Journal of Organometallic Chemistry 694 (2009) 309–312

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

Intramolecular hydroamination catalysed by Ag complexes stabilised *in situ* by bidentate ligands

Sophie R. Beeren, Serin L. Dabb, Barbara A. Messerle *

School of Chemistry, The University of New South Wales, NSW, Australia

ARTICLE INFO

Article history:
Received 5 September 2008
Received in revised form 17 October 2008
Accepted 22 October 2008
Available online 30 October 2008

Keywords:
Hydroamination
Silver catalyst
Bidentate ligand
Alkynylamine
Triflate
Cyclisation

ABSTRACT

A series of silver complexes generated *in situ* from $AgOSO_2CF_3$ (AgOTf) and a range of bidentate ligands were investigated as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine. A variety of P- and N-donor ligands were tested including the novel pyrazole-phosphine ligand 1-(2-(diphenylphosphino)phenyl)pyrazole. The best catalyst was formed from equimolar amounts of the P,N-donor ligand 1-(2-(diphenylphosphino)ethyl)pyrazole and AgOTf, which achieved a turnover rate of 129 h^{-1} for the cyclisation of 4-pentyn-1-amine.

1. Introduction

Nitrogen containing heterocycles are sub-units in biologically active compounds which are important in the pharmaceutical and agrochemical industries. Their synthesis via convenient and direct approaches is therefore highly desirable. Catalysed cyclisation of alkynyl- and alkenylamines via intramolecular hydroamination has shown great potential for the energy efficient synthesis of *N*-heterocycles [1]. Lanthanide [2], early [3] and late [4–10] transition metal complexes have been shown to successfully catalyse this reaction. The advantage of late transition metals is their lower oxophilicity (compared to early transition metal or lanthanide metal catalysts), which leads to higher functional group tolerance and less sensitivity to water or oxygen exposure.

There are a number of examples of silver catalysed hydroamination reactions [5,7,9–12], however, there are only a few examples of the use of silver as a catalyst for the cyclisation of alkynylamines to form *N*-heterocycles [5,7,9,10]. These previous studies have primarily focussed on the use of silver salts rather than silver complexes as catalysts, and it has been found that these salts have a tendency to decompose at high temperatures and become inactive before the complete conversion of substrate is reached. However, a more active Ag(I) catalyst may be obtained by complexation of the silver centre with a suitable ligand, where the ligand stabilises and/or improves the efficiency of the catalytically active Ag centre [7,9,11]. Most recently, $Ag(phen)(OSO_2CF_3)$ (10 mol%), which contains the N,N-donor ligand phenanthroline (phen), has been shown to promote a conversion of 95% of 4-pentyn-1-amine (**1**) to 2-methylpyrroline (**2**) after 4 h at 70 °C, whereas $AgOSO_2CF_3$ (AgOTf) alone only promotes a conversion of 55% after the same time [9].

In this paper, we report the use of silver complexes generated *in situ* from AgOTf and a series of bidentate N,N-, P,N- and P,P-donor ligands as intramolecular hydroamination catalysts. Of particular interest for the development of efficient metal centred catalysts are mixed P,N-donor ligands which combine hard (nitrogen) and soft (phosphorus) centres [13]. Rhodium(I) and iridium(I) complexes containing the P,N-donor ligand 1-(2-(diphenylphosphino)ethyl)pyrazole (**3**) have shown high activity as hydrothiolation [14], hydroalkoxylation [15] and hydroamination [8] catalysts.

