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Rapid threefold cross-couplings with sterically bulky triarylbismuths under Pd–Cu dual catalysis†

Maddali L. N. Rao* and Ritesh J. Dhanorkar

The threefold cross-coupling reactivity of sterically highly demanding bulky triarylbismuths was addressed with task specific Pd–Cu dual catalytic conditions. In this study, an unprecedented hitherto unknown cross-coupling reactivity of sterically bulky triarylbismuths was demonstrated with a diverse range of aryl iodides and bromides. The intermediacy and *in situ* formation of arylcopper was probed with mesitylcopper in support of the proposed dual catalysis. This study opened up an easy way forward for application of sterically bulky bismuth reagents in threefold aryl–aryl coupling reactions.

The cross-couplings of organobismuth reagents demonstrated a remarkable reactivity under palladium-catalyzed conditions.¹⁻⁵ The studies of 5,6,7,12-tetrahydrodibenz[$c_i f$][1,5]azabismocines and monoorganobismuth alkoxides reflected the consistent and facile reactivity in aryl-aryl bond formations.² As a step forward in this direction, triarylbismuths excelled in an exemplary way with the use of sub-stoichiometric one-third amount delivering threefold cross-couplings in a one-pot operation.³⁻⁵ In this regard, the utilization of triarylbismuths in coupling reactions offer many synthetic advantages which includes high coupling reactivity, sub-stoichiometric loading of the reagents, short reaction durations *etc.*

Aryl-aryl bond formation is one of the most studied process in cross-coupling chemistry as biaryl scaffolds are high in demand in various applications.⁶ The coupling reactivity of sterically bulky organometallic nucleophiles has been a challenging task. These studies using various organometallic reagents have been addressed consistently with rational design of ligand and/or catalytic conditions.⁷ For example, recent studies of Giri *et al.* revealed the facile reactivity of organoindiums under copper-catalyzed conditions involving consecutive transmetalations.⁷

Another recent report by Espinet *et al.* on Stille couplings also showed novel couplings using bulky organotin reagents under gold catalysis.^{7b} Similarly, other coupling studies with bulky organoboron,^{7c-e} organozinc,^{7f} organolithiums,^{8a} organomagnesium,^{8b} organotitanium^{8c} and organoindium^{8d} *etc.* have been explored under various metal cross-coupling conditions often invoking the support from specialized ligand as demanded by the difference in reactivity of several of these organometallic nucleophiles. Surprisingly, the corresponding coupling reactivity using sterically bulky *ortho* substituted bismuth reagents such as **1a–1f** (Fig. 1) was largely unknown.^{9,10} In that context, there is a desperate need to explore the couplings of sterically bulky triarylbismuth reagents for the development of viable protocol conditions.

The threefold coupling reactivity of sterically demanding triarylbismuth reagents is complicated due to unavoidable sterics rendered with the presence of *ortho* functionalization. To circumvent this steric burden, it was reasoned that the development of a dual catalytic protocol comprising Pd–Cu system would pave the way for the desired coupling process. Here the plan was to generate monoarylcopper species *in situ* from copper halide and arylbismuths involving transmetalation during dual catalytic coupling process. The envisioned supportive role of copper halide in Pd catalysis was favored by



Fig. 1 Structures of **1a–1d** and **1f** from single crystal XRD; **1e** is DFT optimized structure (by GAUSSIAN 09 at B3LYP/LANL2DZ level).

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, India. E-mail: maddali@iitk.ac.in; Fax: +91-512-2597532; Tel: +91-512-2597532

[†] Electronic supplementary information (ESI) available: Experimental procedures, characterization data and spectral data for all products was given. CCDC for **1a** (1005303), **1b** (1005301), **1c** (1005300), **1d** (1005302) and **1f** (1005299). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra23311a

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literature reports¹¹ involving aryl/heteroaryl transfer from tin or boron in the Stille^{11*b,c*} and Suzuki^{11*d*} coupling reactions. To our surprise, this role of copper was never invoked so far in Pdcatalyzed bismuth coupling reactions. This made us to curiously investigate this reactivity for the advantage of couplings with sterically demanding bismuth reagents. In fact, this approach lived up to its expectation to deliver an unprecedented aryl-aryl facile couplings of sterically bulky triarylbismuth reagents under task specific Pd–Cu dual catalytic conditions as elaborated hereunder.

