SYNTHESIS, STRUCTURE AND REACTIVITY OF TRIPHENYLBISMUTH BIS(2-THIOPHENECARBOXYLATE)

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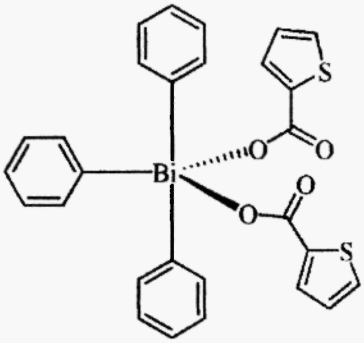
Abstract: Triphenylbismuth bis(2-thiophenecarboxylate) was prepared and its X-ray structure determined. The structure features two independant molecules, each of which adopt trigonal-bipyramidal geometries, with the carboxylato groups showing a strong bidentate apical coordination. Under copper catalysis, triphenylbismuth bis(2-thiophenecarboxylate) led to modest to moderate yields of *O*- or *N*-phenylation products.

INTRODUCTION

Copper-catalyzed *O*- and *N*-arylation reactions involving triarylbismuth diacetates [1,2] or aryllead triacetates [3] are ligand coupling reactions [4] which were discovered in the eighties independently by Barton's and Dodonov's group. These reagents lead generally to efficient arylation under mild neutral conditions (room temperature or 40°C, no added basic reagent). Recently, the scope of these main group metal catalyzed reactions was broadened when Chan [5] and Evans [6] reported that organoboron compounds can be used as the source of the organic aryl ligand. Subsequently, organosiloxanes [7] and diaryliodonium salts [8] proved also to be efficient reagents for these mild copper catalyzed *O*- and *N*-arylation reactions.

Since Liebeskind's first report, copper 2-thiophenecarboxylate, [9] [Cu(I)TC], has been gaining growing interest for copper-catalyzed substitution reactions. Its use appeared fruitful in a variety of C-C coupling reactions [10] as well as in Atom Transfer Radical Polymerization. [11] It has also been used recently for the synthesis of enamides. [12] As the success of these catalytic systems is dependent upon the presence of the thiophenecarboxylate ligand, we considered that this ligand could further improve the efficiency of copper catalyzed *O*- and *N*-arylation reactions involving triarylbismuth diacetates. At first sight, Cu(I)TC - $Ph_3Bi(OAc)_2$ would appear as the simplest system. However, the TC ligand would be present at the catalytic level when the acetate ligand would be present at the stoichiometric level. As ligand redistribution cannot be excluded under these conditions, the exact role of TC could not be ascertained. Recently, the influence of the nature of the C-Bi ligands present on pentavalent organobismuth compounds was reported, [13] but the influence of the acyloxy group has barely been addressed. [14] In the related lead (IV) chemistry, the replacement of acetate ligands by 2-thiophenecarboxylate ligands has shown a beneficial effect on alcohol oxidations with lead tetraacylate. [15] As part of our studies on the selective arylation of heterocyclic amines by triarylbismuth diacylates, [16] we require mild and efficient arylation reaction systems. Therefore we decided to investigate the synthesis and X-ray structure of triphenylbismuth bis(2-thiophenecarboxylate) [Ph_3BiTC_2] and to compare it to other copper or copper salts-catalyzed / triphenylbismuth diacetate *O*- and *N*-arylation reaction systems.



Scheme 1

MATERIALS AND METHODS

Melting points were taken on a Büchi capillary apparatus and are uncorrected. NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer. Column chromatography were performed with Merck "Silicagel-60" 60-230 mesh.