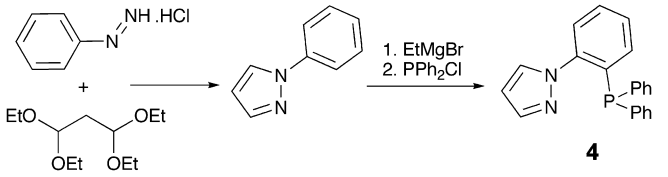
2. Results and discussion

2.1. Synthesis of 1-(2-(diphenylphosphino)phenyl)pyrazole (**4**)

To further investigate the use of P,N-donor ligands in hydroamination catalysis the novel pyrazole-phosphine ligand 1-(2-(diphenylphosphino)phenyl)pyrazole (**4**) was synthesised (Scheme 1). In this ligand, modelled on the previously reported ligand **3** [14], a phenyl bridge replaces the ethyl backbone. By thus expanding the range of pyrazole-phosphine ligands available we can consider the importance of the relative flexibility of the ligand backbone in catalysis. 1-Phenylpyrazole was synthesised via a condensation reaction between 1,1,3,3-tetraethoxypropane and phenylhydrazine hydrochl-

* Corresponding author. Tel.: +61 2 9385 4653; fax: +61 2 9385 6141.
E-mail address: b.messerle@unsw.edu.au (B.A. Messerle).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.10.038



Scheme 1. Synthesis of ligand **4**.

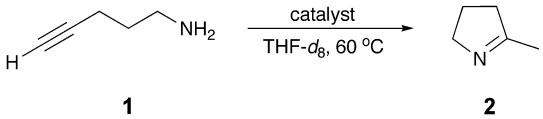
oride [16,17]. Ethyl magnesium bromide was used to deprotonate 1-phenylpyrazole at the ortho-position, to form 2-(1-pyrazolyl)phenylmagnesiumbromide *in situ*. Addition of chlorodiphenylphosphine to the reaction mixture afforded the air stable ligand **4** cleanly, after the crude product was recrystallised from hot methanol. Ethyl magnesium bromide was used in place of *n*-butyl lithium, which has previously been used in the synthesis of 3,5-dimethyl(1-(2-(diphenylphosphino)phenyl))pyrazole [18], due to the preference of *n*-butyl lithium to deprotonate the 3 or 5 position of the pyrazole ring over the phenyl protons [19,20].

2.2. Catalysis

The efficiency of a range of Ag catalysts generated *in situ* from $AgOSO_2CF_3$ (AgOTf) and a series of bidentate ligands, including **3** and the new ligand **4**, was investigated using the intramolecular hydroamination of 4-pentyn-1-amine (**1**) to form 2-methylpyrroline (**2**) (Scheme 2). The catalysis was carried out at 60 °C in THF-d_8 under a N_2 atmosphere. Reaction progress was monitored by the acquisition of ^{1}H NMR spectra at regular intervals and %conversion was determined by integration of relevant peaks in the NMR spectra.

As a control experiment the reaction was first carried out in the presence of AgOTf with no added ligand at different loadings – 2 mol%, 5 mol% and 10 mol% (Table 1). At each of these concentrations the catalyst was initially highly active, as indicated by the consistently high turnover rates measured at 50% conversion. When using only 2 mol% AgOTf the catalytic activity dropped before complete conversion of the substrate, with no more than 90% conversion reached even after 7 days. In the presence of 5 mol% and 20 mol% of AgOTf, the rate of reaction was sufficiently fast that >98% conversion was reached quickly, before the complete decomposition of the catalyst.

With the aim of generating reactive, but stable, Ag catalysts AgOTf was reacted with each of the ligands shown in Fig. 1 in solution. The complexes thus generated *in situ* were tested for catalytic



Scheme 2. Hydroamination of 4-pentyn-1-amine (**1**) to 2-methylpyrroline (**2**).

Table 1
Catalytic efficiency of AgOTf for the hydroamination of 4-pentyn-1-amine (**1**).

AgOTf (mol%)	Time at 80% conversion (h)	Time at >98% conversion (h)	N_t (h^{-1})[a]
2	1.5	164 (90%[b])	62
5	0.6	11.5	48
20	1.5	1.25	50

[a] Turnover rates (N_t, h^{-1}) = (moles of product)/(moles of catalyst)/hour, calculated at 50% coversion.
[b] Complete conversion of substrate in the presence of 2 mol% AgOTf was not observed.

