conditions, but the fragments of M⁺–Cl and M⁺–2Cl are very abundant, which revealed that the Te–Cl bonds in **2** are easily broken.

Table 2 (continued)

Compound	IR(cm ⁻¹)	¹ H NMR: δ (ppm)
2l	3055w, 2975w, 2880w, 1625s, 1575s, 1560m, 1490s, 1460s, 1250vs, 1180s, 1040m, 875m, 820s, 760s, 735m, 680m	9.13 (s, 1H, H-1); 8.19 (d, 2H, <i>J</i> = 8.8 Hz, H-10); 8.04 (dd, 2H, <i>J</i> = 7.6 Hz, 2.0 Hz, H-2, 6); 7.90 (d, 1H, <i>J</i> = 8.4 Hz, H-7); 7.76 (dd, 1H, <i>J</i> = 8.8 Hz, 2.4 Hz, H-8); 7.65 (m, 3H, H-3, 4, 5); 7.29 (d, 2H, <i>J</i> = 8.8 Hz, H-11); 7.23 (d, 1H, <i>J</i> = 2.4 Hz, H-9); 4.16 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 1.39 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2m	3060w, 2970w, 2890w, 1620s, 1575s, 1560s, 1490s, 1468s, 1460s, 1255vs, 1180s, 1040s, 875w, 820s, 800m, 760s, 700m, 680s	9.13 (s, 1H, H-1); 8.19 (d, 2H, <i>J</i> = 8.8 Hz, H-10); 8.04 (d, 2H, <i>J</i> = 7.2 Hz, H-2, 6); 7.88 (dd, 1H, <i>J</i> = 7.6 Hz, 2.0 Hz, H-8); 7.82 (d, 1H, <i>J</i> = 8.8 Hz, H-7); 7.65 (m, 3H, H-3, 4, 5); 7.37 (s, 1H, H-9); 7.29 (d, 2H, <i>J</i> = 8.8 Hz, H-11); 4.16 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 1.39 (t, 3H, <i>J</i> = 7.0 Hz, CH ₃)
2n	3050w, 2995w, 2975w, 2880w, 1620s, 1582s, 1490m, 1475s, 1250s, 1180s, 1035s, 865w, 820s, 760s, 690s	9.07 (s, 1H, H-1); 8.19 (d, 2H, <i>J</i> = 8.8 Hz, H-10); 8.02 (dd, 2H, <i>J</i> = 7.0 Hz, 2.0 Hz, H-2, 6); 7.90 (d, 1H, <i>J</i> = 8.8 Hz, H-7); 7.62 (m, 3H, H-2, 3, 4); 7.26–7.29 (m, 3H, H-8, 11); 6.87 (d, 1H, <i>J</i> = 2.5 Hz, H-9); 4.16 (q, 2H, <i>J</i> = 7.0 Hz, OCH ₂); 3.72 (s, 3H, OCH ₃); 1.39 (t, 3H, <i>J</i> = 7.2 Hz, CH ₃)

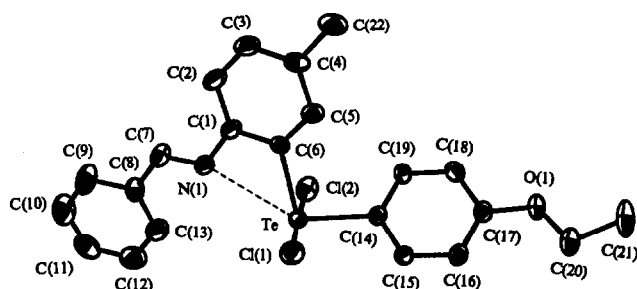


Fig. 1. Molecular structure of 2a.

2.3. X-ray crystal structure of 2a

The X-ray crystal structure of 2a was determined in order to investigate the effect of *ortho* imino nitrogen atom on the structure of transmetallation products.

TABLE 3. Selected bond lengths and angles for the title compound (estimated standard deviations in parentheses)

Bond length (Å)		Bond length (Å)	
Te–Cl(1)	2.5373(9)	C(5)–C(6)	1.381(4)
Te–Cl(2)	2.4968(9)	C(7)–C(8)	1.478(5)
Te–N(1)	2.905(2)	C(8)–C(9)	1.394(5)
Te–C(6)	2.120(3)	C(8)–C(13)	1.373(6)
Te–C(14)	2.125(3)	C(9)–C(10)	1.389(6)
O(1)–C(17)	1.368(4)	C(10)–C(11)	1.316(6)
O(1)–C(20)	1.441(4)	C(11)–C(12)	1.367(6)
N(1)–C(1)	1.412(4)	C(12)–C(13)	1.365(5)
N(1)–C(7)	1.269(4)	C(14)–C(15)	1.386(4)
C(1)–C(2)	1.396(4)	C(14)–C(19)	1.394(4)
C(1)–C(6)	1.393(5)	C(15)–C(16)	1.392(5)
C(2)–C(3)	1.385(5)	C(16)–C(17)	1.386(5)
C(3)–C(4)	1.395(6)	C(17)–C(18)	1.388(4)
C(4)–C(5)	1.385(4)	C(18)–C(19)	1.372(4)
C(4)–C(22)	1.509(5)	C(20)–C(21)	1.508(5)