Preparation of triphenylbismuth bis(2-thiophenecarboxylate) from triphenylbismuth carbonate Triphenylbismuth carbonate [17] (4.2 g, 8.4 mmole) was added to a solution of 2-thiophenecarboxylic acid (2.37 g, 18.5 mmole) in methylene dichloride (30 cm^3). The slurry was stirred at room temperature for one hour. After filtration, the solvent was distilled under reduced pressure and the solid residue recrystallized from CH_2Cl_2/pentane (1/1) to afford Ph_3BiTC_2 (5.3 g, 91 %), mp 169 °C. lit. [18] mp 168 °C; ^{1}H-NMR δ ($CDCl_3$) 6.96 (dd, 2H, J = 3.8 and 4.9 Hz, H-4'), 7.34 (dd, 2H, J = 1.1 and 4.9 Hz, H-5'), 7.43 (t, 3H, J = 7.9 Hz, H-4), 7.59 (t, 6H, J = 7.8 Hz, H-3), 7.60 (dd, 2H, J = 1.1 and 4.8 Hz, H-3'), 8.32 (d, 6H, J = 8.3 Hz, H-2). ^{13}C-NMR δ ($CDCl_3$) 127.27 (C-5'), 130.60 (C-4'), 130.88 (C-4), 131.27 (C-3), 132.01 (C-3'), 134.03 (C-2), 137.72 (C-2'), 159.22 (C-1), 167.45 (CO). $C_{28}H_{21}BiO_4S_2$ (694.58) requires C: 48.42, H: 3.05%. Found C: 48.38, H: 3.01%.

Preparation of triphenylbismuth bis(2-thiophenecarboxylate) from triphenylbismuth diacetate. A mixture of triphenylbismuth diacetate [19] (5 g, 8.9 mmole) and 2-thiophenecarboxylic acid (2.9 g, 23.14 mmole) in methylene dichloride (100 cm^3) was stirred at room temperature for 15 hours. After filtration, the solvent was distilled under reduced pressure and the solid residue washed with acetone (100 cm^3). Recrystallization from CH_2Cl_2/pentane (1/1) afforded pure Ph_3BiTC_2, (4.53 g, 78 %).

Metallic copper catalyzed phenylation with triphenylbismuth bis(2-thiophenecarboxylate) - **General Procedure:** A mixture of the substrate (0.4 mmole, 1 equiv.), Ph_3BiTC_2 (1.1 equiv.) and metallic copper powder (0.1 equiv.) or copper diacetate (0.1 equiv.) in methylene dichloride (4 or 20 cm^3) was stirred at room temperature for the time indicated (Table 5). The mixture was filtered and the solvent distilled under reduced pressure. Column chromatography of the residue afforded the *O*- or *N*-phenylation products, which were identical to previously prepared samples. The yields are reported in Table 5.

3-Phenoxy-2,2-dimethylpropan-1-ol (1a): [20] colourless oil, (ether/pentane 1/4), ^{1}H-NMR δ ($CDCl_3$) 1.02 (s, 6H, CH_3), 3.52 (s, 2H, H-1), 3.75 (s, 2H, H-3), 6.91 (d, 2H, J = 7.7 Hz, H-6), 6.95 (t, 2H, J = 7.0 Hz, H-7), 7.28 (t, 1H, J = 8.1 Hz, H-8). ^{13}C-NMR δ ($CDCl_3$) 21.54 (CH_3), 36.24 (C-2), 69.54 (C-1), 74.43 (C-3), 114.39 (C-6), 120.66 (C-8), 129.31 (C-7), 158.93 (C-5).

3,5-Di-*tert*-butylphenyl phenyl ether (2a): mp 72-73 °C, lit. [21] mp 71-72 °C (ether/pentane 1/4), ^{1}H-NMR δ ($CDCl_3$) 1.35 (s, 18H, CH_3), 6.95 (d, 2H, J = 2.6 Hz, H-4), 7.06 (m, 2H, H-2), 7.26 (m, 2H, H-9), 7.34 (m, 2H, H-10), 7.43 (t, 1H, J = 8.6 Hz, H-11). ^{13}C-NMR δ ($CDCl_3$) 31.30 (Me), 34.87 ($Me_3\underline{C}$), 113.60 (C-2, C-6), 117.34 (C-4), 118.01 (C-2', C-6'), 121.56 (C-4'), 129.52 (C-3', C-5'), 152.57 (C-3, C-5), 156.17 (C-1), 157.73 (C-1').