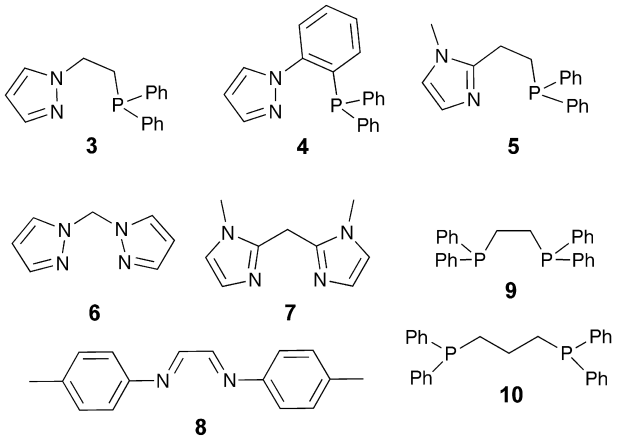


Fig. 1. Bidentate P- and N-donor ligands reacted with AgOTf to generate hydroamination catalysts *in situ*.

Table 2
Hydroamination of 4-pentyn-1-amine (**1**): relative efficiencies of Ag^+ catalysts formed *in situ* from AgOTf and various bidentate P and N-donor ligands.[a]

Catalyst	Conversion at N_t (h^{-1})	
	2 h (%)	
AgOTf + **3**	>98	129
AgOTf + **9**	90	64
AgOTf	82	62
AgOTf + **5**	43	–
AgOTf + **7**	40	–
AgOTf + **4**	37	–
AgOTf + **8**	37	–
AgOTf + **6**	28	–
AgOTf + **10**	12	–

[a] Reactions were performed using 2 mol% AgOTf and 2 mol% of ligand.

activity for the intramolecular hydroamination reaction (Table 2). Specifically, AgOTf was treated with each of the three bidentate P,N-donor ligands; 1-(2-(diphenylphosphino)ethyl)pyrazole (**3**), 1-(2-(diphenylphosphino)phenyl)pyrazole (**4**) or 2-(2-(diphenylphosphino)ethyl)-1-methylimidazole (**5**) [21], to form catalysts *in situ*. Ligands **3** and **5** were first synthesised within our research group and Ir and Rh complexes incorporating **3** and **5** have previously shown catalytic efficiency for the hydroamination reaction [14,21]. When 2 mol% of AgOTf and 2 mol% of ligand **3** were combined, a highly active and stable catalyst was generated which catalysed the complete conversion of **1** in 1.7 h with a turnover rate of 129 h^{-1}. This is the best reported result to date for the cyclisation of **1** using a silver catalyst [9]. In particular the turnover rate exceeded that of AgOTf alone (62 h^{-1}). Both the more rigid pyrazole-phosphine ligand **4** and the imidazole-phosphine ligand **5** generated poor catalysts which did not promote more than 30% conversion of substrate to product.

Three bidentate N-donor ligands were combined with AgOTf to form complexes *in situ* which were tested as catalysts for hydroamination. The ligands studied were bis(pyrazol-1-yl)methane (**6**) [22], bis(*N*-methylimidazol-2-yl)methane (**7**) [23] and glyoxal bis(4-methylphenylimine) (**8**) [24] (Fig. 1). Ligands **6**, **7**, and **8** all formed catalysts that were initially highly active and promoted the conversion of 25% of the substrate within 15 min. The reaction rate then slowed significantly and catalysis dropped below detectable amounts, most likely due to decomposition of the Ag^+ complexes.

