Journal of Advances in Science and Technology
Vol. III, No. IV, February-2012, ISSN 2230-9659

Study on the Reactions of Long Chain (C*n*h2*n*+1) Azolium Chloride and Bromide Salts

Anand Vasudeo Mehta[1] Dr. Anurag Tiwari[2]

[1]Research Scholar, CMJ University, Shillong, Meghalaya

[2]Assistant Professor, Govt. College, Kanpur (U.P.), Guide No - 198

Abstract - Metal–NHC chemistry has been reviewed by pioneers in the field. When Herrmann and Bertrand published excellent reviews in 2000 concerning the synthesis of metal–NHCs, few Ag(I)–NHCs were known [1,3b]. Indeed interest in the synthesis of Ag(I)–NHCs and their application in transmetallation reactions has only greatly increased in recent years. In this regard, we reviewed Ag(I)–NHCs in 2004 [77] providing general trendsin Ag(I)–NHC chemistry. Arnold also had a mini review onAg(I)–NHCs in 2002 [78]. Recently, Garrison and Youngs published a review on Ag(I)–NHCs in 2005 [79], focusing mainlyon the structural parameters. We note that 62 papers dealingwith Ag(I)–NHCs have been published since the Youngs'review. When we look at the present trends in the chemistry ofmetal–NHCs (up to 31 July 2006), the Ag(I)–NHCs comprise various NHC systems ranging from five membered to seven membered rings, including imidazolium, benzimidazolium, imidazolinium, triazolium, pyrazolium, quinoxaline and naphthaanellated imidazolium, imidazo[1,5-a]pyridine, bipiperidine and biisoquinoline derived imidazolium, bisimidazoliums with arene backbone, six-membered ring pyrimidinium, sevenmembered ring amidinium moieties, etc. (Scheme 1). Therefore, it was our intention to provide an updated and comprehensive review on the subject of Ag(I)–NHCs, which may further accelerate work on this topic. The main features of this review were to evenly focus on (a) the ease and limitations in the synthesis of Ag(I)–NHCs, (b) the parameters influencing the solid state structures of Ag(I)–NHCs, and (c) the efficacy of transmetallation reaction by Ag(I)–NHCs. In particular, the authors would like to evaluate the widely applied Ag2O technique in the synthesisof Ag(I)–NHCs and their transmetallation efficiency to afford other important metal–NHCs.

Key Words ; NHC Systems, Membered Rings, Including Imidazolium, Benzimidazolium, Imidazolinium, Triazolium, Pyrazolium, Quinoxaline And Naphthoanellated Imidazolium.

◆

INTRODUCTION

As depicted in Scheme 2, different approaches such as (1) reaction of azolium salts with silver base, (2) reaction of free NHC with silver salts, and (3) reaction of azolium salts with silver salts under basic PTC conditions, have been used to prepare Ag(I)–NHCs. As early as 1993, Arduengo reported the first Ag (I)–NHC by the reaction of Ag(I) salt with a free NHC [80]. Later, Bertrand in 1997, reported that the reaction between triazolium triflate salt and a silver base such as Ag (OAc) (OAc = acetate), yielded a polymeric Ag(I)–NHC [81]. The reaction of another silver base, Ag2O, with azolium salts to afford

Ag(I)–NHCs was first reported in 1998 by Lin and co-workers [9a]. This result was serendipitous. While using different bases for the deprotonation of azolium salts, in an attempt to synthesize Au(I)–NHCs, the employment of Ag2O as a mild base effectively produced the Au(I)–NHCs. This study implied the generation of Ag (I)–NHCs *in situ*, and their role as transmetallating agents to prepare other metal–NHCs. Based on this obser-Scheme 2. Methods prescribed to prepare Ag(I)–NHCs.

The first example of Ag (I)–NHC formed via Ag2O technique vation, efforts were initiated by Lin to isolate the Ag (I)–NHCs in the solid state.