***N*-(*tert*-Butyl)-*N*-phenylamine (3a)**: [14] colourless oil, (ether/pentane 1/4), ^{1}H-NMR δ (DMSO-d_6) 1.27 (s, 9H, CH_3), 3.41 (br s, 1H, NH), 6.57 (t, 1H, J = 6.0 Hz, H-4), 6.73 (d, 2H, J = 8.8 Hz, H-2), 7.06 (t, 2H, J = 8.8 Hz, H-3). ^{13}C-NMR δ (DMSO-d_6) 29.36 (CH_3), 50.70 (Me_3C), 115.92 (C-2), 116.30 (C-4), 127.64 (C-3),146.88 (C-1).

***N*-Phenyl-1,2,3,4-tetrahydroisoquinoline (4a)**: mp 45 °C, lit. [22] mp 45-46 °C (ether/pentane 1/4), ^{1}H-NMR δ (DMSO-d_6) 2.88 (t, 2H, J = 5.9 Hz, H-3), 3.50 (t, 2H, J = 5.8 Hz, H-4), 4.36 (s, 2H, H-1), 6.73 (t, 1H, J = 7.1 Hz, H-12), 6.98 (d, 2H, J = 8.1 Hz, H-10), 7.15-7.20 (m, 4H, H-5, 6, 7, 8), 7.22 (t, 2H, J = 8.00 Hz, H-11). ^{13}C-NMR δ (DMSO-d_6) 27.83 (C-4), 45.40 (C-3), 49.51 (C-4), 114.41 (C-10), 117.66 (C-12), 125.56 (C-6), 125.99 (C-7), 126.31 (C-8), 128.08 (C-5), 128.75 (C-11), 135.23 (C-4a), 136.68 (C-8a), 146.29 (C-9).

X-Ray structure determination of triphenylbismuth bis(2-thiophenecarboxylate): [23]

Suitable crystals for X-ray analysis were obtained by recrystallization in CH_2Cl_2/pentane. The crystal was measured at room temperature on an Enraf Nonius Kappa CCD diffractometer [24] with monochromated MoKα (λ = 0.71070 Å) radiation. A set of 90 frames was measured for Ph_3BiTC_2, through a 180° φ scan in the following conditions : 2° φ steps, 120 seconds per frame repeated twice. All intensities were corrected for Lorentz polarization and for absorption. [25] Calculations were performed by direct methods using SHELXL-97 program. [26] All non hydrogen atoms were refined anisotropically through cycles of full-matrix least squares using SHELXL-97. The residual highest electron density peak is equal to 1.62 and is located at 0.85 Å from Bi(2).

RESULTS AND DISCUSSION

Triarylbismuth diacylates can be obtained by two main methods: *type a* = oxidation of the corresponding triarylbismuthane in the presence of the required carboxylic acid or *type b* = ligand exchange on a preformed pentavalent organobismuth compound. As *type a* oxidations are generally performed in the presence of an excess of the carboxylic acid, we preferred to prepare triphenylbismuth bis(2-thiophenecarboxylate) by the *type b* ligand exchange reaction which requires the use of only a small excess of the acyl ligand. Reaction of triphenylbismuth carbonate [17] with a slight excess (1.1 molar equiv.) of 2-thiophenecarboxylic acid at room temperature for 1 hour afforded Ph_3BiTC_2 in 91% yield. This product was prepared by Domagala *et al.* by a slightly different procedure in a modest 47% yield. [18] Under appropriate conditions, this reaction is mild and high yielding, but the synthesis of Ph_3BiCO_3 results from a two steps process: oxidation of the triarylbismuthane to dihalotriarylbismuth followed by reaction with potassium carbonate. In an alternative approach, ligand exchange between a triarylbismuth diacetate and a strongly acidic ligand leads to high yields of the exchange products. [27] Triphenylbismuth diacetate was prepared in one step by treating triphenylbismuthane with sodium perborate in acetic acid. [19] It was then treated with a small excess (1.3 molar equiv.) of 2-thiophenecarboxylic acid in methylene dichloride at room temperature for 15 hours. In spite of the only slightly more acidic character of 2-thiophenecarboxylic acid (p_KA 3.5 in H_2O), [28] the ligand exchange was nearly complete, and Ph_3BiTC_2 was isolated in 78% yield after recrystallization.

