Chlorination of *p*-substituted triarylpnictogens by sulfuryl chloride: Difference in the reactivity and spectroscopic characteristics between bismuth and antimony

A.F.M. Mustafizur Rahman, Toshihiro Murafuji *, Motoko Ishibashi, Youhei Miyoshi, Yoshikazu Sugihara [1]

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

Abstract

Competitive oxidative chlorination of *p*-substituted triarylstibines **3** [(*p*-XC$_6$H$_4$)$_3$Sb; **a**: X = OMe, **c**: X = Cl, **d**: CO$_2$Et, **e**: CF$_3$, **f**: CN, **g**: NO$_2$] by sulfuryl chloride was carried out against **3b** (X = H) and the electronic effect of these substituents on the chlorination of **3** was compared with that of homologous triarylbismuthanes **1**. The relative ratios **4/4b** (Ar$_3$SbCl$_2$/Ph$_3$SbCl$_2$) decreased with increasing electron-withdrawing ability of the substituents (**a**: 53/47, **c**: 49/51, **d**: 46/54, **e**: 44/56, **f**: 40/60, **g**: 37/63), but the tendency was not so pronounced as observed in the chlorination of **1**. A Hammett plot of the **4/4b** ratios against the σ_p constants exhibited a good linear relationship with a negative slope, the value of which was almost half of that deduced from the **2/2b** (Ar$_3$BiCl$_2$/Ph$_3$BiCl$_2$) ratios. The difference in the reactivity between **1** and **3** may be explained by the effect of the electron-withdrawing substituents in the aromatic rings, which affects the p-character of the lone pair on the pnictogen atoms by increasing the positive metal charge and appears more remarkably in **1** than in **3**. The ^{13}C NMR study of **3** revealed that the chemical shifts of the ipso carbons (C1) attached to the antimony show a linear relationship against the σ_p constants with a positive slope (14.5). The value was smaller than that deduced from **1** (17.0), suggesting that the antimony center of **3** is less sensitive to the substituent effect. This is in accord with the tendency of the chlorination.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Antimony; Bismuth; Oxidative chlorination; ^{13}C NMR study; Hammett plot

1. Introduction

Recently, we have reported the effect of substituents on the reactivity and spectroscopic characteristics of triarylbismuthanes **1** and their dichlorides **2** [1]. Competitive chlorination of **1** against **1b** by sulfuryl chloride revealed that the reactivity of **1** is dramatically lowered by the electron-accepting substituents. Thus,

1g bearing a nitro group does not show any reactivity in the chlorination (**2g/2b** = 0/100). Such a marked electronic effect should be stressed since the lone pair of the bismuth atom is inherently an s-character and cannot efficiently overlap with the 2p orbitals of the aromatic ring carbons. To know how the electronic effect affects the reactivity of triarylpnictogen more clearly, homologous antimony system was chosen for comparison [2]. We describe here the oxidative chlorination of *p*-substituted triarylstibines **3** together with the spectroscopic characteristics of **3** and their dichlorides **4**, in comparison with the bismuth congeners (see Chart 1).

* Corresponding author. Fax: +81 83 933 5738.
 E-mail addresses: murafuji@yamaguchi-u.ac.jp (T. Murafuji), sugihara@yamaguchi-u.ac.jp (Y. Sugihara).
 [1] Fax: +81 83 933 5730.

1: M = Bi
3: M = Sb

2: M = Bi
4: M = Sb

X = **a**: MeO, **b**: H, **c**: Cl, **d**: CO2Et,
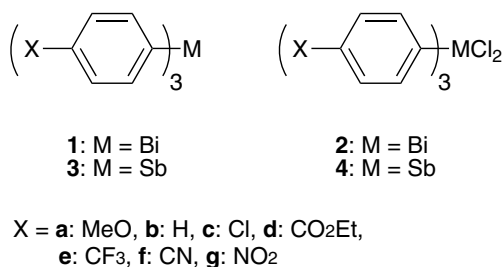   **e**: CF3, **f**: CN, **g**: NO2

Chart 1.