REVIEW OF LITERATURE

In the very first approach, addition of *N*,*N*_-diethylbenzimidazolium bromide to Ag2O in CH2Cl2 at room temperature easily afforded the Ag(I)–NHC ([Ag]/[salt] = 1) via *in situ* deprotonation (Scheme 3) [9a]. The formation of Ag(I)–NHC was monitored by the gradual disappearance of the Ag2O suspension in the solution.

After this report, the Ag2O technique was regarded as a convenient strategy to prepare Ag(I)–NHCs. The special attributes of the Ag2O technique such as (a) reactions can be carried out in air, (b) solvent pre-treatments are not required, (c) no additional base is needed, (d) deprotonation usually takes place at C2-carbene, and (e) the tolerance of Ag2O towards some active hydrogen atoms, were considered as some of the reasons to highlight this technique in metal–NHC chemistry. There are some reports of reactions being conducted in inert conditions without mentioning the reasons. Out of the 158 reports published until now on the preparation of Ag (I)–NHCs and their transmetallation, 142 deal with the Ag2O technique. The following content was divided into two major categories.

MATERIAL AND METHOD

In this section, we will discuss first the reports on the Ag2O method and then discuss other methods. Due to their easy accessibility, a large number of mono-azolium halide salts (containing one azole ring) were employed to react with Ag2O to access Ag(I)–NHCs. In addition to mono-azolium salts, various bisazolium and tris-azolium salts (containing two or three azole rings) with different linkers in pincer, cyclophane, and tripodal architectures were also investigated.

According to the available reports, mono-azolium halides can produce Ag(I)–NHCs of various ionic and neutral structures (types 1–7; Scheme 4) in the solid state. The salts with nonhalide salts usually formed simple bis-carbene complexes (type- 7; Scheme 4). The structures displayed by the Ag(I)–NHCs formed from bis- and poly-azolium salts will be discussed in later sections. These observations were based mainly on single crystal X-ray studies. Other techniques such as NMR and mass spectrometry were also used for the characterization of Ag(I)–NHCs. Nevertheless, fluxional behavior between the ionic and neutral complexes was observed in solution for most of the compounds.

The stoichiometric reaction of short chain azolium halides, i.e. (*N*,*N*_-Me2 or *N*,*N*_-Et2 substituted) benzimidazolium, imidazolium and triazolium chloride or bromides with Ag2O ([salt]/[metal] = 1) progressed smoothly in CH2Cl2 to produce either type-1 ion-pair complexes or type-2 and type-3 neutral complexes (Scheme 5a–e) [9a,9c,82]. The ion-pair Ag(I)–NHCs (Scheme 5a and b) based on *N*,*N*-dimethylbenzimidazolium and imidazolium moieties show extended Ag· · ·Ag interactions due to the planar shape of the ligand. With the triazolium NHC moiety, each pair of neutral type-3 Ag(I)–NHC (Scheme 5e) further interacts with neighboring pairs by extended Ag· · ·halide interactions, and form an infinite one-dimensional polymer, in which the Ag(I) adopts a tetrahedral geometry. Various *N*,*N*dialkyl, *N*,*N*-diaryl and hetero-disubstituted *N*-alkyl, *N*_-aryl imidazolium chloride and bromide salts were also employed to react with Ag2O, to afford normally the type-1 ionic or type- 2 neutral complexes [10,16,83–86], but no extended Ag· · ·Ag or Ag· · ·X interactions were observed in the reported crystal structures.

The reactions of long chain (C*n*H2*n*+1) azolium chloride and bromide salts (*n* = 10, 12, 14, 16 and 18) with Ag2O were investigated (Scheme 6) [9c,82b]. For the chloride salts of benzimidazolium or imidazolium, recrystallization of the crude product from CH2Cl2/hexane gave chloride bridged type-3 neutral Ag(I)–NHC complexes (Scheme 6a and d). Under similar experimental conditions, the bromide salts of long chain benzimidazolium produced type-1 ion-pair complexes (Scheme 6b). The reaction of long chain bromide salts of imidazolium with Ag2O afforded a product with an empirical formula of [Ag(NHC)Br].

