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To Anlyse the Ag2o Technique Has Been the Most Popular Method in the Synthesis of Ag (I)–Nhcs

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Abstract – The present work revealed that the Ag2O technique has been the most popular method in the synthesis of Ag(I)–NHCs and in their subsequent uses as transmetallating agents. The Ag2O technique is tolerant of activated hydrogen atoms adjacent to functional groups. The use of normal azolium halide led to the formation of ionic or neutral Ag(I)–NHCs in the solidstate, depending on factors such as counter-ions, carbene cores, N-substituents and the crystallization conditions. A fluxional behavior between the ionic and neutral complexes was observed in solution for most of the compounds. The ionic or neutral compounds displayed structural diversity to give monomeric, dimeric and polymeric forms depending on the steric bulkiness around the Ag(I)–NHCs. In some instances non-stoichiometric X−/AgX2− were reported; this happened because the AgX2− was in equilibrium with AgX(s) and X−. This problem can be resolved if the halide ion was replaced by non-coordinating anions.

Depending on the nature of the imidazolium salts, the synthetic reactions conducted with excess Ag2O yielded interesting products. For example, the reaction of long N-alkyl chain containing imidazolium or benzimidazolium salts with excess Ag2O produced stable AgNPs in solution along with the AgNHCs.

When N-pyridyl functionalized imidazolium salts reacted with excess Ag2O, the triangulo-[Ag3(_-NHC)3]+3 complexes (Scheme 17a and b) with bridging _2-carbenes and unusual Ag· · ·Ag interactions were generated.

Key Words; Non-Coordinating, Yielded, Interactions

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INTRODUCTION

Ag(I)–NHC complexes with NHCs other than imidazol-2-ylidene carbene were also obtained via the Ag2O method.

Buchmeiser and co-workers reported the first six-membered tetrahydropyrimidin-2-ylidene based Ag(I)–NHC from a tetrahydro-pyrimidinium bromide salt [38]. Herrmann et al. reported the first crystal structure of tetrahydropyrimidin-2-ylidene based Ag(I)–NHC (Scheme 21i) [115]. The large down Scheme 13. polymeric (a) and dimeric (b) Ag(I)–NHC cyclophanes. Scheme 14. Formation of Ag(I)–NHC cyclophane complexes with different bridging groups. Scheme 15. Ag(I)–NHCs obtained from tripodal imidazolium salts. field shift of the carbene-C resonance from that of the free salt was attributed to a strong Ag–C bond. Heinicke et al. reported that the reaction of electron deficient quinoxaline- and naphthylanellated salts with Ag2O produced neutral or bis-NHC complexes (Scheme 21ii and iii) [39,54]. Very recently, Herrmann et al. reported the formation of Ag (I)–NHCs from chiral imidazolium salts derived from 2,2_-bipyridine or from partially reduced biisoquinoline [49], but no characterization was provided.

Other than the Ag2O technique, reactions of azolium salts with Ag2CO3, Ag(OAc), or with Ag(I) salts under PTC conditions or by transmetallation from other metal–NHCs were Scheme 16. Homoleptic triangulo-[(Ag3_-NHC)3]+3 complexes (a–c). Scheme 17. Ag (I)–NHC cyclophanes (a and b) obtained with excess Ag2O. Scheme 18. A typical reaction of Ag2O with imidazolium salts having the substituents at the C2-position. also reported. Danopoulos' group observed that longer reaction times were needed when Ag2CO3 was used instead of Ag2O Recently, reports by Hoveyda and Gilbertson mentioned the validity of Ag2CO3 in the preparation of Ru–NHCs [56, 73].

Charette explored the use of a combination of Ag(OAc) and Na2CO3 to prepare Ag(I)–NHCs from *N*-benzoylimidazolium Scheme 19. Iodide anchored trinuclear Ag(I)–NHC. sylide in refluxing THF (Scheme 22i) [67]. Formation of a dimeric structure linked through C2-, N-atoms rather than C2-, O-atoms was claimed to be due to the long Ag–C bond.