As the success of copper-catalyzed *O*- and *N*-arylation reactions with pentavalent organobismuth derivatives is strongly dependent upon the presence of a bidentate carboxylic acid-type ligand, we performed an X-ray structure determination of Ph_3BiTC_2 to investigate the role of the sulfur atom as a possible coordinating ligand in the bidentate structure of the acyl groups. X-ray structures of pentavalent organobismuth dicarboxylates are not extensively represented in the literature, as a limited number of such structures has been reported: *i.e.* triphenylbismuth bis(2-furanecarboxylate), [29] triphenylbismuth bis(trifluoroacetate), [30] triphenylbismuth bis(formate), [31] and a series of bis(hydroxypropanoato)- and bis(hydroxybutanoato)-triarylbismuth. [32] These triarylbismuth dicarboxylates have a distorted trigonal bipyramidal structure with the aryl groups in equatorial positions and the carboxylato groups in apical positions. Moreover, the two oxygen atoms of each carboxylato groups coordinate to the central bismuth atom resulting in a coordination number of seven. Two of the aromatic rings are perpendicular to the Bi-O bond while the third one is parallel to it. Although the structure of triphenylantimony bis(2-thiophenecarboxylate) [18] has been described, the structure of triphenylbismuth bis(2-thiophenecarboxylate) was not reported.

The title compound crystallizes with two independent molecules in the asymmetric unit [$Ph_3Bi(1)TC_2$ and $Ph_3Bi(2)TC_2$], as well as with one included solvent molecule of CH_2Cl_2. The structure of this complex is shown in Figure 1. Selected geometrical parameters are collected in Tables 1-4 according to the numbering scheme displayed in Figure 1. Considering the shortest distances between the Bi atoms and their ligand atom donors [O(2), O(4), C(11), C(17) and C(27) for Bi(1) molecule and O(5), O(7), C(39), C(45) and C(51) for Bi(2) molecule, respectively], the geometry around the bismuth atoms can be described as a trigonal bipyramid. However, in the two independent molecules, each of the two carboxylic ligands is bound to the central Bi atom by one short bond, [Bi(2)-O(5) and Bi(2)-O(7): mean distance 2.310 (4) Å], and a weaker intramolecular Bi-O bond, [Bi(2)-O(6) and Bi(2)-O(8): mean distance 2.699 (4) Å], and the polyhedron around Bi could be viewed as a distorted pentagonal bipyramid, in which the four oxygens of the carboxylate and C(39) atoms are in the equatorial plane, while C(45) and C(51) are in the apical positions (see Tables 2 and 3). The same feature is observed with Bi(1) molecule, but with Bi-O short bonds close to 2.310 (4) Å and weak bonds close to 2.856 (4) Å. However, as the O(2)-Bi(1)-O(4) angle is 172.30 (14)° for the Bi(1) molecule and the O(5)-Bi(2)-O(7) angle is 175.43 (15)° for the Bi(2) molecule, it is more accurate to consider the structures as distorted trigonal bipyramids in which the three phenyl groups occupy the equatorial plane and the carboxylato groups occupy the apical positions.