2. Results and discussion

Substituted triarylstibines **3** were synthesized from the corresponding aryllithium or aryl-magnesium in accordance with the method for the synthesis of **1** [3]. Competitive chlorination of **3** was carried out against **3b** (Eq. (1)) and the result is summarized in Table 1. The relative ratios **4/4b** (estimated by ^{1}H NMR) decreased with increasing electron-withdrawing nature of the *p*-substituent, but the tendency was not so pronounced as that of **2/2b**. As shown in Fig. 1, a Hammett plot of **4/4b** against σ_p constants [4] showed a good linear relationship ($n = 6$, $r = 0.95$) with a negative slope (-0.51), which is almost half of the **2/2b** value (-0.97). The nuclear quadrupole resonance study of certain substituted triarylstibines has suggested that the efficient means of transmission of the substituent effect to the antimony atom is through the Sb–C σ bonds owing to the mismatch with the p orbitals

of the ring carbons used in π interaction and that changes in the σ and π network are competitive [5]. The effect of electron-withdrawing substituents on the structure and stabilities of compounds containing heavier main group elements has been studied from the viewpoint of sp-hybridization [6]. In substituted lead compounds, an increasing positive metal charge due to electronegative substituents increases the size differences between the 6s and 6p orbitals by greater contraction of the 6s orbital and makes the efficient sp-hybridization less favorable [6a]. This destabilizes electronegatively substituted Pb(IV) compounds. Thus, such an effect of the electron-withdrawing substituents may reduce the p-character of the lone pair on the pnictogen atoms, lowering the reactivity of **1** and **3**. It is known that configurational inversion at the trivalent antimony and bismuth centers can take place via the edge inversion process [6b] when these central atoms are substituted by electron-withdrawing substituents [6c,6d], although the inversion at the pnictogen centers is a slow process except for the classical vertex inversion typified by nitrogen. The trigonal transition state of the classical vertex inversion is destabilized by the similar electronic effect while the T-shaped transition state of the edge inversion is rather favorable [6e]. The pronounced substituent effect in **1** compared to that in **3** seems to be due to the larger orbital size and more electropositive nature of bismuth atom than antimony atom. We have observed the predominant chlorination of **3b** over **1b** (**4b/2b** = 62/38) in the competitive chlorination and ascribed this result to the higher p-character of the lone pair on the antimony atom [1]. This is reflected in the C–Sb–C bond angles of **3b** [98.0(3)°, 96.0(3)°, 95.7(3)° and 97.5(3)°, 95.5(4)°, 95.1(3)° for the two independent molecules in the asymmetric unit] [7], which are larger than the C–Bi–C bond angles of **1b** [96(1)°, 94(1)° and 92(1)°] [8].

Table 1
Relative ratios in the competitive reaction

	(a)	(c)	(d)	(e)	(f)	(g)
2/2b	53/47	33/67	29/71	35/65	16/84	0/100
4/4b	53/47	49/51	46/54	44/56	40/60	37/63

Fig. 1. Hammett plots.

$$Ar_3Sb \ (Ar \neq Ph) + Ph_3Sb \xrightarrow[\text{CH}_2\text{Cl}_2, \ r.t.]{SO_2Cl_2 \ (1.0 \ mmol)} Ar_3SbCl_2 + Ph_3SbCl_2$$

$$\begin{array}{cccc} \mathbf{3} & \mathbf{3b} & & \mathbf{4} & \mathbf{4b} \\ (1.0 \ mmol) & (1.0 \ mmol) & & & (+ \ recovery \ of \ \mathbf{3} \ and \ \mathbf{3b}) \end{array}$$

$$(1)$$

The chemical shifts (δ_C) of the aromatic ring carbons of **3** and **4** are shown in Table 2. The signals due to the ipso carbons (C1) attached to the antimony shifted downfield from about 9 to 12 ppm relative to those of the parent monosubstituted benzenes **5** [9], but the tendency was not so pronounced as observed in **1** and **2** (25–30 ppm). The signals due to the C2 atoms were observed downfield from about 6 to 8 ppm relative to those of **5** but the C3 and C4 signals appeared at the region close to the corresponding signals of **5**. With respect to the C2, C3 and C4 atoms, the chemical shifts of **3** and **4** were approximately comparable to those of **1** and **2**, respectively. An outstanding spectroscopic feature is in the chemical shifts of the C1 atoms. The C1 signals shifted downfield with increasing electron-withdrawing nature of the *p*-substituents and the chemical shifts of these signals showed linear relationships against the Hammett σ_p constants ($n = 7$) with positive slopes (**3**: 14.5, $r = 0.86$, **4**: 12.7, $r = 0.83$) as well as those of **1**, **2** and **5** (**1**: 17.0, $r = 0.89$, **2**: 11.7, $r = 0.81$, **5**: 12.0, $r = 0.88$). It is known that the chemical shifts of the C1 atoms of **5** are correlated with the σ_p constants and total charge density on these carbons [10]. The smaller value of **3** than that of **1**, therefore, implies that the antimony center of **3** is less sensitive to the electronic effect. This is in accord with the tendency of the chlorination. Furthermore, the small difference in the slope values between **3** and **4** compared to that of the bismuth congeners shows that the bismuth system is more sensitive to the electronic effect with change in the geometry of the metal center (see Chart 2).