When this compound was crystallized from acetone, a type-3 complex (Scheme 6c) was obtained. However, upon crystallization from CH2Cl2/hexane, a type-4 complex (Scheme 6e) was isolated. Extended Ag· · ·Ag interactions were not possible for the long-chain Ag(I)–NHCs, presumably, packing to obtain better chain–chain interactions were more important than Ag· · ·Ag interactions. Besides chain–chain interactions, both long chain and short chain Ag(I)–NHCs were stabilized by many secondary attraction forces such as extended hydrogen bonding and intermolecular Ag· · ·halide interactions. A structural comparison of both the short and long chain compounds according to the crystal structure analysis.

Actually, the long chain Ag(I)–NHCs were designed to study the possible formation of liquid crystals (LC); unfortunately none of them were mesomorphic, probably due to insufficient core–core interactions [9d,82b]. However, when mixed with their corresponding imidazolium salts they exhibited LC properties. Recent studies have projected this special type of organic–inorganic hybrids to serve as good singlesource-precursors for silver nanomaterials [82b]. The stoichiometric reactions of azolium [NO3], [PF6], and [BF4] salts produced simple bis-carbene complexes (type-7 as shown in Scheme 4) with or without basic PTC conditions [82b]. Usually the exclusion of light was not required in the Ag2O technique. Iodide salts prefer to form ion-pair complexes with poly silver-iodide ion rather than neutral species [87]. The short chain *N*,*N*_-dimethylimidazolium iodide produces the type-1 ion-pair complex, Scheme 7a from DMSO (Scheme 7) [88] The poly silver-iodide anion and the [Ag(NHC)2]+ cation were linked together by weak intermolecular Ag· · ·I interactions in the crystal packing. Replacing one methyl side arm with an allyl group led to the formation of a type-4 tetranuclear complex (Scheme 7b) upon recrystallization from DMSO [88]. However, the use of *N*-Me,*N*_-anthracenyl substituted imidazolium salt produced an iodide bridged type- 5 neutral Ag(I)–NHC (Scheme 7c) in CH2Cl2 (Scheme 7) [89]. Despite the above observations, the interaction of *N*,*N*_- dimethyl-benzimidazolium or imidazolium iodides with Ag2O inCH2Cl2 produced Ag(I)–NHC at room temperature with chloride anion instead of iodide [82a,90]. Under similar conditions no metathesis of bromide by chloride occurred. The chlorinated solvent may be the source of the chloride. Liu used the same imidazolium iodide but isolated the final Ag(I)–NHC as [Ag(Me2-imy)2][Ag4I6] from hot DMSO [88].

The interaction of Ag2O with several saturated imidazolinium salts [91–93] with simple N-substituents was also studied using different solvent system including water. Type-2 mononuclear or type-3 halide bridged dinuclear Ag(I)–NHCs were normally formed from imidazolinium halides, and type-7 [Ag(NHC)2]+ complexes from non-halide salts similar to those of unsaturated imidazolium analogues. Some of the representative drawings were given in Scheme 8. Notably, the non-planar Ag2I2 unit in compound Scheme 8a exhibited both Ag· · ·Ag and Ag· · ·I interactions [91]. In contrast to the preparations above, the failure of the reaction of ferrocenyl substituted imidazolinium salt withAg2Owas attributed to reduced acidity (Scheme 8i) [94]. However, the unsaturated imidazolium salt with ferrocenyl substituents successfully produced a bis-carbene of the type-7.

In a recent advance, Nolan and Clyburne emphasized the influence of halide ions and the solvent on the structural formulae of Ag(I)–NHCs [84]. The reaction of *N*,*N*_-dialkyl or diaryl substituted imidazolium and imidazolinium chloride salts with Ag2O in CH2Cl2 was shown to form type-2 neutral complexes (Scheme 9) as observed from a single crystal X-ray study.