In the two molecules, the weakly coordinating oxygen atoms of the two carboxylato ligands located at 2.859 (4) Å and 2.854 (5) Å from the bismuth atom in Bi(1) molecule, and located at 2.722 (5) Å and 2.677 (7) Å from the bismuth atom in Bi(2) molecule, are *cis* to each other respectively. It is likely that this causes the significant deviation of the C-Bi-C angles from 120° in the equatorial planes [C(11)-Bi(1)-C(17) = 148.40 (2)° for Bi(1) molecule, and C(45)-Bi(2)-C(51) 151.7 (3)° for Bi(2) molecule]. The non-bonding Bi-O distances are only 24% longer for the Bi(1) molecule and 16 % longer for the Bi(2) molecule, which are among the shortest coordinating bonds observed in such pentavalent triarylbismuth diacylates. Interestingly, these distances are 34% longer in the case of the corresponding triphenylantimony bis(2-thiophenecarboxylate). [18] It must also be noted that the thiophene rings in the Bi(1) molecule, [S(1) and S(2) atoms], are in *cis* position while the position is *trans* for the Bi(2) molecule, [S(3) and S(4) atoms].

If we consider the dihedral angles between the planes of the thiophene groups A and B, and the phenyl group C [C(23)-C(28) for molecule Bi(1) and C(39)-C(44) for molecule Bi(2)], we can observe, in the case of the Bi(2) molecule that the phenyl C plane has a value close to 8.9 (3)° respectively to planes A and B (see Table 4). The two phenyl D and E planes have only a 1.7 (3)° angle difference. The phenyl C plane, parrallel to the Bi-O bond, is nearly perpendicular to the other two phenyl groups (CD and CE angles close to 95°). In the case of the Bi(1) molecule, the helical shape is more pronounced, as the angles between planes AC, BC and DE range between 15 and 29° and the angles between the phenyl planes are less important (CD and CE angles close to 81°).

The bond distances and angles of the thiophene rings are essentially the same as found in 2-thiophenecarboxylic acid. [33] Coordination of the thiophene sulfur atoms to the bismuth atoms can be excluded, as intermolecular distances smaller than the sum of the van der Waals radii do not exist.

Figure 1 ORTEP view of the two molecules of Ph_3BiTC_2.

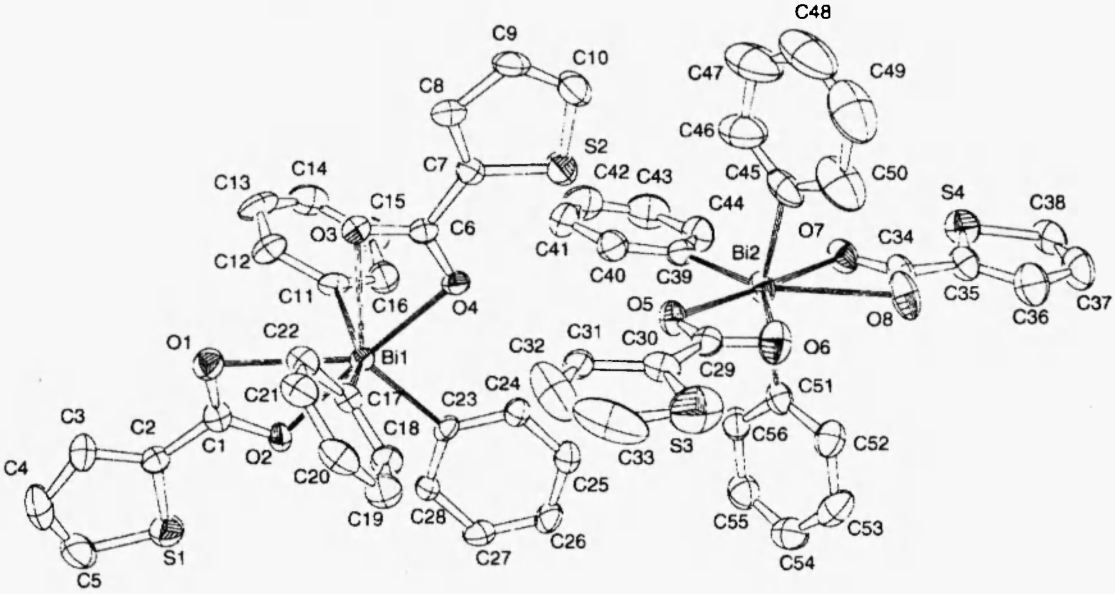


Table 1: Crystal data for triphenylbismuth bis(2-thiophenecarboxylate)