Table 2
^{13}C NMR spectral data (δ) of **3** and **4** in CDCl$_3$

	C1	C2	C3	C4	C5	CH$_2$	CH$_3$
3							
a	129.07	137.32	114.65	160.07			55.06
b	138.40	136.24	128.87	128.59			
c	135.83	137.29	129.31	135.54			
d	143.99	136.11	129.69	131.08	166.43	61.10	14.30
e[1]	142.21	136.41	125.73	131.44	123.94		
f	143.61	136.57	132.39	113.49	118.20		
g	145.81	136.92	123.83	148.91			
4							
a	130.39	135.78	114.95	162.12			55.44
b	139.92	134.11	129.59	131.74			
c	137.36	135.40	129.85	138.88			
d	144.13	134.01	130.45	133.73	165.38	61.61	14.26
e[1]	143.09	134.65	126.55	134.21	123.25		
f	143.85	134.80	133.65	116.47	117.18		
g	145.15	135.33	124.45	150.15			

[1] Quartet, J_{CF} = around 3.6, 33.0 and 271.3 Hz for C3, C4 and C5, respectively.

Chart 2.

Table 3
The difference in the chemical shifts between **3** and **4** (Δ_4)

	(C1)	(C2)	(C3)	(C4)
a	1.32	−1.54	0.30	2.05
b	1.52	−2.13	0.72	3.15
c	1.53	−1.89	0.54	3.34
d	0.14	−2.10	0.76	2.65
e	0.88	−1.76	0.82	2.77
f	0.24	−1.77	1.26	2.98
g	−0.66	−1.59	0.62	1.24

Table 3 shows the difference in the chemical shift between **3** and **4** ($\Delta_4 = \delta_4 - \delta_3$), which is suggestive of the tendency of polarization on the aromatic rings of **4** when the geometry of the antimony center changes from tricoordinate to pentacoordinate. π-Polarization is found to arise in the aromatic rings of **2** on the basis of the chemical shifts of **1** and **2** ($\Delta_2 = \delta_2 - \delta_1$), where the charge distribution of the C1 and C2 atoms are negative while that of the C3 and C4 atoms positive [1]. Furthermore, dependence of the electronic effect on the π-polarization is marked in the C1 atoms. In contrast to the Δ_2(C1) values which dramatically increase negatively from 1.67 (**a**) to −4.08 (**g**), the Δ_4(C1) values did not show such pronounced changes, although gradually increased negatively like the Δ_2(C1) values. The Δ_4 values of the C2, C3 and C4 atoms were also not so large as the Δ_2 values. These findings indicate that the charge distribution of the C1, C3 and C4 is positive while that of the C2 negative, thus similar π-polarization taking place. The ipso carbons attached to the silicon of the pentacoordinate silicates are known to appear more downfield compared to those of the parent tetracoordinate silanes due to the π-polarization induced by the electronic fields of the charged substituents [11]. This may be applicable to the bismuth and antimony system [12]. Thus, the upfield shift of the C1 signals of **2** relative to those of **1** is attributed to the positively polarized bismuth center of **2** due to the electron-withdrawing chlorine atoms. In contrast, the downfield shift of the C1 signals of **4** compared to those of **3** is considered to show that the antimony center of **4** is not so polarized as the bismuth center of **2** with increasing electron-withdrawing nature of the *p*-substituents.