We performed the study of aryl–aryl coupling employing sterically congested **1a** under palladium-catalyzed conditions (Table 1). In general, electronically rich aryl halides are known to be poor reactive.^{7,8} Hence, we explored our study with electronically rich 4-iodotoluene employing Pd(OAc)₂/PPh₃, K₃PO₄ in DMF at 90 °C conditions. This reaction proceeded poorly to give biaryl **2.1** in 9% yield (entry 1). This prompted us to test the envisioned role of copper halide in co-promoting the cross-coupling process.

The initial attempt with stoichiometric amount of CuCl delivered a dramatic improvement with 60% cross-coupling yield (entry 2). Encouraged by this, further study was conducted with different copper halides (entries 3–7). This denoted the beneficial role of different copper halides and the best outcome was obtained using CuI in 81% yield (entry 7). The inhibitory role of phosphine ligand during the transmetalation step of the catalytic cycle and CuI serving as a scavenger of the phosphine was reported in non-polar solvents.^{11b} To check this possibility if any, we performed a control reaction with deliberate lowering of PPh₃ from 0.4 equiv. (entry 7) to 0.2 equiv. amount (entry 8) and this resulted in moderate coupling reactivity. This indicated that copper halide is not serving as a scavenger of phosphine in

our polar DMF solvent.^{11b} This result unambiguously revealed the effective and catalytic role of CuI in furnishing high crosscoupling reactivity under palladium-catalyzed conditions and it was considered as our standardized protocol (entry 7). In all, the above screening resulted in the development of a robust Pd– Cu dual catalytic protocol for efficient coupling of sterically congested bismuth reagent under mild reaction conditions.

To further elaborate, the cross-coupling reactivity of **1a** was further explored with electronically diverse aryl iodides (Table 2). This with different aryl iodides delivered the facile threefold reactivity of **1a** to give *ortho* substituted biaryls **2.1–2.6** in 77– 87% yields. Our developed Pd–Cu protocol proved to be efficient with electronically rich aryl iodides to give high yields of biaryls **2.1** and **2.3**. Our dual catalytic protocol tolerated sensitive formyl group (**2.4**) and also gave chemoselective iodo couplings in the presence of bromide terminus (**2.7** and **2.8**). Further, chloro (**2.5**) and trifluoromethyl (**2.6**) substituted phenyl iodides also participated with excellent reactivity.

The fabulous coupling reactivity of 1a encouraged our further examination with a few more sterically bulky BiAr₃ reagents 1b-1e (Fig. 1) to obtain ortho functionalized biaryls (Table 3). The coupling reactivity of tri-o-tolylbismuth reagent 1b with 2-iodobenzaldehyde furnished ortho disubstituted biaryl 3.1 in 92% yield. The sterically more demanding trimesitylbismuth (1c) and tri(2,6-dimethylphenyl)bismuth (1d) reagents also coupled with functionalized aryl iodides to afford the corresponding tri- and tetrasubstituted biaryls (3.2-3.5) in 71-84% yields. The reaction of 3-bromophenyl iodide gave chemoselective iodo coupled product 3.4 in 76% yield. These couplings with tri(naphthalen-1-yl)bismuth (1e) gave the corresponding 1-phenylnaphthalenes (3.6-3.9) in 85-98% yields. This evaluation demonstrated successful couplings of sterically bulky BiAr₃ reagents with electronically diverse aryl iodides under the optimized Pd-Cu dual catalytic conditions.





^{*a*} Reaction conditions: **1a** (0.25 mmol, 1 equiv.), 4-iodotoluene (0.875 mmol, 3.5 equiv.), K₃PO₄ (1.5 mmol, 6 equiv.), Pd(OAc)₂ (0.025 mmol, 0.1 equiv.), PPh₃ (0.1 mmol, 0.4 equiv.), CuX, DMF (3 mL), 90 °C, time. ^{*b*} Isolated yields. ^{*c*} Homo-coupled biaryl formed in minor amount. ^{*d*} With 0.2 equiv. of PPh₃.

4

4

81

57



CuI (0.2 equiv.)

CuI (0.2 equiv.)