Formula	$C_{57}H_{44}Bi_2Cl_2O_8S_4$	Formula weight	1474.02
Crystal system	Triclinic	Crystal size, mm	0.25x0.15x0.1
Space group	P-1	*a*, Å	9.2335 (2)
b, Å	16.1710 (5)	*c*, Å	19.5592 (5)
β, °	77.368 (1)	*V*, Å^3	2739.2 (1)
Z	2	Diffractometer	Kappa CCD
Temperature, K	193 (2)	μ(MoK_), cm^{-1}	6.719
Trans. Factors	0.912, 1.077	D_{calcd}, g cm^{-3}	1.787
F(000)	1428	θ_{max} °	26.37
Reflns meas.	10336	Reflns unique, R_{int}	10258, 0.051
Reflns with I > 4 σ(*F*)	8404	Weighting scheme	calcd [a]
$R(F^2)$, $R_w(F^2)$	0.036, 0.096	ρ, e.Å^{-3}	1.62; -2.03
Programs used	SHELXL 97 (Sheldrick, 1997); Kappa CCD (Nonius, 1998)		
Deposition number	CCDC 167053		

[a] $w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 2.0512P]$ where $P = (F_o^2 + 2F_c^2)/3$

The arylating properties of Ph_3BiTC_2 under copper catalysis were tested with four substrates: two hydroxyl containing compounds (2,2-dimethyl-1,3-propanediol **1** and 3,5-di-*tert*-butylphenol **2**) and two amino compounds (*tert*-butylamine **3** and 1,2,3,4-tetrahydroisoquinoline **4**). When 0.1 M solutions of the substrates in methylene dichloride were treated with Ph_3BiTC_2 (1.1 mol-equiv.) in the presence of a catalytic amount of a copper species (either metallic copper or copper(II) diacetate, 0.1 mol-equiv.) at room temperature, poor to modest yields of the expected *O*- or *N*-phenylation products were obtained (Table 5).

Table 2: Selected bond lengths (A) for Ph_3BiTC_2

Bi(1)-O(1)	2.859 (4)	Bi(2)-O(5)	2.297 (4)
Bi(1)-O(2)	2.310 (4)	Bi(2)-O(6)	2.722 (5)
Bi(1)-O(3)	2.854 (5)	Bi(2)-O(7)	2.328 (4)
Bi(1)-O(4)	2.311 (4)	Bi(2)-O(8)	2.677 (7)
Bi(1)-C(11)	2.202 (5)	Bi(2)-C(39)	2.222 (6)
Bi(1)-C(17)	2.207 (5)	Bi(2)-C(45)	2.209 (7)
Bi(1)-C(23)	2.226 (5)	Bi(2)-C(51)	2.197 (6)

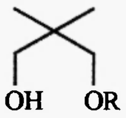
Table 3: Selected angles (°)

C(23)-Bi(1)-O(4)	85.95(18)	C(39)-Bi(2)-O(5)	88.31(19)
C(23)-Bi(1)-O(2)	87.44(18)	C(39) -Bi(2)-O(7)	87.2(2)
O(2)-Bi(1)-O(4)	172.30(14)	O(5)-Bi(2)-O(7)	175.43(15)
C(11)-Bi(1)-C(17)	148.4(2)	C(45)-Bi(2)-C(51)	151.7(3)
C(11)-Bi(1)-C(23)	108.6(2)	C(39)-Bi(2)-C(45)	101.8(3)
C(17)-Bi(1)-C(23)	103.0(2)	C(39)-Bi(2)-C(51)	106.5(2)
C(11)-Bi(1)-O(2)	89.55(17)	C(45)-Bi(2)-O(6)	79.8(2)

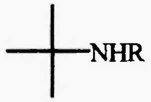
Table 4: Dihedral angles between selected planes of Ph_3BiTC_2 (°)