Bond angle (°)		Bond angle (°)	
Cl(1)–Te–Cl(2)	177.31(4)	C(4)–C(5)–C(6)	119.6(3)
Cl(1)–Te–N(1)	104.09(6)	C(1)–C(6)–C(5)	123.0(3)
Cl(1)–Te–C(6)	88.39(9)	N(1)–C(7)–C(8)	121.7(4)
Cl(1)–Te–C(14)	88.84(9)	C(7)–C(8)–C(9)	118.9(3)
Cl(2)–Te–N(1)	78.31(6)	C(7)–C(8)–C(13)	122.4(4)
Cl(2)–Te–C(1)	85.42(7)	C(9)–C(8)–C(13)	118.6(3)
Cl(2)–Te–C(6)	92.15(9)	C(8)–C(9)–C(10)	119.0(4)
Cl(2)–Te–C(14)	88.48(9)	C(9)–C(10)–C(11)	120.9(5)
N(1)–Te–C(6)	53.6(1)	C(10)–C(11)–C(12)	121.2(4)
N(1)–Te–C(14)	147.19(9)	C(11)–C(12)–C(13)	119.7(4)
C(6)–Te–C(14)	97.7(2)	C(8)–C(13)–C(12)	120.6(4)
C(17)–O(1)–C(20)	118.2(3)	C(15)–C(14)–C(19)	121.0(3)
C(1)–N(1)–C(7)	120.9(3)	C(14)–C(15)–C(16)	119.9(3)
N(1)–C(1)–C(2)	127.5(3)	C(15)–C(16)–C(17)	118.5(3)
N(1)–C(1)–C(6)	115.4(3)	O(1)–C(17)–C(16)	122.9(3)
C(2)–C(1)–C(6)	117.0(3)	O(1)–C(17)–C(18)	115.7(3)
C(1)–C(2)–C(3)	120.4(3)	C(16)–C(17)–C(18)	121.4(3)
C(2)–C(3)–C(4)	121.6(4)	C(17)–C(18)–C(19)	120.0(4)
C(3)–C(4)–C(5)	118.5(3)	C(14)–C(19)–C(18)	119.1(3)
C(3)–C(4)–C(22)	120.2(3)	O(1)–C(20)–C(21)	105.8(4)
C(5)–C(4)–C(22)	121.3(3)		

TABLE 4. Atomic coordinates and equivalent isotropic thermal parameters (estimated standard deviations in parentheses)

Atom	x	y	z	B (Å ²)
Te	0.13855(2)	0.18670(6)	0.11251(2)	3.024(8)
Cl(1)	0.11482(9)	−0.0966(3)	0.15410(9)	4.89(5)
Cl(2)	0.16381(8)	0.4707(3)	0.07630(8)	4.76(4)
O(1)	0.2221(3)	0.4877(8)	0.3619(2)	4.8(1)
N(1)	0.0550(2)	0.2066(9)	−0.0008(2)	3.8(1)
C(1)	0.0215(3)	0.252(1)	0.0357(3)	3.6(2)
C(2)	−0.0365(3)	0.298(1)	0.0195(4)	4.8(2)
C(3)	−0.0633(3)	0.341(1)	0.0608(4)	5.1(2)
C(4)	−0.0331(3)	0.343(1)	0.1194(3)	4.3(2)
C(5)	0.0245(3)	0.299(1)	0.1359(3)	3.7(2)
C(6)	0.0509(3)	0.258(1)	0.0943(3)	3.1(1)
C(7)	0.0328(3)	0.198(1)	−0.0550(3)	4.5(2)
C(8)	0.0675(3)	0.156(1)	−0.0941(3)	4.2(2)
C(9)	0.0397(4)	0.131(2)	−0.1525(4)	7.2(3)
C(10)	0.0724(5)	0.094(2)	−0.1894(4)	7.6(3)
C(11)	0.1288(4)	0.083(1)	−0.1699(4)	5.9(2)
C(12)	0.1570(4)	0.108(2)	−0.1128(4)	6.7(3)
C(13)	0.1264(4)	0.144(2)	−0.0751(4)	5.8(2)
C(14)	0.1674(3)	0.2886(9)	0.1976(3)	2.8(1)
C(15)	0.2010(3)	0.184(1)	0.2410(3)	3.2(1)
C(16)	0.2214(3)	0.248(1)	0.2970(3)	3.6(2)
C(17)	0.2048(3)	0.414(1)	0.3083(3)	3.4(1)
C(18)	0.1711(3)	0.518(1)	0.2647(3)	3.8(2)
C(19)	0.1526(3)	0.457(1)	0.2092(3)	3.5(2)
C(20)	0.2461(4)	0.376(1)	0.4107(3)	5.2(2)
C(21)	0.2469(5)	0.483(2)	0.4632(4)	7.3(3)
C(22)	−0.0638(4)	0.387(2)	0.1634(4)	6.2(2)