7

8^d

Table 3 Couplings of aryl iodides with 1b–1e reagents^a



 a Reaction conditions: BiAr₃ (0.25 mmol, 1 equiv.), aryl iodide (0.875 mmol, 3.5 equiv.), K₃PO₄ (1.5 mmol, 6 equiv.), Pd(OAc)₂ (0.025 mmol, 0.1 equiv.), PPh₃ (0.1 mmol, 0.4 equiv.), CuI (0.05 mmol, 0.2 equiv.), DMF (3 mL), 90 °C, 3 h; isolated yields; biaryls formed in minor amounts.

To further showcase the efficacy of our Pd–Cu dual catalysis, cross-couplings of sterically bulky BiAr₃ reagents with aryl bromides were planned. It was studied elaborately by employing both electronically rich and poor aryl bromides. Initially, the

cross-coupling ability of **1a** was tested with electronically poor aryl bromides under Pd–Cu dual catalytic conditions (Table 4). Simultaneously, these couplings were addressed under CuI free palladium catalysis. This was to establish the difference in coupling reactivity with and without copper conditions. In this endeavour, we have witnessed effective couplings of o-, m- and p-substituted functionalized aryl bromides in high yields.

The corresponding couplings attempted with CuI free Pd conditions invariably gave poor yields indicating definitive role of CuI in the coupling process. To note, electronically different and *ortho*-substituted aryl bromides reacted with equal ease, rendering high product yields (2.4 and 4.1-4.4). Again, the diverse *meta*- and *para*- substituted aryl bromides also involved with excellent reactivity (4.5-4.12). In this investigation, 1a was effectively cross-coupled with various electronically deficient aryl bromides functionalized with formyl, cyano, acetate, chloro, fluoro, trifluoromethyl and nitro groups.

Encouraged by this magnificent coupling reactivity of **1a**, this study was extended to other bismuths **1b–1f** with varied steric demand (Table 5).

The coupling reactivity of **1b** with different aryl bromides resulted in high profile couplings giving *ortho* substituted biaryls **3.1** and **5.1–5.5** in 75–96% yields. Importantly, bismuth reagent **1d** with sterically demanding *ortho* disubstituted 2,6dimethylphenyl group participated superbly to afford tri- and tetrasubstituted biaryls **5.6–5.8** and **3.5** in 80–96% yields. Additionally, couplings with tri(naphthalene-1-yl)bismuth **1e** also gave high yields (**3.7**, **3.8**, **5.13** and **5.14**). Similarly, sterically bulky trimesitylbismuth **1c** furnished tetrasubstituted biaryls **5.9–5.11** and **3.3** in 60–83% yields. More so, sterically



^{*a*} Reaction conditions: tri(*o*-anisyl)bismuth (0.25 mmol, 1 equiv.), aryl bromide (0.875 mmol, 3.5 equiv.), K_3PO_4 (1.5 mmol, 6 equiv.), $Pd(OAc)_2$ (0.025 mmol, 0.1 equiv.), PPh_3 (0.1 mmol, 0.4 equiv.), CuI (0.05 mmol, 0.2 equiv.), DMF (3 mL), 90 °C, 3–4 h; isolated yields; biaryls formed in minor amounts. ^{*b*} Yields from CuI free Pd conditions given in parenthesis.



^{*a*} Reaction conditions: $BiAr_3$ (0.25 mmol, 1 equiv.), aryl bromide (0.875 mmol, 3.5 equiv.), K_3PO_4 (1.5 mmol, 6 equiv.), $Pd(OAc)_2$ (0.025 mmol, 0.1 equiv.), PPh₃ (0.1 mmol, 0.4 equiv.), CuI (0.05 mmol, 0.2 equiv.), DMF (3 mL), 90 °C, 3–4 h; isolated yields; biaryls formed in minor amounts. ^{*b*} Yields under CuI free Pd protocol given in parenthesis.

demanding **1f** with 2,4-dimethoxyphenyl gave biaryl **5.12** in 96% yield. A random check of the corresponding cross-couplings using CuI free Pd conditions gave poor yields (given in parenthesis in Table 5). This evaluation with sterically bulky triarylbismuths delivered facile threefold reactivity with diverse aryl iodides and electronically poor aryl bromides under the established Pd–Cu dual catalytic conditions.