When Stahl and co-workers tried to synthesize a Pd(II)–NHC from a seven-membered NHC ligand by the use of AgOAc, a type-2 Ag(I)–NHC was unexpectedly obtained (Scheme 22ii) [116]. Transfer of NHC from a putative Pd(II)–NHC to Ag (I) was anticipated. Buchmeiser and co-workers reported that six-membered tetrahydropyrimidin-2-ylidene complex of Rh (I) also transferred the NHC to Ag(I) upon reaction with excess Ag(CF3COO) (Scheme 22iii) [117]. Formation of a pyrazol-3- ylidene Ag (I), by the reaction of pyrazolium carboxylate with Ag(CF3SO3) was described by Schmidt, based on mass spectroscopic data [118]. Earlier, Liu and co-workers reported that very unstable Ag(I)–NHCs based on a saturated imidazolinium moiety can be obtained by the transmetallation ofWIII, MoIII, CrIII, PtII and PdII–NHCs [119].However, some of these Ag(I)–NHCs were stable enough to be isolated by the Ag2O technique [91].

The work by Lin and Catalano described the interaction of non basic Ag(I) salts with azolium salts under PTC/OH− conditions which also yielded Ag(I)–NHCs (Scheme 22iv and v) [9a,13b].

REVIEW OF LITERATURE

Regarding the implementation of Arduengo's free NHC route, so far only three mono-NHCs (1,3-Mes2-imy, 1,3, 4,5-Me4-imy, and 1,3-*i*Pr2-4,5-Me2-imy; imy = imidazol-2-ylidene), and one bis-NHC (1,1_-(pyridine-2,6-diyl) bis(3-benzyl-2,3-dihydro-1*H*-imidazole-2-ylidene) were employed to prepare Ag (I)–NHCs [80,84,120–122]. The use of mono-NHCs produced either type-2 neutral or type-7 bis carbene complexes depending on the Ag (I) precursor (Scheme 23i and ii). When a bis-carbene with pyridyl linker was used, an interesting double helical structure of Ag(I)–NHC [122] (Scheme 23iii), similar to that of reported Hg(II)–NHC [123] was found.

Carbene transfer reactions of Ag(I)–NHCs

In the present metal–NHC chemistry, Ag(I)–NHCs have proven popular mainly because of their role as NHC transfer agents in the development of many other important metal–NHCs. Practical difficulties encountered in the synthesis of metal–NHCs by other methods [for example, Refs. 11,12,20,31,33,34,56,74,75] suggested that the Ag2O method was a good choice. Many authors suggested that active hydrogen atoms other than C2–H can be protected effectively by this method. Although many studies have indicated that transmetal-Scheme 21. The formation of Ag(I)–NHCs from pyrimidinium, naphtha- and quinoxaline imidazolium salts via the Ag2O technique.

Preparation of Ag(I)–NHCs by different methods other than the Ag2O method. Lotion can be conducted in air, inert conditions were mentioned in few instances. The available literature revealed that NHC ligand transfers from Ag(I)–NHCs to various metal ions including Au(I), Pd(II), Cu(I), Cu(II), Ni(II), Pt(II), Ir(I), Ir(III), Rh(I), Rh(III), Ru(II), Ru(III) and Ru(IV) were successfully achieved.

However, there were some limitations and unexpected products Scheme 23. Ag(I)–NHCs via the free NHC route. Encountered in some studies, such as contamination of Ag-ions and the formation of unexpected metal–NHC geometries. Nevertheless, the transfer of NHC not only depended on the nature of Ag(I)–NHCs, but also on the nature of the receiving metalprecursors and the reaction conditions. The authors would like to review some of these problems.

With the first successful transfer ofNHCfrom an Ag(I)–NHC to Au(I) and Pd(II), the lack of 107,109Ag–13C coupling in the 13CNMRspectrum and the labile nature of the Ag(I) complexes were proposed to be part of the reasons for the NHC migration (Scheme 24) [9a]. However, there was some evidence that Ag(I)–NHCs with non-fluxional Ag–C bonds were also able to transfer the NHCs [9a,42].