Figure 1 shows the molecular structure of 2a. Selected bond lengths and bond angles are listed in Table 3, and atomic coordinates in Table 4. The coordination about the tellurium atom can be considered as essentially pseudo-octahedral, with a lone pair of electrons occupying the fourth equatorial site. The distances of Te–C(6) (2.120(3) Å) and Te–C(14) (2.125(3) Å) are in good agreement with the sum of Pauling's single-bond covalent radii of Te (1.37 Å) and sp²-hybridized carbon atom (0.74 Å) [13], and with the values in the crystal structures of the analogous compounds, 4-EtOC₆H₄-TeCl₃ [14], (C₇H₇O)₂TeCl₂ [15] and 2-phenylazophenyltellurium trichloride [5], in which the bond lengths of Te–C are in the range 2.09–2.16 Å. The Te–Cl bond lengths, 2.4968(9) and 2.5373(9) Å, are longer than the sum of the covalent radii (2.36 Å) [13], or the Te–Cl distance in TeCl₄ (mean, 2.311 Å [16]) but agree well with the values commonly found for analogous compounds [4,5,17]. The Te–N(1) distance of 2.905(2) Å is longer than those reported for 2-phenylazophenyltellurium trichloride, 2.417 Å [5], and for 2-(pyridyl)phenyl tellurium tribromide, 2.244 Å [9], but shorter than the sum of the van der Waals radii of Te and N (about 3.7 Å) [18], indicating a substantial secondary intramolecular coordination between Te and

N(1). It is of interest to note that the twist angle of both the *N*-phenyl and the *C*-phenyl rings out of the plane C(8)–C(7)=N(1)–C(1) in the Schiff base moiety is very small (less than 8°). This structure forms a striking contrast with those of substituted benzylideneanilines, in which the twist angle of the *N*-phenyl ring out of the plane C–C=N–C ranges from 44.1° to 55.2° [19]. The greater changes in the structure of the Schiff base moiety upon the *ortho* position of the *N*-phenyl ring displaced by Te atom may be caused by the N → Te intramolecular coordination, which holds the Schiff base moiety in near-planar geometry. The bond angles of 115.4(3)° for N(1)–C(1)–C(6) and 112.9(3)° for C(1)–C(6)–Te are less than 120°. This can also be explained in terms of the secondary intramolecular interaction between Te and N(1). The small value of the N(1)–Te–C(6) angle (53.6(1)°) is due to the constraint of the four-membered chelate ring.

3. Experimental details

3.1. Materials and instruments

All reactions were carried out in reagent-grade solvents. 1,4-Dioxane was treated according to the literature method [20] before use. Compounds **1a–1n** were synthesized by the procedure as described in literature [11] and were characterized by melting-point and IR data. 4-Ethoxyphenyltellurium trichloride was obtained from the reaction of ethoxybenzene with TeCl₄ in refluxing chloroform [3]. Melting points were measured on a WC-1 apparatus and are uncorrected. Elemental analysis was determined with a Carlo-Erba 1106. IR spectra were recorded on a Shimadzu IR-435 spectrometer using KBr pellets. ¹H NMR spectra were obtained on a Bruker AM-400 at 20°C in dimethylsulphoxide-*d*₆ with tetramethylsilane (TMS) as an internal reference standard ($\delta = 0$ ppm). Mass spectra were recorded on a HP 5988A mass spectrometer operating at 70 eV. The sample was introduced by direct inlet techniques with a source temperature of about 250°C.

3.2. General procedure for the transmetallation reactions

4-Ethoxyphenyltellurium trichloride (0.71 g, 2 mmol) was added to the Schiff-base-type arylmercury compounds **1a–1n** (2 mmol) in 1,4-dioxane (30 ml). The mixture was refluxed for 3 h; then cooling the mixture gave the crystals of HgCl₂ which were removed by filtration. The filtrate was evaporated to dryness *in vacuo*, and subsequently the resulting solids were extracted with chloroform (30 ml) and the undissolved solids removed. Concentration of the extract by vacuum distillation gave the corresponding transmetallation products **2a–2n** which were recrystallized from the

mixed solvent of chloroform and methanol. The results of the reactions are listed in Table 1. The spectral data of the products are formulated in Table 2.