However, the corresponding reactivity was found to be poor with electronically rich aryl bromides (Table 6). For example, reaction of *o*-tolyl bromide with **1a** using Pd–Cu catalytic conditions delivered **6.1** in 25% yield (Table 6, entry 1). To improve this reactivity, a brief screening was conducted with P(p-tolyl)₃ and dppf ligands (entries 2–4). From this, catalytic protocol with dppf ligand was proved to be effective for couplings with electronically rich aryl bromides (entry 3).

This protocol but without CuI gave very poor yield (entry 5) indicating the important role of CuI in this coupling process. This screening afforded an effective protocol involving with dppf (0.2 equiv.), $Pd(OAc)_2$ (0.1 equiv.), K_3PO_4 (6 equiv.), CuI (0.2 equiv.), DMF, 90 °C and 4 h conditions (entry 3). With this, the reactivity of various electronically rich aryl bromides was tested using bulky triarylbismuth reagents, **1a–1f** (Table 7).

Table 6 Screening with o-tolyl bromide^{*a,b*}



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1	PPh_3 (0.4 equiv.)	25
2	$P(p-tolyl)_3$ (0.4 equiv.)	67
3	dppf (0.2 equiv.)	78
1	dppf (0.1 equiv.)	64
5^b	dppf (0.2 equiv.)	9

^{*a*} Reaction conditions: *o*-tolyl bromide (0.875 mmol, 3.5 equiv.), **1a** (0.25 mmol, 1 equiv.), K_3PO_4 (1.5 mmol, 6 equiv.), $Pd(OAc)_2$ (0.025 mmol, 0.1 equiv.), phosphine ligand, CuI (0.05 mmol, 0.2 equiv.), DMF (3 mL), 90 °C, 4 h; isolated yields; biaryls formed in minor amounts. ^{*b*} Without CuI.

This scrutiny produced high coupling performance as the reactivity of **1a** with simple phenyl bromide or its electronically rich variants gave biaryls (**2.2, 2.3, 6.1** and **6.2**) in 62–91% yields. Similar cross-couplings with other bismuth reagents **1b–1f** also afforded high yields (**3.2, 3.6, 6.3–6.5**) demonstrating enduring efficacy of the established Pd–Cu dual protocol.

Furthermore, the cross-coupling of *ortho* disubstituted and electronically rich 2-bromo-1,3-dimethylbenzene was tested with **1a** using XPhos ligand (Scheme 1) to obtain *ortho* trisubstituted biaryl system. In fact, this reaction successfully furnished biaryl **7.1** in 64% yield. Under similar conditions, couplings of **1a** and **1f** with pentafluorophenyl bromide gave biaryls **7.2** and **7.3** in 66% and 79% yields (Scheme 1).

To highlight, our established three Pd–Cu dual catalytic conditions elegantly reacted with exemplary ease and utility in



^{*a*} Reaction conditions: BiAr₃ (0.25 mmol, 1 equiv.), aryl bromide (0.875 mmol, 3.5 equiv.), K_3PO_4 (1.5 mmol, 6 equiv.), $Pd(OAc)_2$ (0.025 mmol, 0.1 equiv.), dppf (0.05 mmol, 0.2 equiv.), CuI (0.05 mmol, 0.2 equiv.), DMF (3 mL), 90 °C, 4 h; isolated yields; biaryls formed in minor amounts. ^{*b*} Yield under CuI free Pd protocol given in parenthesis.



couplings of sterically bulky BiAr₃ reagents with electronically diverse aryl iodides and bromides. Very importantly, with the variation of phosphine alone (PPh₃, dppf and XPhos), we could derive facile couplings with different electrophilic coupling partners employing mild Pd-Cu dual catalytic conditions. The straightforward impact of the nature of phosphines facilitating the couplings of different aryl halides under Pd-Cu dual catalvsis demonstrated the independent role being played by both Pd and Cu reagents in the coupling process. To understand this, a few control reactions have been performed as given in Scheme 2. Firstly, the cross-coupling of 1c using CuI free Pd catalytic conditions furnished 5.9 in 15% yield (eqn (1)). Whereas, it gave 5.9 in 60% yield using Pd-Cu catalytic conditions (Table 5). The intermediacy and effective role of arylcopper was further evaluated. The required mesitylcopper was separately prepared¹² and employed in catalytic amount in lieu of CuI in our established conditions (eqn (2)). This reaction gave the desired product 5.9 in 63% yield and thus established the catalytic role of anylcopper in the coupling process. Further coupling of 4bromoacetophenone and 1c without Pd catalyst and with catalytic CuI did not give the cross-coupling product (eqn (3)). This confirmed the specific role of Pd in Pd-Cu dual catalytic cycle. Furthermore, a stepwise process involving in situ formation of oxidative addition product and its coupling with mesitylcopper using the established conditions gave cross-coupled product 5.9 in 59% yield (eqn (4)).