A literature survey revealed that the NHC transfer technique has most frequently been applied to the synthesis of Au(I), Pd(II) and Rh(I)–NHCs. Therefore, we will first focus on Au(I)–NHCs. Common methods used to synthesize Au(I)–NHCs [124] include: (a) cleavage of electron rich olefins with Au(I) sources, (b) direct reaction of Au(I) sources with azolium salts under PTC conditions, (c) direct reaction of Au(I) sources with preformed NHCs, (d) protonation or alkylation of gold azolyl compounds, and (e) transmetallation with Ag(I)–NHCs. Recent trends revealed that transmetallation has become popular. The reaction between an Ag(I)–NHC and gold precursors such as Au(SMe2)Cl or Au(tht)Cl, or Au(PEt3)Cl afforded Au(I)–NHC effectively. Lin generalized the preparation of various [Au(NHC)Cl] compounds (Scheme 25i), which can be used as good precursors to prepare Au(I)–NHC-core containing compounds [9a–c]. Herrmann and co-workers also Scheme 24. Fluxional behavior of Ag(I)–NHCs and NHC transfer. reported the easy synthesis of a neutral [Au(NHC)Cl] via transmetallation Recently, Nolan and co-workers described that in the preparation of certain neutral [Au(NHCs)Cl]s, the technique of transmetallation was superior to that of the free NHC method [11]. Baker et al.

reported that in an attempt to isolate neutral [Au(NHC)Cl] by using the preformed NHC, a cationic Au(I)–NHC was obtained [12]; transmetallation easily controlled the formation of pure [Au(NHC)Cl]. It is noticeable that the use of imidazolium bromide in transmetallation to prepare [Au(NHC)Cl] may sometimes generate traces of [Au(NHC)Br].

If this is the case, the use of chloride salt may provide better quality [Au(NHC)Cl] [12]. Catalano et al. utilized pyridyl and picolyl substituted Ag (I)–NHCs to prepare Au(I)–NHCs, which served as excellent precursors to obtain a variety of polymeric gold compounds [13].Meyer observed that the transmetallation

of a tripodal Ag(I)–NHC afforded a tripodal Au(I)–NHC under inert conditions, but not in air (Scheme 26i) [14]. Zhang and co-workers reported that the transfer of ether bridged macrocyclic NHCs from dinuclear Ag(I)–NHCs gave Au(I)–NHCs smoothly under inert conditions (Scheme 26ii) [15]. With long *N*-alkyl chains, the ratio between the Ag to Au influenced the Au (I)–NHC formed; when the Ag/Au molar ratiowas 2, a mixed Ag2Au2 compound (Scheme 26iii) was produced [9d], but with a molar ratio of 1, the reaction afforded only Au (I)–NHCs [90] (Scheme 26iv). Corber´an et al. reported the preparation of *N*-methyl menthoxide and *N*-*n*Bu substituted Au(I)–NHCs via transmetallation [16].

MATERIAL AND METHOD

Regarding the synthesis of Pd(II)–NHCs, in addition to the transmetallation, other methods such as direct metallation of azolium salt with Pd(OAc)2 or with Pd(II)-precursor in the presence of external base were also evaluated in some cases. The work by Cavell and co-workers [20], Tilset and co-workers [31], Gade and co-workers [33], and Shreev and co-workers [34] specified the failure of direct metallation to prepare Pd (II)–NHCs.

Therefore transmetallation by Ag(I)–NHCs became of general interest. With non-functionalized NHCs (only with *N*-alkyl or *N*aryl substituents), transmetallation normally produced simple Pd(NHC)2Cl2 complexes as shown in Scheme 24 [18,19]. Whereas, with functionalized NHCs, Pd(II)–NHCs of different structures were obtained, depending on the nature of the Pd(II) precursor, the reaction conditions, and stoichiometry of the reactants. For example, Cavell and co-workers showed that equimolar reactions between a picolyl substituted Ag(I)–NHC and Pd(MeCN)2Cl2 or PdMe(cod)Cl produced nonchelated Pd(II)–NHCs (Scheme 27i and ii) [20a]. A chelated mono-carbene complex, however, was obtained upon reaction Scheme 25. Au(I)–NHCs of short alkyl chains from Lin's work.

The formation of mono and polynuclear Au(I)–NHCs by transmetallation. of Ag(I)–NHC with two equivalents of PdMe(cod)Cl (Scheme 27iii) [20a]. Wang et al. reported that the reaction of a trinuclear Ag(I)–NHC containing an *N*-picolyl sidearm with ~3M equivalents of Pd(PhCN)2Cl2 produced a chelated NHC complex (Scheme 27iv) [21]. Douthwaite also described the influence of reaction stoichiometry on the transfer reaction between a chiral dimeric Ag(I)–NHC and Pd(MeCN)2Cl2 [22c]. Burgess and colleagues described that sometimes the Ag(I)–NHCs with bulky N-substituents did not favor the NHC migration to Pd(II) (Scheme 27) [23]; in this situation, the use of microwave conditions was recommended (Scheme 27v). However, there was some evidence that NHCs with bulky N-substituents could still be transferred effectively to Pd(II) and different metal ions [for example, Ref.