3. Experimental

Dichloromethane and THF were distilled from calcium hydride under nitrogen before use. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ on a BRUKER AVANCE 400S spectrometer with TMS as an internal standard. IR
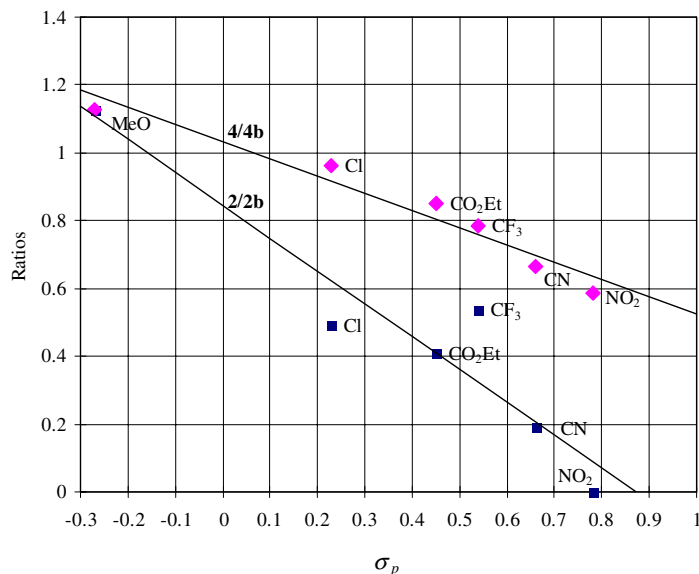
spectra were observed as KBr pellets on a Nicolet Impact 410 spectrophotometer. Triphenylstibine (**3b**) was purchased from Tokyo Kasei Kogyo Co., Ltd. Triarylstibines **3a**, **3c** and **3e** were synthesized from the corresponding Grignard reagents and antimony(III) chloride.

Tris(4-methoxyphenyl)stibine (**3a**): yield 52%; m.p. 182–185 °C; ^{1}H NMR δ 3.80 (s, 9H), 6.88 (d, 6H, $J = 8.6$ Hz), 7.33 (d, 6H, $J = 8.6$ Hz).

Tris(4-chlorophenyl)stibine (**3c**): yield 42%; m.p. 112–112.5 °C (lit. [5], 110–111 °C); ^{1}H NMR δ 7.26 (s, 12H).

Tris(4-trifluoromethylphenyl)stibine (**3e**): yield 48%; m.p. 130–132 °C (lit. [5], 130–132 °C); ^{1}H NMR δ 7.54 (d, 6H, $J = 7.8$ Hz), 7.61 (d, 6H, $J = 7.8$ Hz).

3.1. Synthesis of triarylstibines 3d and 3f: general procedure

To a solution of 4-iodoarene (3 mmol) in THF (10 ml) was added dropwise at −40 °C a solution of isopropylmagnesium bromide (3.6 mmol) in the same solvent (6 ml) and the mixture was stirred for 30 min, during which time the temperature was raised to −20 °C. The aryl-Grignard reagent thus generated in situ was cooled to −40 °C, a solution of antimony(III) chloride (1 mmol) in THF (5 ml) was added dropwise, and the resulting mixture was gradually raised to ambient. The reaction was quenched with brine and insoluble substances were filtered off. The mixture was extracted with ethyl acetate (3 × 10 ml). The combined extracts were dried (Na$_2$SO$_4$) and concentrated to leave an oily residue, which was crystallized from methanol to give a pure product.

Tris(4-ethoxycarbonylphenyl)stibine (**3d**): yield 48%; m.p. 74–76 °C; ^{1}H NMR δ 1.38 (t, 9H, $J = 7.2$ Hz), 4.37 (q, 6H, $J = 7.2$ Hz), 7.48 (d, 6H, $J = 8.2$ Hz), 7.99 (d, 6H, $J = 8.2$ Hz); IR (cm^{-1}): 2986, 1730, 1589, 1386, 1280, 1121, 1056, 1013, 747, 694. Anal. Calc. for C$_{27}$H$_{27}$O$_6$Sb: C, 56.97; H, 4.78. Found: C, 56.77; H, 4.91%.

Tris(4-cyanophenyl)stibine (**3f**): yield 22%; m.p. 202–205 °C; ^{1}H NMR δ 7.50 (d, 6H, $J = 8.2$ Hz), 7.64 (d, 6H, $J = 8.2$ Hz); IR (cm^{-1}): 2228, 1586, 1483, 1385, 1056, 1013, 828, 550. Anal. Calc. for C$_{21}$H$_{12}$N$_3$Sb: C, 58.92; H, 2.83; N, 9.82. Found: C, 59.15; H, 2.98; N, 9.97%.