Planes*	$Ph_3Bi(1)TC_2$	$Ph_3Bi(2)TC_2$
AB	2.8(5)	2.4(4)
AC	15.4(4)	8.9(3)
BC	16.1(4)	8.8(5)
CD	94.8(3)	81.7(3)
CE	95.4(3)	80.7(3)
DE	29.4(3)	1.7(3)

*	$Ph_3Bi(1)TC_2$	$Ph_3Bi(2)TC_2$
Plane A:	S(2)-C(7)-C(8)-C(9)-C(10)	[S(3)-C(30)-C(31)-C(32)-C(33)]
Plane B:	S(1)-C(2)-C(3)-C(4)-C(5)	[S(4)-C(35)-C(36)-C(37)-C(38)]
Plane C:	C(23)-C(24)-C(25)-C(26)-C(27)-C(28)	[C(39)-C(40)-C(41)-C(42)-C(43)-C(44)]
Plane D:	C(17)-C(18)-C(19)-C(20)-C(21)-C(22)	[C(51)-C(52)-C(53)-C(54)-C(55)-C(56)]
Plane E:	C(11)-C(12)-C(13)-C(14)-C(15)-C(16)	[C(45)-C(46)-C(47)-C(48)-C(49)-C(50)]



1, R = H
1a, R = Ph



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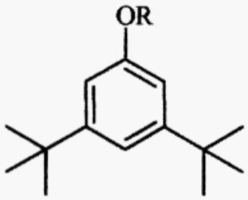
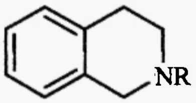


2, R = H
2a, R = Ph



4, R = H
4a, R = Ph

Surprisingly, after a 5-fold dilution, the reaction appeared to proceed more efficiently. Indeed, when 0.02 M concentrations were used instead of 0.1 M, relatively good yields were then obtained in the *O*-phenylation reactions.

This result may be related to the unusual structure of the bismuth compound Ph_3BiTC_2, revealed by the X-ray analysis. The thiophenecarboxylic ligand seems to be more strongly bonded to the bismuth atom in a bidentate manner than in any other triarylbismuth dicarboxylates. Therefore, oxidative addition on the catalytic copper species can be expected to be less efficient. When the reaction is performed under more diluted conditions, structural equilibration between the various conformers may then occur, leading to a better transmetallation.

Table 5: Copper catalysed phenylation reactions with Ph_3BiTC_2

Substrate	Reactions Conditions	Product (%)[a]	Product (%)[b]
1	Cu, 12 h, RT	**1a** (20)	**1a** (80)
1	$Cu(OAc)_2$, 12 h, RT	**1a** (19)	**1a** (51)
2	Cu, 12 h, RT	**2a** (15)	**2a** (76)
2	$Cu(OAc)_2$, 12 h, RT	**2a** (15)	**2a** (50)
3	Cu, 12 h, RT	**3a** (6)	
3	$Cu(OAc)_2$, 12 h, RT	**3a** (5)	
4	Cu, 12 h, RT	**4a** (13)	
4	$Cu(OAc)_2$, 12 h, RT	**4a** (12)	

[a] Reactions performed at 0.1 M concentration in CH_2Cl_2
[b] Reactions performed at 0.02 M concentration in CH_2Cl_2

In conclusion, triphenylbismuth bis(2-thiophenecarboxylate) can be easily synthesized in high yields by ligand exchange through reaction of either Ph_3BiCO_3 or $Ph_3Bi(OAc)_2$ with 2-thiophenecarboxylic acid. Its X-ray structure analysis revealed the presence of two independant molecules with significantly different modes of crystallization. Introduction of the 2-thiophenecarboxylic acid ligand leads to an unusually strongly bonded bidentate structure, which results in an unexpectedly modest activity as an arylating reagent in the copper-catalyzed phenylation of OH or NH containing substrates.

ACKNOWLEDGEMENT

The authors are very grateful to Dr Michel Giorgi (Universite d'Aix-Marseille 3) for his help and advice during the X-ray crystallographic studies.

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**Received: August 30, 2001 - Accepted: September 10, 2001 –
Accepted in publishable format: October 2, 2001**