However, the triazolium salt produced a Ag(I)–NHC in CH2Cl2 with the coexistence of both ionic (type-1) and neutral forms (type-2) in the solid state (Scheme 9). An increase in the solvent polarity increased the population of ionic bis-carbene (type-1) (Scheme 9). This aspect was further indicated by the use of the *N*,*N*-dimesityl substituted iodide salt, where only the ionic bis-carbene of type-1 complexes were formed in highly polar MeCN as determined by 13C NMR and single crystal X-ray study (Scheme 9). This was proposed to be due to the higher polarizability of iodide than chloride. Type-2 [(NHC)AgCl] is identical to that of Nolan's work were also reported by Hahn and co-workers [92].

When mono-azolium salts (both halide and non-halide) with functional groups at one or two N-side arms were employed to react with Ag2O, the Ag(I)–NHCs were also isolated as type-1 ion-pair, type-2 mononuclear neutral complexes, type-3 halide bridged complexes, type-4 Ag2X4 2− bridged tetranuclear complexes, and type-7 bis-carbene complexes as determined by crystal structure and spectroscopic analysis (Scheme 10) [13a,20a,b,22a,c,24c,25,26,31,33,44,55,70,95–101]. Some representative examples were given in Scheme 10. Normally the functional group was not bonded to the Ag(I), but in a few reports coordination of functional groups to Ag(I) were illustrated [55a,70,95,100] (Scheme 10). The work by Cavell and co-workers has shown the nonstoichiometric X−/AgX2 − anion in some Ag(I)–NHCs, upon using imidazolium halides [20]. In such cases, it was suggested that replacing the halide by non-halide ion can avoid the ambiguity [20,42]. Arnold reported that the reaction of alcohol functionalized imidazolium halides with Ag2O led to the deprotonation of both C2–H and –OH protons and yielded the type-6 halide free Ag(I)–NHC–alkoxyl complexes (Scheme 11i and iii) [62,101]. However, this phenomenon depends on steric factors (Scheme 11, Eq. (ii)). These observations were described on the basis of EA and NMR data only. Further in this work, the formation of an amine coordinated Ag(I)–NHC with the imidazolium salt having an alkylammonium side arm (Scheme 11iv) [101], suggested that Ag2O was not sufficiently basic to deprotonate the secondary amine. Hoveyda and co-workers reported the preparation, crystal structure characterization and catalytic application of the halide free Ag(I)–NHC-phenoxyl complexes (Scheme 11v) [66a,b].

Several bis-imidazolium salts connected by a simple alkylenyl linker or by pyridyl, ether, and amine functional group linkers were designed to prepare Ag(I)–NHCs [15,20c,d,22b,d, 23,27b,30,57,63,82a,90,101–105]. Bis-imidazolium salts with an arene backbone were also explored recently to afford Ag(I)–NHCs [48]. Structural drawings for some of the examples were given in Scheme 12. The use of halide salts produced either neutral or ionic Ag(I)–NHCs. Functional groups did not appear to play any role in the coordination. Youngs and co-workers reported the first Ag(I)–NHC with antimicrobial properties (Scheme 13) [106]. Two neighboring bis-carbene units were bridged by Ag(I) to form a polymeric structure (Scheme 13a). Addition of NH4PF6 to this watersoluble polymer produced a water-insoluble discrete dinuclear Ag(I)–NHC (Scheme 13b).

Youngs and co-workers also pioneered the use of bis-imidazolium salts to prepare Ag (I)–NHC-cyclophanes (Scheme 14) [107]. Stoichiometric reactions (1:2) of imidazolium linked cyclophanes (Scheme 14a and b) with Ag2O produced dinuclear complexes (Scheme 14i), in which two Ag(I) ions bridged the NHC units of two different macrocyclic rings. The complex with *gem*-diol bridging functionality (from salt b, Scheme 14) was encapsulated to tecophilic fiber mats, to serve as a precursor for nanosilver, which exhibited excellent bacterial activity [107b].