3.3. X-ray crystal structure determination for **2a**

Single crystals of **2a** suitable for the X-ray diffraction study were obtained by slow evaporation of dilute solution of **2a** in a mixed solvent of chloroform and methanol (3:1 v/v) at room temperature.

The crystal data are as follows: C₂₂H₂₁Cl₂NO₂Te; *M* = 512.91; monoclinic; space group, *C*2/*c* with cell dimensions *a* = 24.337 (2) Å, *b* = 7.689 (1) Å, *c* = 24.257 (2) Å and $\beta = 107.02$ (1)°; *Z* = 8; *V* = 4342.2 Å³; *D*_c = 1.570 g cm⁻³; *F*(000) = 2032; $\mu = 134.76$ cm⁻¹.

Data collection and reduction were performed as follows. A single crystal of approximate dimensions 0.22 mm × 0.19 mm × 0.06 mm was mounted on the end of a glass fibre. The X-ray diffraction intensity data of 4720 independent reflections, of which 3473 with *I* > 3σ(*I*) were observable, were collected with an Enraf–Nonius CAD-4 four-circle diffractometer at 298 K using graphite-monochromated Cu Kα radiation ($\lambda = 1.54184$ Å) with the ω–2θ scan mode within the range 0° ≤ θ ≤ 70°. Throughout the data collection the intensities of three standard reflections were monitored at regular intervals (3600 s) to check the stability of the system. Empirical absorption and Lorentz–polarization corrections for all intensities were applied.

Structure solution and refinement were carried out as follows. The structure was solved by Patterson methods using an Enraf–Nonius SDP program package [21] on a PDP 11/44 computer. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic of their carrier atoms. The final values of *R* and *R*_w were 0.057 and 0.062 respectively. The final positional parameters are given in Table 4.

Full tables of bond lengths and angles, torsional angles, hydrogen coordinates, anisotropic thermal parameters and the figure of unit cell are available from the authors.

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References

- 1 K.L. Ding, Y.J. Wu, Y. Wang, Y. Zhu and L. Yang, *J. Organomet. Chem.*, 463 (1993) 77, and references cited therein.

- 2 M.R. Detty, H.R. Luss, J.M. McKelrey and S.M. Gerr, *J. Org. Chem.*, 51 (1986) 1692.
- 3 M.R. Detty and S.M. Luss, *J. Org. Chem.*, 48 (1983) 5149.
- 4 H.J. Gysling, H.R. Luss and S.A. Gardner, *J. Organomet. Chem.*, 184 (1980) 417.
- 5 M.A.K. Ahmed and W.R. McWhinnie, *J. Organomet. Chem.*, 281 (1985) 205.
- 6 R.E. Cobbleddick, F.M.B. Einstein, W.R. McWhinnie and F.H. Musa, *J. Chem. Res. M*, (1979) 1901.
- 7 H.B. Singh and W.R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, (1985) 821.
- 8 V.I. Minkin, I.D. Sadekov, A.A. Maksimenko, O.E. Kompan and Yu.T. Struchkov, *J. Organomet. Chem.*, 402 (1991) 331.
- 9 N. Al-Salim, A.A. West, W.R. McWhinnie and T.A. Hamor, *J. Chem. Soc., Dalton Trans.*, (1988) 2363.
- 10 G.T. Morgan and M.D.K. Drew, *J. Chem. Soc.*, (1925) 2307.
- 11 K.L. Ding, Y.J. Wu, H.W. Hu, L.F. Shen and X. Wang, *Organometallics*, 11 (1992) 3849.
- 12 Y.J. Wu, K.L. Ding, Z.Y. Yu, D.H. Wu and L.F. Shen, *Chem. Res. Chin. Univ.*, 8 (1992) 253.
- 13 L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, NY, 1960.
- 14 P.H. Bird, V. Kumar and B.C. Pant, *Inorg. Chem.*, 19 (1980) 2487.
- 15 R.H. Jones and T.H. Hamor, *J. Organomet. Chem.*, 262 (1984) 151.
- 16 B. Buss and B. Krebs, *Angew. Chem., Int. Edn.*, 9 (1970) 463.
- 17 J. Bergman and L. Engman, *J. Organomet. Chem.*, 181 (1979) 335.
- 18 V.I. Minkin, A.A. Maksimenko, G.K. Mehrotra, A.G. Maslakov, O.E. Kompan, I.D. Sadekov, Yu.T. Struchkov and D.S. Yufit, *J. Organomet. Chem.*, 348 (1988) 63.
- 19 H.B. Burgi and J.D. Dunitz, *Helv. Chim. Acta*, 53 (1970) 1749.
- 20 N.L. Cheng and S.S. Hu, *Handbook of Solvents*, Chemical Industry Press, Beijing, 1986, p. 407.
- 21 B.A. Frenz & Assoc., Inc., College Station, TX, USA; Enraf-Nonius, Delft, Netherlands, 1985.