The activity of *in situ* silver catalysts formed from AgOTf and two bidentate phosphorus donor ligands, 1,2-bis(diphenylphos-

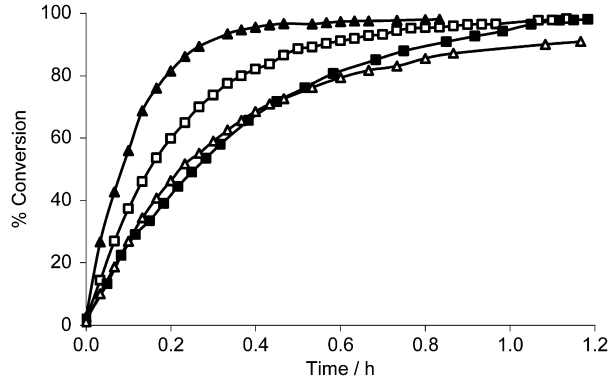


Fig. 2. Reaction profile for the cyclisation of 4-pentyn-1-amine (**1**) catalysed by 5 mol% AgOTf (Δ) and 5 mol%. AgOTf in the presence of 2 mol% (□), 5 mol% (▲) and 10 mol% (■) of **3**.

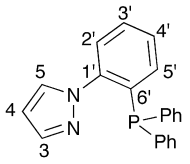


Fig. 3. Numbering system for **4** for reporting of NMR spectroscopic data.

phino)ethane (**9**) and 1,3-bis(diphenylphosphino)propane (**10**) was also investigated. Ligand **9** generated an effective catalyst that promoted 90% conversion of 4-pentyn-1-amine (**1**) in 2.1 h with a turnover rate of 64 h^{-1}. The same reactivity was not observed in the case of ligand **10**, which contains a longer alkyl chain between phosphine donors. Instead, AgOTf and **10** formed a complex that catalysed only 12% conversion of **1** in 2 h.

Having established that the most efficient catalyst of those tested here for the hydroamination of **1** was formed *in situ* from 2 mol% of AgOTf and 2 mol% of P,N-donor ligand **3**, a series of experiments were performed to establish which stoichiometric ratio of AgOTf and ligand would generate the most effective catalyst. The reaction was carried out in the presence of 5 mol% of AgOTf in combination with 2, 5 and 10 mol% of **3** (Fig. 2). A turnover rate of 130 h^{-1} was achieved using 5 mol% of AgOTf and 5 mol% of **3** and complete conversion to imine **2** was reached in 50 min. By comparison, turnover rates of 48 h^{-1}, 66 h^{-1} and 38 h^{-1} were observed when 0, 2 and 10 mol% of **3** were used, respectively. It was concluded, therefore, that the most efficient catalyst is formed from equimolar amounts of AgOTf and **3**.

The catalysed cyclisation of 5-hexyn-1-amine (**11**) to form 2-methyl-3,4,5,6-tetrahydropyridine (**12**) was also investigated using the catalyst generated *in situ* from AgOTf and **3**. Previous results have shown that the cyclisation of alkynylamines to form six-membered rings is typically harder to achieve than five-membered rings [4,9], which was also shown to be the case here. The combination of AgOTf (2 mol%) and **3** (2 mol%) promoted a conversion of **11** to **12** of only 34% after 21 h, with no significant improvement after this time.

3. Conclusion

The use of silver complexes generated *in situ* from AgOTf and a series of bidentate ligands were investigated as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine (**1**). A variety of P- and N-donor ligands were tested, including the novel pyrazole-phosphine ligand 1-(2-(diphenylphosphino)phenyl)pyrazole (**4**). It was determined that an efficient catalyst is generated only when the ligand introduced provides the correct balance between reactivity and stabilisation of the Ag(I) metal centre, the best example studied here being 1-(2-(diphenylphosphino)ethyl)pyrazole (**3**). In the presence of equimolar concentrations of AgOTf and **3**, the hydroamination of 4-pentyn-1-amine (**1**) was catalysed to completion with a turnover rate of 129 h^{-1}.