Baker also isolated a variety of Ag(I)–NHC cyclophane complexes from salts given in Scheme 14c–f [108]. While the reactions of salts c and d and f with Ag2O easily afforded the dinuclear Ag(I)–NHCs in Eq. (i), reaction of salt e with Ag2O was very slow. The bromide ions of Ag(I)–NHCs obtained from salts d and f were replaced with [PF6] or [BPh4] to avoid the nonstoichiometric Br−/AgBr2 − problem. EA and NMR data of the Ag (I)–NHC obtained from salt e were consistent with the formulation as neutral [Ag(NHC)Br], but single crystal study showed that a Ag2Br2 core was intercalated between two [Ag(NHC)Br] (Eq. (ii)).

Meyer and Periss designed tripodal-imidazolium salts with carbon or nitrogen anchors (Scheme 15a–c) to prepare Scheme 10. Ag(I)–NHCs (a–h) with functional groups in the N-side arms. Ag (I)–NHCs [41a,109]. The solid state structures of Ag(I)–NHCs (Scheme 15i) obtained from salts a and b showed that two tripodal NHCs were bridged by three Ag(I) ions via each of the three pendant arms to provide three units of bis-carbene Ag(I) complexes (Scheme 15) [109].

The synthesis conducted in the presence of excess Ag2O [(Ag)/(salt)≥1] sometimes showed results different from that of the normal stoichiometric reactions [(Ag)/(salt)≤1]. This phenomenon was found to depend on the nature of the imidazolium salt and the solvent. Reports by Lin and co-workers [82b], Catalano et al. [13b, c, 110], Youngs and co-workers [111,112] and Crabtreeand co-workers [40b,113] summarized this special type of observation. Lin noted that [82b] when excess Ag2O was used to react with *N*-methyl or ethyl substituted imidazolium halides ([Ag]/[salt]≥1.2) in CH2Cl2 for >18 h, the solution turned yellow, and a silver mirror together with brown powdery solid was coated on the reaction vessel. When the ratio of [Ag]/[salt] was ≤1.0, no yellow solution nor silver mirror was observed. When long chain imidazolium halides react with excess Ag2O, a yellow solution was observed but not the silver mirror nor the brown solid. The UV–vis spectrum of the yellow solution showed intense surface plasmon resonance (SPR) bands at ~426 nm, suggesting the formation of nano-silver particles.

It appears that long chain imidazolium halides can stabilize AgNPs better than short chain imidazolium salts. The yellow colloidal AgNPs can be removed by activated carbon. Catalano's work showed that when excess Ag2O reacts with imidazolium salts containing picolyl or quinolyl N-side arms [(Ag)/(salt) =~10], the homoleptic triangulo-[Ag3(_-NHC)3]+3 complexes (Scheme 16a and b) are produced, with bridging _2-carbenes and unusual Ag· · ·Ag interactions (~2.7A°) [(Scheme 16) [13b,c,110], whereas, a simple [Ag(NHC)2]+ is obtained from the usual stochiometric reaction [(Ag)/(salt) = 1]. Identical compounds were obtained upon addition of AgBF4 to the pre-formed [Ag(NHC)2]+ complexes in acetonitrile [110]. Youngs also reported a similar trinuclear complex (Scheme 16c) by using a similar imidazolium salt containing a terminal alkanol functionality [111], however, this time the ratio of [Ag]/[salt] was = 1.2.

In the preparations of Ag(I)–NHC-cyclophane complexes (Scheme 17), Youngs demonstrated that a tetranuclear complex (Scheme 17a) was formed when four equivalents of Ag2O were treated with one equivalent of the [PF6] salt of imidazoliumcyclophane in DMSO [112a]. Under similar conditions, the bromide salt produced only a dinuclear compound (Scheme 17b) in water [112a]. These results indicated that the solubility of the products kinetically controlled the reaction.