3.2. Synthesis of triarylstibine 3g

To a solution of 4-iodonitrobenzene (3 mmol) in THF (20 ml) was added dropwise at −100 °C a solution of phenyllithium (3.8 mmol) in cyclohexane–Et$_2$O solution (3.8 ml). A solution of antimony(III) chloride (1 mmol) in THF (5 ml) cooled to −100 °C was then transferred immediately into the dark purple solution of 4-nitrophenyllithium obtained above, and the resulting mixture was gradually raised to ambient. The reaction was quenched with brine and insoluble substances were filtered off. The mixture was extracted with ethyl

acetate (3 × 10 ml). The combined extracts were dried (Na$_2$SO$_4$) and concentrated to leave a residue, which was crystallized from methanol to give a pure product.

Tris(4-nitrophenyl)stibine (**3g**): yield 34%; m.p. 214–216 °C; ^{1}H NMR δ 7.61 (d, 6H, $J = 8.6$ Hz), 8.22 (d, 6H, $J = 8.6$ Hz); IR (cm^{-1}): 1593, 1570, 1519, 1345, 851, 736, 702. Anal. Calc. for C$_{18}$H$_{12}$N$_3$O$_6$Sb: C, 44.30; H, 2.48; N, 8.61. Found: C, 44.10; H, 2.20; N, 8.80%.

3.3. Reaction of 3 with sulfuryl chloride: general procedure

To a solution of triarylstibine **3** (1 mmol) in dichloromethane (5 ml) was added at room temperature a 1.0 M solution of sulfuryl chloride in the same solvent (1 ml). After completion of the reaction (checked by TLC), the resulting mixture was concentrated to leave a residue, which was crystallized by an addition of hexane to give a pure product.

Tris(4-methoxyphenyl)antimony dichloride(**4a**): yield 89%; m.p. 108–110 °C; ^{1}H NMR δ 3.86 (s, 9H), 7.05 (d, 6H, $J = 9.0$ Hz), 8.16 (d, 6H, $J = 9.0$ Hz); Anal. Calc. for C$_{21}$H$_{21}$Cl$_2$O$_3$Sb: C, 49.07; H, 4.12. Found: C, 48.89; H, 3.90%.

Triphenylantimony dichloride (**4b**): yield 92%; m.p. 139–141 °C (lit. [13], 139–142 °C); ^{1}H NMR δ 7.56 (m, 9H), 8.24 (m, 6H).

Tris(4-chlorophenyl)antimony dichloride (**4c**): yield 91%; m.p. 193–194 °C; ^{1}H NMR δ 7.54 (d, 6H, $J = 8.6$ Hz), 8.56 (d, 6H, $J = 8.6$ Hz). Anal. Calc. for C$_{18}$H$_{12}$Cl$_5$Sb: C, 41.00; H, 2.29. Found: C, 41.22; H, 2.50%.

Tris(4-ethoxycarbonylphenyl)antimony dichloride (**4d**): yield 72%; m.p. 128–130 °C; ^{1}H NMR δ 1.41 (t, 9H, $J = 7.1$ Hz), 4.42 (q, 6H, $J = 7.1$ Hz), 8.22 (d, 6H, $J = 8.6$ Hz), 8.30 (d, 6H, $J = 8.6$ Hz); IR (cm^{-1}): 2986, 1733, 1587, 1390, 1301, 1184, 1125, 1053, 1010, 851, 754, 689. Anal. Calc. for C$_{27}$H$_{27}$Cl$_2$O$_6$Sb: C, 50.66; H, 4.25. Found: C, 50.38; H, 4.41%.

Tris(4-trifluoromethylphenyl)antimony dichloride (**4e**): yield 89%; m.p. 127–129 °C; ^{1}H NMR δ 7.85 (d, 6H, $J = 8.1$ Hz), 8.38 (d, 6H, $J = 8.1$ Hz). Anal. Calc. for C$_{21}$H$_{12}$Cl$_2$F$_9$Sb: C, 40.17; H, 1.93. Found: C, 40.34; H, 1.88%.