4. Experimental section

Chemicals were purchased from Aldrich or Lancaster and used without further purification. Nitrogen (>99.5%) was obtained from Linde Gas Pty. Ltd. and used as supplied. THF-d_8 was purchased from Cambridge Isotopes and dried over sodium prior to use. 4-Pentyn-1-amine (**1**) was synthesised by the Organic Synthesis Centre, School of Chemistry, University of Sydney and was dried over calcium hydride prior to use. All spectra were obtained at 298 K unless otherwise reported and ^{1}H and ^{13}C spectra are referenced to internal solvent references. ^{31}P NMR chemical shifts were externally referenced to H_3PO_4 (85% in D_2O) at 0 ppm. 1-Phenylpyrazole [16,17], 1-(2-(diphenylphosphino)ethyl)pyrazole (**3**) [14], 2-(2-(diphenylphosphino)ethyl)-1-methylimidazole (**5**) [21], bis(pyrazol-1-yl)methane (**6**) [22], bis(*N*-methylimidazol-2-yl)methane (**7**) [23], and glyoxal bis(4-methylphenylimine) (**8**) [24] were synthesised by literature procedures.

4.1. Synthesis of 1-(2-(diphenylphosphino)phenyl)pyrazole (*4*)

Ethyl magnesium bromide (14 mL, 1 M in THF) was added to a solution of 1-phenylpyrazole (2.00 g, 13.9 mmol) in THF (5 mL) under an atmosphere of nitrogen. This mixture was refluxed overnight in an oil bath at 100 °C. The red/brown mixture that formed was cooled to room temperature and then on ice before the slow addition of diphenylphosphine chloride (3.07 g, 139 mmol). After stirring for 3 h at room temperature, water was added in air to quench the reaction. The product was extracted into ethyl acetate (3 × 15 mL), dried over magnesium sulfate and the solvent evaporated *in vacuo* to yield a red solid. Recrystallisation from hot methanol yielded **4** as a yellow crystalline solid (1.67 g, 37%) m.p. 104–105 °C.

Found: C, 76.90; H, 5.31; N, 8.68%. $C_{21}H_{17}N_2P$ requires C, 76.82; H, 5.22; N, 8.53. ν_{max}/cm^{-1} 3064 (br), 1598, 1569, 1517, 1473, 1452, 1433, 1433, 1412, 1392, 1330, 1194, 1075, 1045, 1019, 934, 845, 767, 749, 697, 658, 620, 514, 501, 490, 420. (See Fig. 3 for numbering) δ_H (300 MHz; benzene-d_6; Me_4Si) 7.58 (1H, d, $^3J_{H3-H4}$ = 1.4 Hz, H3), 7.47 (1H, d, $^3J_{H5-H4}$ = 2.5 Hz, H5), 7.38 (1H, ddd, $^3J_{H3'-H4'}$ = 7.9 Hz, $^3J_{H3'-P}$ = 4.0 Hz, $^4J_{H3'-H5'}$ = 1.3 Hz, H3′), 7.35–7.28 (4H, m, *o*-CH of PPh_2), 7.14 (1H, ddd, $^3J_{H6'-H5'}$ = 7.0 Hz, $^4J_{H6'-P}$ = 3.5 Hz, $^4J_{H6'-H4'}$ = 1.5 Hz, H6′), 7.05–7.00 (6H, m, *m*-CH and *p*-CH of PPh_2), 6.96 (1H, ddd apparent dt, ^3J = 7.6 Hz, $^4J_{H4'-H6'}$ = 1.4 Hz, H4′), 6.84 (1H, ddd apparent dt, ^3J = 7.5 Hz, $^4J_{H5'-H3'}$ = 1.3 Hz, H5′), 6.04 (1H, dd apparent t, ^3J = 2.0 Hz, H4) ppm. $\delta_{P\{H\}}$ (121 MHz; benzene-d_6; Me_4Si) −14.0 ppm. $\delta_{C\{H\}}$ (75 MHz; $CDCl_3$; Me_4Si) 144.8 (d, $^1J_{C2'-P}$ = 21.1 Hz, C2′), 140.6 (C3), 136.7 (d,$^1J_{C-P}$ = 11.6, *i*-C of PPh_3), 134.9 (C6′), 134.1 (d, $^3J_{C-P}$ = 20.3 Hz, *m*-C of PPh_2) 133.9 (d, $^2J_{C1'-P}$ = 20.3 Hz, C1′) 131.3 (d, $^4J_{C5-P}$ = 5.8 Hz, C5), 129.8 (C4′), 129.0 (*p*-C of PPh_2), 128.7 (d, $^2J_{C-P}$ = 7.3 Hz, *o*-C of PPh_2), 128.4 (C5′), 126.4 (d, $^2J_{C3'-P}$ = 2.9 Hz, C3′), 106.4 (C4) ppm. ES-MS (MeOH) (ES^+): *m/z* 330 ([**4**+H]$^+$, 100%).