CONCLUSION

Crystal studyrevealed additional contacts (~2.3–2.5A°) between the nonbridging Ag and the NHCs. A similar tetranuclear complex was also obtained from pyridyl and pyrrole bridged imidazolium salt by utilizing excess of Ag2O [112b]. An unprecedented observation in the Ag2O technique was reported by Crabtree (Scheme 18) [40b,113]. When the imidazolium rings were occupied with substituents in all the positions (1–5 positions), those salts with methyl, benzyl and even ethyl substituents at the C2-position (Scheme 18ii) produced normal C2-bonded Ag(I)–NHCs by reaction with a four-fold excess of Ag2O. Reaction of 1,2,3,4-tertramethyl imidazolium iodide with Ag2O also produced normal C2-bonded Ag(I)–NHC. Metallic silver observed in these reactions suggested its role in the cleavage of the C–C bond at the C2-position. However, C–C bond cleavage did not occur when the C2-substituent was isopropyl. This different behavior was attributed to the steric effect caused by the C2-substituent. It has been proposed that 2-carbonyl imidazolium species were intermediates in the above C–C bond cleavage reaction. To support this proposition, the reaction of 2-benzoylimidazolium salt was performed; indeed a normal Ag(I)–NHC was formed. This result provided a clue to the development of another potentially useful method that carbonylimidazolium species can be used as starting materials to prepare Ag(I)–NHC and other metal–NHCs (Scheme 18) [40b,113].

A report by Alcarazo et al. described the formation of abnormal Ag(I)–NHCs from 2-phenyl imidazo[1,5-a]pyridinium salt (Scheme 18, Eq. (iii)) [51].

Very recently a report by Wang et al. reported that an iodide anchored trinuclear Ag(I)–NHC structure was obtained when a picolyl functionalized imidazolium iodide salt was reacted with 3 mol excess of Ag2O (Scheme 19) [21]. Previously, Cavell and co-workes reported an identical reaction [20a]; formation of an [Ag(NHC)2]+ with non-stoichiometric I−/AgI2− anion was observed at 2:1 molar ratio of [imidazolium salt]/[Ag2O]. Scheme 12. Ag(I)–NHCs (a–e) obtained from bis-imidazolium salts. Chiu et al. reported that when Ag(I) salts were added to a type-2 Ag(I)–NHC having an *N*-pyrazole and *N*_-aryl sidearm (Scheme 20a), a variety of Ag(I)–NHCs were obtained (Scheme 20) [114]. When the aryl was benzyl, the addition of AgNO3 generated a coordination polymer [Ag(NHC)(NO3)]*n* (Scheme 20b) in MeCN at room temperature. However, when aryl was *N*-naphthyl or fluorobenzyl, a metallomacrocycle (Scheme 20c) was obtained with the addition of AgNO3 or AgBF4. A simple bis-carbene with a *N*-fluorobenzyl substituent (Scheme 20d) was obtained upon the addition of AgNO3 in refluxing methanol.

REFERENCES

[1] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39.

[2] R.H. Crabtree, J. Organomet. Chem. 690 (2005) 5451.

[3] (a) W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290; (b) T. Weskamp, V.P.W. B¨ohm, W.A. Herrmann, J. Organomet. Chem. 600 (2000) 12.

[4] P.J. Barnard, M.V. Baker, S.J. Berners-Price, D.A. Day, J. Inorg. Biochem. 98 (2004) 1642.

[5] W.A. Herrmann, C. K¨oher, L.J. GooDen, G.R.J. Artus, Chem. Eur. J. 2 (1996) 1627.

[6] M.F. Lappert, J. Organomet. Chem. 358 (1988) 185.

[7] H.-W. Wanzlick, H.-J. Schonherr, Angew. Chem. 80 (1968) 154; H.-W. Wanzlick, H.-J. Schonherr, Angew. Chem. Int. Ed. Engl. 7 (1968) 141.

[8] K.M. Lee, C.K. Lee, I.J.B. Lin, Angew. Chem. Int. Ed. 36 (1997) 1850.