22b, 24, 26, 28, 42–45,52,53,55,56]. Perhaps, the nature the of Pd(II) precursor used was a part of the reason.

The work by Mangeney and co-workers also demonstrated the influence of Pd(II) precursor in the NHC transfer process [24]. Ag(I)–NHCs with *N*-benzyl substituents transferred NHC smoothly to Pd(MeCN)2Cl2 (Scheme 28i) [24a], but not with N-*i*Pr and *N*-(*S*)-1-phenylethyl substituents. In the latter case, reaction occurred when Pd(allyl)Cl2 was used (Eq. (ii)) [24b]. Coleman and co-workers showed that the transfer of NHC from imine-functionalized Ag(I)–NHC to two different Pd(II) precursors produced chelated Pd(II)–NHCs (Scheme 28iii and iv) [25a]. Imine-functionalized Ag (I)–NHC with methylene-spacer produced a tautomerized Pd(II)–NHC (Scheme 28v) [25b]. In addition, several chelated Pd(II) complexes with achiral tridentate amino–NHC–amino [20b], achiral tridentate NHC–amino–NHC [22d], bidentate amino–NHC [24c] have been prepared easily via the carbene transfer technique.

Poyatos et al. observed that the imidazolium salt with one *N*oxazole side arm produced a chelated Pd(II)–NHC via transmetallation, and a non-chelated Pd(II)–NHC via direct-metallation (Scheme 29i and ii) [26]. The different halides used in the two reactions may cause the different chelation behaviors. Lee et al.

reported that the imidazolium salt with two *N*-phosphine side arms formed only a chelated Pd(II)–NHC via either transmetallation or the direct-metallation with PdCl2 (Scheme 29iii and iv) [27a]. Notably no base was added in the latter reaction; the high acidity of the salt along with the *N*-phosphine side arms suitable for chelation was proposed to be the reasons for the ease of C2–H bond activation. Lee and co-workers also suggested the use of more polar solvents for a smooth progression of the transmetallation reactions [27b].

The influence of reaction stoichiometry and bulkiness of the N-substituents in the preparation of Pd(II)–NHCs.

Transmetallation with a variety of Pd (II) precursors. Pd (II)–NHCs by transmetallation and direct metallation. A Pd (II) complex consisting of a variety of unsymmetrical pyridyl supported pyrazolyl–NHC ligands was also obtained by the transmetallation method (Scheme 30) [28].

Danopoulos reported that the transfer of NHC from [Ag(NHC)halide] to Pd(II) was accompanied with the mixed anions Cl/AgCl2 − [29b,c]. In such a case, addition of AgBF4 before the transmetallation produced pure Pd(II)–NHCs In contrast to many reports which described carbene transfer from Ag(I)–NHCs to Pd(II) as being quite successful [18–39], work by Herrmann et al. showed that the intended carbine transfer of a six-membered NHC containing bulky mesityl Nsubstituents to Pd (MeCN)2Cl2 failed (Scheme 32i) [115]. The presence of a strong Ag–Ccarbene bond (as observed by the large down field shifts of the carbene-C resonance) was proposed to be a reason for the failure of NHC transfer. A similar result was observed by Buchmeiser and co-workers with the identical Ag(I)–NHC [38,125]. However, with N-*i*Pr substituents, transmetallation was successful (Scheme 32ii) [38]. Hahn and co-workers reported that the transmetallation of a saturated five-membered imidazolin-2-ylidene with bulky *N*-mesityl and *N*-2,6-*i*Pr2–Ph substituents, to PdI2 and [(*p*-cymene)RuCl(-Cl)] 2 failed (Scheme 32, iii) [92]. A seven-membered ring based NHC with two *N*-neo-pentyl substituents also did not undergo NHC transfer reaction (Scheme 32iv) [116]. When a bis-imidazolium salt linked by a highly electron withdrawing carbonyl groupwas used to react with Ag2Oand Pd(MeCN)2Cl2 in a one pot reaction, a palladacyclobutan-3-one complex instead of a Pd(II)–NHC was produced (Scheme 32v), presumably due to the additional stabilization of the bonding mode in the former [126]. Despite that many imine-NHC functionalized Ag(I)–NHCs effectively produced the Pd(II)–NHCs, a recent report by Flahaut and co-workers reported the failure of the transfer of an imine-NHC to Pd(II) [24c]. Huynh et al. mentioned that when N-*i*Pr substituted benzimidazolium salt was used, transmetallation gave a mixture of products with very low yields of Pd(II)–NHC [127]. This is quite unusual with simple azolium salts, but no experimental details were provided.