4.2. General procedure for catalytic reactions

All catalytic reactions were performed on a small scale in NMR tubes fitted with a Young's concentric Teflon valve. All reactions were carried out and samples prepared under an atmosphere of nitrogen. Samples were prepared by addition of 4-pentyn-1-amine

(**1**) (0.5–0.6 mmol) to AgOTf and the ligand (if present) in THF-d_8 (0.5–0.6 mL). The reaction was performed at 60 °C by heating in an oil bath or within the spectrometer.

The progress of the reaction was monitored by acquiring ^{1}H NMR spectra at regular intervals. In the preparation of each sample, as soon as all reactants had been added to the NMR tube it was frozen in liquid nitrogen. The first spectrum was measured when the sample had been thawed to room temperature and inserted into the spectrometer. The moment of this first acquisition was taken to be time zero. Conversion of starting material to product was determined by integration of the product resonances relative to the substrate resonances. The turnover rate (N_t, h^{-1}) was calculated as the number of moles of product/moles of catalyst/hour and was determined at the point of 50% conversion.

Acknowledgements

Financial support from the Australian Research Council and The University of New South Wales is gratefully acknowledged. We are grateful to Dr. K. Vuong, Dr. D. Kennedy and Dr. S. Rumble for the synthesis of ligands **5**, **6** and **8**, respectively.