Tris(4-cyanophenyl)antimony dichloride (**4f**): yield 86%; m.p. 176–178 °C; ^{1}H NMR δ 7.87 (d, 6H, $J = 8.5$ Hz), 8.37 (d, 6H, $J = 8.5$ Hz); IR (cm^{-1}): 2231, 1483, 1390, 1010, 828, 547. Anal. Calc. for C$_{21}$H$_{12}$Cl$_2$N$_3$Sb: C, 50.55; H, 2.42; N, 8.42. Found: C, 50.30; H, 2.22; N, 8.18%.

Tris(4-nitrophenyl)antimony dichloride (**4g**): yield 89%; m.p. 230–233 °C (decomp.); ^{1}H NMR δ 8.44 (d, 6H, $J = 9.1$ Hz), 8.47 (d, 6H, $J = 9.1$ Hz); IR (cm^{-1}): 1599, 1531, 1390, 1356, 850, 735. Anal. Calc. for C$_{18}$H$_{12}$Cl$_2$N$_3$O$_6$Sb: C, 38.68; H, 2.16; N, 7.52. Found: C, 38.40; H, 2.06; N. 7.43%.

Acknowledgement

References

[1] A.F.M. Mustafizur Rahman, T. Murafuji, M. Ishibashi, Y. Miyoshi, Y. Sugihara, J. Organomet. Chem. 689 (2004) 3395.
[2] (a) Hypervalent organoantimony compounds, see: S. Kojima, R. Takagi, H. Nakata, Y. Yamamoto, K.-y. Akiba, Chem. Lett. (1995) 857;
(b) Y. Yamamoto, H. Fujikawa, H. Fujishima, K.-y. Akiba, J. Am. Chem. Soc. 111 (1989) 2276;
(c) K.-y. Akiba, T. Okinaka, M. Nakatani, Y. Yamamoto, Tetrahedron Lett. 28 (1987) 3367;
(d) Hypervalent organopnictogen compounds, see: Y. Matano, H. Nomura, H. Suzuki, Inorg. Chem. 41 (2002) 1940;
(e) Y. Matano, H. Nomura, H. Suzuki, M. Shiro, H. Nakano, J. Am. Chem. Soc. 123 (2001) 10954.
[3] T. Murafuji, K. Nishio, M. Nagasue, A. Tanabe, M. Aono, Y. Sugihara, Synthesis (2000) 1208.
[4] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.
[5] T.B. Brill, G.G. Long, Inorg. Chem. 11 (1972) 225.
[6] (a) M. Kaupp, P.v.R. Schleyer, J. Am. Chem. Soc. 115 (1993) 1061;
(b) A.J. Arduengo III, C.A. Stewart, Chem. Rev. 94 (1994) 1215;
(c) D.A. Dixon, A.J. Arduengo III, J. Am. Chem. Soc. 109 (1987) 338;
(d) Y. Yamamoto, X. Chen, S. Kojima, K. Ohdoi, M. Kitano, Y. Doi, K.-y. Akiba, J. Am. Chem. Soc. 117 (1995) 3922;
(e) S. Nagase, Kikan Kagaku Sosetsu 34 (1998) 113;
(f) S. Nagase, Acc. Chem. Res. 28 (1995) 469.
[7] E.A. Adams, J.W. Kolis, W.T. Pennington, Acta Cryst. C 46 (1990) 917.
[8] D.M. Hawley, G. Ferguson, J. Chem. Soc. A (1968) 2059.
[9] (a) E. Breitmaier, W. Voelter, Carbon-13 NMR Spectroscopy, VCH, Weinheim, 1987 (Chapter 4);
(b) D.F. Ewing, Org. Magn. Reson. 12 (1979) 499.
[10] (a) G.L. Nelson, G.C. Levy, J.D. Cargioli, J. Am. Chem. Soc. 94 (1972) 3089;
(b) H. Spiesecke, W.G. Schneider, J. Chem. Phys. 35 (1961) 731.
[11] K. Tamao, T. Hayashi, Y. Ito, Organometallics 11 (1992) 182.
[12] A.F.M. Mustafizur Rahman, T. Murafuji, K. Kurotobi, Y. Sugihara, N. Azuma, Organometallics 23 (2004) 6176.
[13] D.V. Moiseev, A.V. Gushchin, A.S. Shavirin, Y.A. Kursky, V.A. Dodonov, J. Organomet. Chem. 667 (2003) 176.