NHC transfer was also widely employed to form the Rh(I)–NHCs. In Crabtree's work, if the excess Ag2O was removed before the transmetallation reaction, the bis-imidazolium salts with short linkers (*n* = 1, 2) produced neutral non-chelated [Rh(NHC)Cl]2 under refluxing conditions (Scheme 33i) [40a]. However, chelated ionic Rh(I)–NHCs were isolated from the salts with long linkers (*n* = 3.4) under similar reaction conditions in the presence of KPF6 (Scheme 33ii). Chelated complexes as chloride salts were not characterized structurally due to decomposition.

With the *n* = 2 linker, a chelated ionic Rh(I)–NHC was also formed in the presence of excess Ag2O and KPF6 under refluxing conditions. On the other hand, non-chelated neutral Rh(I)–NHCs were produced if the transmetallation was performed at room temperature for *n* values of 1–4 (Scheme 33i). Here it is noticeable that Viciano et al. were able to obtain chelated Ir(I)–NHCs at room temperature from the The formation of Pyridyl supported pyrazolyl-NHC Pd(II) complexes. Transmetallation by the use of [Ag(NHC)2][BF4] complex. bis-imidazolium salts with linkers of *n* = 2–4 [59a].Youngs and co-workers also obtained a non-chelated dinuclear Rh(I)–NHC compound from dinuclear Ag(I)–NHC (Scheme 33iii) [30]; yet a chelated Pd(II)–NHC was formed from the same Ag(I)–NHC (Scheme 33iv).Areport by Peris pointed out that a square planar but not tripodal Rh(I)–NHC or Ir(I)–NHCwas obtained from the tripodal imidazolium salts (Scheme 33vi) [41a].

Slaughter demonstrated the use of a di-carbene complex, [Ag (NHC) 2]2[BF4]2, to produce a chelated Rh(I)–NHC An important feature of this work was that NHCs with bulky *N*-mesityl substituents transferred effectively to Rh(I). As well, the reports by the groups of Tsuji and coworkers [43] and Liu and co-workers [44] also described the transfer of bulky NHCs such as dendrimer-NHC and *N*-pyridyl NHC to the Rh(I). Youngs achieved NHC transfer from a dinuclear Ag(I)–NHC to radioactive 105Rh(III) in hot DMSO (Scheme 35i) [57]. Peris and co-workers showed that the ratios between the pyridylsubstituted imidazolium salt and the metal-precursors (Rh(I) and Ir(I)) influenced the oxidation state of the metal ions in the final product [41b]. When the salt/M ratio was 1 (M= Rh, Ir), mono-NHC Rh(I) and Ir(I) complexes were shown to be formed via *in situ* Ag(I)–NHCs (Scheme 35ii). The coordination behavior of the pyridine side arm was uncertain in the mono-NHC complexes. On the other hand, when the salt/M ratio was 2, oxidation of the metal ions occurred to form chelated Rh(III) and Ir(III)–NHCs (Scheme 35iii). Ag(I) was proposed to oxidize the metal ions, since Ag(0) was observed. Arnold also came up with a similar observation with ruthenium ion [69]. However, a non-chelated neutral Ir(I)–NHC was formed from the 4,5- dichlorosubstituted imidazolium salt under similar conditions [59b].

In another approach, Youngs and co-workers demonstrated that a caffeine derived NHC was transferred efficiently from Ag(I)–NHC to Rh(I) in hot DMSO [45].