References

[1] (a) For selected reviews see: T.E. Müller, M. Beller, Chem. Rev. 98 (1998) 675;
(b) F. Pohlki, S. Doye, Chem. Soc. Rev. 32 (2003) 104;
(c) F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 104 (2004) 3079.
[2] (a) For example: Y. Li, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 707;
(b) I. Aillaud, J. Collin, C. Duhayon, R. Guillot, D. Lyubov, E. Schulz, A. Trifonov, Chem. Eur. J. 14 (2008) 2189;
(c) S. Datta, M.T. Gamer, P.W. Roesky, Organometallics 27 (2008) 1207;
(d) X. Yu, T.J. Marks, Organometallics 26 (2007) 365;
(e) S. Hong, T.J. Marks, Acc. Chem. Res. 37 (2004) 673 (and references therein).
[3] (a) For example S. Majumder, A.L. Odom, Organometallics 27 (2008) 1174;
(b) D.A. Watson, M. Chiu, R.G. Bergman, Organometallics 25 (2006) 4731;
(c) C. Müller, C. Loos, N. Schulenberg, S. Doye, Eur. J. Org. Chem. (2006) 2499;
(d) L. Ackermann, R.G. Bergmann, R.N. Loy, J. Am. Chem. Soc. 125 (2003) 11956;
(e) P.D. Knight, I. Munslow, P.N. O'Shaughnessy, P. Scott, Chem. Commun. (2004) 894.
[4] S. Burling, L.D. Field, B.A. Messerle, S.L. Rumble, Organometallics 26 (2007) 4335.
[5] T.E. Müller, M. Grosche, E. Herdtweck, A. Pleier, E. Walter, Y. Yan, Organometallics 19 (2000) 170.
[6] (a) For example: X.-Z. Shu, X.-Y. Liu, H.-Q. Xiao, K.-G. Ji, L.-N. Guo, Y.-M. Liang, Adv. Synth. Catal. 350 (2008) 243;
(b) C.F. Bender, R.A. Widenhoefer, Chem. Commun. (2006) 4143;
(c) S. Burling, L.D. Field, B.A. Messerle, P. Turner, Organometallics 23 (2004) 1714;
(d) E.B. Bauer, G.T.S. Andavan, T.K. Hollis, R.J. Rubio, J. Cho, G.R. Kuchenbeiser, T.R. Helgert, C.S. Letko, F.S. Tham, Org. Lett. 10 (2008) 1175;
(e) Z. Liu, J.F. Hartwig, J. Am. Chem. Soc. 130 (2008) 1570.
[7] T.E. Müller, A.-K. Pleier, J. Chem. Soc., Dalton Trans. (1999) 583.
[8] L.D. Field, B.A. Messerle, K.Q. Vuong, P. Turner, T. Failes, Organometallics 26 (2007) 2058.
[9] J.M. Carney, P.J. Donoghue, W.M. Wuest, O. Wiest, P. Helquist, Org. Lett. 10 (2008) 3903.
[10] (a) B.C.J. van Esseveldt, P.W.H. Vervoort, F.L. van Delft, F.P.J.T. Rutjes, J. Org. Chem. 70 (2005) 1791;
(b) S. Robinson, M.C. Dovey, D. Gravestock, Tetrahedron Lett. 45 (2004) 6787.
[11] J. Sun, S.A. Kozmin, Angew. Chem., Int. Ed. 45 (2006) 4991.
[12] (a) J.S. Prasad, L.S. Liebeskind, Tetrahedron Lett. 29 (1988) 4253;
(b) Y. Koseki, S. Kusano, T. Nagasaka, Tetrahedron Lett. 39 (1998) 3517;
(c) A.M. Prior, R.S. Robinson, Tetrahedron Lett. 49 (2008) 411;
(d) Q. Ding, X. Yu, J. Wu, Tetrahedron Lett. 49 (2008) 2752;
(e) T.J. Harrison, J.A. Kozak, M. Corbella-Pané, G.R. Dake, J. Org. Chem. 71 (2006) 4525;
(f) R.S. Robinson, M.C. Dovey, D. Gravestock, Eur. J. Org. Chem. (2005) 505;
(g) N. Lingaiah, N.S. Babu, K.M. Reddy, P.S.S. Prasad, I. Suryanarayana, Chem. Commun. (2007) 278;
(h) Y. Luo, Z. Li, C.-J. Li, Org. Lett. 7 (2005) 2675.
[13] (a) P. Braunstein, J. Organomet. Chem. 689 (2004) 3953;
(b) P. Braunstein, F. Naud, Angew. Chem., Int. Ed. 40 (2001) 680;
(c) P.J. Guiry, C.P. Saunders, Adv. Synth. Catal. 346 (2004) 497;
(d) G.R. Newkome, Chem. Rev. 93 (1993) 2067.
[14] S. Burling, L.D. Field, B.A. Messerle, K.Q. Vuong, P. Turner, J. Chem. Soc., Dalton Trans. (2003) 4181.
[15] B.A. Messerle, K.Q. Vuong, Pure. Appl. Chem. 78 (2006) 385.
[16] R.G. Jones, J. Am. Chem. Soc. 71 (1949) 3994.
[17] I.L. Finar, R.J. Hurlock, J. Chem. Soc. (1957) 3024.
[18] A. Mukherjee, U. Subramanyam, V.G. Puranik, T.P. Mohandas, A. Sarkar, Eur. J. Inorg. Chem. (2005) 1254.
[19] A. Marxer, M. Siegrist, Helv. Chim. Acta 57 (1974) 1988.
[20] D.S. Black, G.B. Deacon, G.L. Edwards, G.M. Gatehouse, Aust. J. Chem. 46 (1993) 1323.
[21] K.Q. Vuong, Ph.D. Thesis, Metal Complex Catalysed C-X (X=S, O and N) Bond Formation, The University of New South Wales, Sydney, 2005.
[22] J. Elguero, S. Julia, J.M.d. Mazo, L. Avila, Org. Prep. Proc. Int. 16 (1984) 299.
[23] P.K. Byers, A.J. Canty, Organometallics 9 (1990) 210.
[24] J.M. Kliegman, T.K. Barnes, J. Org. Chem. 35 (1970) 3140.