Alternative preparation of the oxidative addition product¹³ employing $Pd(PPh_3)_4$ and its reaction with mesitylcopper gave cross-coupling product in 41% yield (eqn (5)). These two reactions (eqn (4) and (5)) collectively demonstrated the involvement of both oxidative addition product and mesitylcopper in our Pd-Cu dual catalytic conditions. Further check with mesitylcopper as co-catalyst in couplings of different bismuths 1a and 1b and 4-bromoacetophenone gave corresponding coupling products 4.10 and 5.5 in 59% and 62% yields respectively (eqn (6) and (7)) demonstrating the general catalytic role of arylcopper under palladium coupling conditions. Additionally, reaction of 1c under dual catalytic conditions but with the absence of 4-bromoacetophenone gave homo-coupled bimesityl (eqn (8)). This investigation employing different bismuth reagents, intermediate mesitylcopper and oxidative products thus emphatically established the specific role of arylpalladium (2a) and arylcopper (2b) as proposed in the following catalytic cycle (Scheme 3).

The proposed mechanism exemplifies the simultaneous involvement of both palladium and copper catalytic cycles with



their task specific role in delivering the cross-coupling product. The catalytic role of palladium in the oxidative addition, transmetalation and reductive elimination steps forms the main catalytic cycle. Additional involvement of catalytic CuI for *in situ* generation of arylcopper^{11d} from arylbismuth and its participation in aryl exchange during transmetalation step of



Scheme 3 Proposed Pd-Cu dual catalytic cycle.

the palladium catalytic cycle was proposed. The efficient reactivity witnessed with the use of catalytic CuX under dual catalytic conditions supports the proposed regeneration of the CuX during the catalytic process. Further, the facile couplings of diverse aryl halides obtained under task specific three different palladium protocols comprising PPh₃, dppf and XPhos ligands and uniformly co-catalyzed by CuI signifies the independent nature of both Pd and Cu catalytic cycles as part of the dual catalytic process.

In summary, we have unravelled an unprecedented crosscoupling reactivity of sterically congested BiAr₃ reagents with a diverse range of aryl iodides and bromides under task specific Pd–Cu dual catalytic conditions. The three Pd–Cu dual protocols with PPh₃, dppf or XPhos ligands and CuI signify the flexible nature of the established dual catalytic conditions besides their versatility and broad synthetic utility. With this, we have unravelled the outstanding reactivity of various sterically congested BiAr₃ reagents in aryl–aryl couplings under mild Pd–Cu dual catalytic conditions using routinely used metal and ligand systems. This study is expected to open up an easy way forward for further applications of these bismuth reagents in organic synthesis.

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Notes and references

- 1 (a) S. Shimada and M. L. N. Rao, *Top. Curr. Chem.*, 2012, **311**, 199; (b) *Organobismuth Chemistry*, ed. H. Suzuki and Y. Matano, Elsevier, Amsterdam, 2001.
- 2 (a) S. Shimada, O. Yamazaki, T. Tanaka, M. L. N. Rao,
 Y. Suzuki and M. Tanaka, *Angew. Chem., Int. Ed.*, 2003, 42, 1845; (b) M. L. N. Rao, S. Shimada and M. Tanaka, *Org. Lett.*, 1999, 1, 1271.
- 3 M. L. N. Rao, O. Yamazaki, S. Shimada, T. Tanaka, Y. Suzuki and M. Tanaka, *Org. Lett.*, 2001, 3, 4103.
- 4 (a) M. L. N. Rao, D. Banerjee and D. N. Jadhav, *Tetrahedron Lett.*, 2007, 48, 2707; (b) M. L. N. Rao, D. Banerjee and D. N. Jadhav, *Tetrahedron Lett.*, 2007, 48, 6644; (c) M. L. N. Rao, D. N. Jadhav and D. Banerjee, *Tetrahedron*, 2008, 64, 5762; (d) M. L. N. Rao, D. Banerjee and R. J. Dhanorkar, *Tetrahedron Lett.*, 2010, 51, 6101.