[9] (a) H.M.J. Wang, I.J.B. Lin, Organometallics 17 (1998) 972; (b) H.M.J. Wang, C.Y.L. Chen, I.J.B. Lin, Organometallics 18 (1999) 1216; (c) H.M.J. Wang, C.S. Vasam, T.Y.R. Tsai, S.-H. Chen, A.H.H. Chang, I.J.B. Lin, Organometallics 24 (2005) 486; (d) C.K. Lee, K.M. Lee, I.J.B. Lin, Organometallics 21 (2002) 10.

[10] S.K. Schneider, W.A. Herrmann, E.Z. Herdtweck, Anorg. Allg. Chem. 629 (2003) 2363.

[11] P. de Fremont, N.M. Scott, E.D. Stevens, S.P. Nolan, Organometallics 24 (2005) 2411.

[12] (a) M.V. Baker, P.J. Barnard, S.K. Brayshaw, J.L. Hickey, B.W. Skelton, A.H. White, Dalton Trans. (2005) 37; (b) M.V. Baker, P.J. Barnard, S.J.B. Price, S.K. Brayshaw, J.L. Hickey, B.W. Skelton, A.H. White, J. Organomet. Chem. 690 (2005) 5625.

[13] (a) V.J. Catalano, M.A. Malwitz, A.O. Etogo, Inorg. Chem. 43 (2004) 5714;

(b) V.J. Catalano, A.L. Moore, Inorg. Chem. 44 (2005) 6558;

(c) V.J. Catalano, A.O. Etogo, J. Organomet. Chem. 690 (2005) 6041.

[14] X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, Organometallics 23 (2004) 755.

[15] (a) J.-W.Wang, H.-B. Song, Q.-S. Li, F.-B. Xu, Z.-Z. Zhang, Inorg. Chim. Acta 358 (2005) 3653;

(b) J.-W.Wang, Q.-S. Li, F.-B. Xu, H.-B. Song, Z.-Z. Zhang, Eur. J. Org. Chem. 2006 (2006) 2232.

[16] R. Corber´an, J. Ram´ırez, M. Poyatos, E. Peris, E. Fern´andez, Tetrahedron: Asymmetry 17 (2006) 1759.

[17] C. Nieto-Oberhuber, S. Lopez, A.M. Echavarren, J. Am. Chem. Soc. 127 (2005) 6178.

[18] C.K. Lee, J.C.C. Chen, K.M. Lee, C.W. Liu, I.J.B. Lin, Chem. Mater. 11 (1999) 1237.

[19] D.C. Li, D.J. Liu, J. Chem. Crystallogr. 33 (2003) 989.

[20] (a) D.S. McGuinness, K.J. Cavell, Organometallics 19 (2000) 741;

(b) A.M. Magill, D.S. McGuinness, K.J. Cavell, G.J.P. Britovsek, V.C.

Gibson, A.J.P. White, D.J. Williams, A.H. White, B.W. Skelton, J. Organomet. Chem. 617/618 (2001) 546;

(c) D.J. Nielsen, K.J. Cavell, B.W. Skelton, A.H. White, Inorg. Chim. Acta 327 (2002) 116;

(d) D.J. Nielsen, K.J. Cavell, B.W. Skelton, A.H. White, Inorg. Chim. Acta 359 (2006) 1855;

(e) D.J. Nielsen, A.M. Magill, B.F. Yates, K.J. Cavell, B.W. Skelton, A.H. White, Chem. Commun. 27 (2002) 2500.

[21] X.Wang, S. Liu, L.-H.Weng, G.-X. Jin, Organometallics 25 (2006) 3565.

[22] (a) L.G. Bonnet, R.E. Douthwaite, B.M. Kariuki, Organometallics 22 (2003) 4187;

(b) L.G. Bonnet, R.E. Douthwaite, R. Hodgson, Organometallics 22 (2003) 4384;

(c) L.G. Bonnet, R.E. Douthwaite, R. Hodgson, J. Houghton, B.M. Kariuki, S. Simonovic, Dalton Trans. 23 (2004) 3528;

(d) R.S. Douthwaite, J. Houghton, M. Kariuki, Chem. Commun. 32 (2004) 698.