- 5 (a) M. L. N. Rao, D. N. Jadhav and P. Dasgupta, Org. Lett., 2010, 12, 2048; (b) M. L. N. Rao and R. J. Dhanorkar, Eur. J. Org. Chem., 2014, 5214; (c) M. L. N. Rao and R. J. Dhanorkar, RSC Adv., 2014, 4, 13134; (d) M. L. N. Rao and R. J. Dhanorkar, RSC Adv., 2013, 3, 6794; (e) M. L. N. Rao, D. N. Jadhav and P. Dasgupta, Eur. J. Org. Chem., 2013, 781.
- 6 (a) K. C. Nicolaou, P. G. Bulger and D. Sarlah, Angew. Chem., Int. Ed., 2005, 44, 4442; (b) G. Bringmann, A. J. P. Mortimer, P. A. Keller, M. J. Gresser, J. Garner and M. Breuning, Angew. Chem., Int. Ed., 2005, 44, 5384.
- 7 Selected references: (a) S. Thapa, S. K. Gurung, D. A. Dickie and R. Giri, Angew. Chem., Int. Ed., 2014, 53, 11620; (b) J. del Pozo, D. Carrasco, M. H. Perez-Temprano, M. Garcia-Melchor, R. Alvarez, J. A. Casares and P. Espinet, Angew. Chem., Int. Ed., 2013, 52, 2189; (c) R. J. Lundgren and M. Stradiotto, Chem.-Eur. J., 2012, 18, 9758; (d) G. A. Molander and B. Biolatto, J. Org. Chem., 2003, 68, 4302; (e) R. Martin and S. L. Buchwald, Acc. Chem. Res., 2008, 41, 1461; (f) J. E. Milne and S. L. Buchwald, J. Am. Chem. Soc., 2004, 126, 13028.
- 8 (a) M. Giannerini, V. Hornillos, C. Vila, M. Fananas-Mastral and B. L. Feringa, Angew. Chem., Int. Ed., 2013, 52, 13329;
 (b) S. Calimsiz, M. Sayah, D. Mallik and M. G. Organ, Angew. Chem., Int. Ed., 2010, 49, 2014; (c) H. W. Lee, F. L. Lam, C. M. So, C. P. Lau, A. S. C. Chan and F. Y. Kwong, Angew. Chem., Int. Ed., 2009, 48, 7436; (d) M. A. Pena, J. P. Sestelo and L. A. Sarandeses, J. Org. Chem., 2007, 72, 1271.
- 9 Y. Monguchi, T. Hattori, Y. Miyamoto, T. Yanase, Y. Sawama and H. Sajiki, *Adv. Synth. Catal.*, 2012, **354**, 2561.
- 10 P. Petiot and A. Gagnon, Eur. J. Org. Chem., 2013, 5282.
- 11 (a) X. Han, B. M. Stoltz and E. J. Corey, J. Am. Chem. Soc., 1999, 121, 7600; (b) V. Farina, S. Kapadia, B. Krishnan, C. Wang and L. S. Liebeskind, J. Org. Chem., 1994, 59, 5905; (c) S. P. H. Mee, V. Lee and J. E. Baldwin, Angew. Chem., Int. Ed., 2004, 43, 1132; Chem.-Eur. J., 2005, 11, 3294; (d) J. Z. Deng, D. V. Paone, A. T. Ginnetti, H. Kurihara, S. D. Dreher, S. A. Weissman, S. R. Stauffer and C. S. Burgey, Org. Lett., 2009, 11, 345; (e) R. Chinchilla and C. Najera, Chem. Rev., 2007, 107, 874.
- 12 T. Tsuda, T. Yazawa, K. Watanabe, T. Fujii and T. Saegusa, *J. Org. Chem.*, 1981, **46**, 192.
- 13 P. Fitton and E. A. Rick, J. Organomet. Chem., 1971, 28, 287.