[23] M.C. Perry,X. Cui, K. Burgess, Tetrahedron: Asymmetry 13 (2002) 1969.

[24] (a) J. Pytkowicz, S. Roland, P. Mangeney, G. Meyer, A. Jutand, J. Organomet. Chem. 678 (2003) 166;

(b) S. Roland, M. Audouin, P. Mangeney, Organometallics 23 (2004) 3075;

(c) A. Flahaut, J.-P. Baltaze, S. Roland, P. Mangeney, J. Organomet. Chem. 691 (2006) 3498.

[25] (a) S. Dastgir, K.S. Coleman, A.R. Cowley, M.L.H. Green, Organometallics 25 (2006) 300;

(b) K.S. Coleman, H.T. Chamberlayne, S. Turberville, M.L.H. Green, A.R. Cowley, Dalton Trans. 29 (2003) 2917.

[26] M. Poyatos, A. Maisse-Francois, S. Bellemin-Laponnaz, L.H. Gade, Organometallics 25 (2006) 2634.

[27] (a) H.M. Lee, J.Y. Zeng, C.-H. Hu, M.-T. Lee, Inorg. Chem. 43 (2004) 6822;

(b) P.L. Chiu, C.Y. Chen, J.Y. Zeng, C.Y. Lu, H.M. Lee, J. Organomet. Chem. 690 (2005) 1682.

[28] F.L. Zeng, Z.K. Yu, J. Org. Chem. 71 (2006) 5274.

[29] (a) A.A.D. Tulloch, S. Winston, A.A. Danopoulos, G. Eastham, M.B. Hursthouse, Dalton Trans. (2003) 699;

(b) A.A. Danopoulos, A.A.D. Tulloch, S. Winston, G. Eastham, M.B. Hursthouse, Dalton Trans. (2003) 1009;

(c) A.A.D. Tulloch, A.A. Danopoulos, G.J. Tizzard, S.J. Coles, M.B. Hursthouse, R.S. Hay-Motherwell, W.B. Motherwell, Chem. Commun. (2001) 1270.

[30] R.S. Simons, P. Custer, C.A. Tessier, W.J. Youngs, Organometallics 22 (2003) 1979.

[31] (a) M. Froseth, A. Dhindsa, H. Roise, M. Tilset, Dalton Trans. (2003) 4516;

(b) M. Frøseth, K.A. Netland, K.W. T¨ornroos, A. Dhindsa, M. Tilset, Dalton Trans. (2005) 1664;

(c) M. Frøseth, K.A. Netland, C. Rømming, M. Tilset, J. Organomet. Chem. 690 (2005) 6125.

[32] B.E. Ketz, A.P. Cole, R.M. Waymouth, Organometallics 23 (2004) 2835.

[33] (a) V. Cesar, S. Bellemin-Laponnaz, L.H. Gade, Organometallics 21 (2002) 5204;

(b) N. Schneider, V. Cesar, S. Bellemin-Laponnaz, L.H. Gade, Organometallics 24 (2005) 4886.

[34] R. Wang, B. Twamley, J.M. Shreeve, J. Org. Chem. 71 (2006) 426.

[35] F. Hannig, G. Kehr, R. Fr¨ohlich, G. Erker, J. Organomet. Chem. 690 (2005) 5959.

[36] G. Zou, W. Huang, Y. Xiao, J. Tang, New J. Chem. (2006) 803.

[37] M. Mayr, M.R. Buchmeiser, Macromol. Rapid Commun. 25 (2004) 231.

[38] M. Mayr, K. Wurst, K. Ongania, M.R. Buchmeiser, Chem. Eur. J. 10 (2004) 1256.

[39] S. Saravanakumar, A.I. Oprea, M.K. Kindermann, P.G. Jones, J. Heinicke, Chem. Eur. J. 12 (2006) 3143.