CONCLUSION

This attempt specifiedthe possible use of biological sources to synthesize various transition metal–NHCs via the Ag2O technique. Coleman et al. reported that while an imino-NHC ligand was transferred to a Scheme 32. Examples of some unsuccessful transmetallation reactions by Ag(I)–NHCs. Scheme 33. The formation of Rh(I)–NHCs via the transmetallation reactions. Rh(I) source in THF, tautomerization of the ligandwas observed similar to that of the Pd(II)–NHC shown in Scheme 28 [25b]. Lee and co-workers described the NHC transfer from a phosphine functionalized trinuclear Ag(I)–NHC to Rh(I) producing a variety of rhodium complexes depending on the conditions (Scheme 36) [46]. The reaction between such an Ag(I)–NHC and [Rh(cod)Cl]2 in dichloromethane, produced *cis*,*mer*-Rh(III)(PCNHCP)(CH2Cl)Cl2 via oxidative addition of dichloromethane to the intermediate Rh(I)(PCNHCP)Cl complex. In the absence of CH2Cl2, this reactive Scheme 34. The formation of chelated Rh(I)–NHC with methylene linkers. The formation of Rh(III), Rh(I), Ir(I) and Ir(III)–NHCs.

Rh(I)(PCNHCP)Cl intermediate was proposed to undergo oxidative degradation in DMF to afford *mer*-Rh(III)(PCNHCP)Cl3 complex (Scheme 36iii). A *mer*-Rh(I)(PCNHCP)(CO)Cl), however, was obtained when [Rh(CO)2Cl]2 was employed (Scheme 36iv); in this case the Rh(I) center was proposed to be stabilized by the _-back bonding of the C O ligand. Transfer of fluorinated NHC to different Rh(I) and Ir(I) reactants has been reported [47]. Saunders and co-worker [47a] showed that a half sandwich Rh(I)–NHC or Ir(I)–NHC complex was formed upon the reaction of Ag(I) fluorinated-NHC complex with [(*η*5-C5Me5)MCl(_-Cl)2] (M= Rh, Ir) in a 1:1 stoichiometry (Scheme 37i). While Whittlesey and co-workers [47b] employed the same Ag(I) fluorinated-NHC to react with [Rh(cod)Cl]2 in a 1:1 stoichiometry to yield the analogous neutral Rh(I)–NHC (Scheme 37ii). An ionic bis-NHC complex of Ir(I) complex was obtained upon the reaction with [Ir(cod) Cl]2 in a 3:1 stoichiometry (NHC/Ir = 3) at 70◦ (Scheme 37iii). This bis-NHC complex was also obtained by heating a neutral mono-NHC Ir(I) (prepared by another method) with the Ag(I)–NHC.

Rh(I) and Ir(I)–NHCs withNHCsother than simple imidazol-2-ylidene moieties were also prepared via transmetallation with Ag(I)–NHCs (Scheme 38). Bielawski used the transmetallation method to prepare a neutral dinuclear Rh(I)–NHC complex containing a bis-NHC with an arene backbone (Scheme 38i)

[48]. Heinicke obtained the neutral mononuclear Rh(I)–NHC containing naphtha(2,3-*d*)imidazol-2-ylidene (Scheme 38ii) [39]. Herrmann et al. utilized chiral imidazolium salts derived from 2,2-bipiperidene and biisoquinoline to prepare Rh(I) and Ir(I)–NHCs via Ag(I)–NHCs formed *in situ* (Scheme 38iii and iv) [49]. The transfer of a saturated imidazolinium based NHCs to Rh(I) was reported by Hemchen and co-worker and Gilbertson and co-worker [55,56]. Crabtree made efforts to generalize the synthesis of abnormal C5-bound Ir(I)–NHCs via the Ag2O technique [58]. The use of a 2-phenyl imidazolium salt generated an unstable C4-bonded Ag(I) complex, which did not afford the Ir(I) complex The formation of abnormal Ir(I)–NHCs via abnormal Ag(I)–NHCs. due to the more basic nature of the C4-carbene. However, the salt designed with two blocking groups at both C2- and C4-positions such as 2,4-diphenyl imidazolium, reacted with Ag2O and then [Ir(cod)Cl]2 in a one pot reaction to give an abnormal C5-bonded Ir(I) complex (Scheme 39i). However, an attempt to prepare abnormal C5-bonded Rh(I)–NHC from 2,4-dimethyl imidazolium salt afforded only a normal C2-bonded Rh(I)–NHC via C2-bonded Ag(I)–NHC [40b], an indication of the influence of the substituent at the C2-position. A report by Lasaletta also described the use of a C2-blocked imidazo[1,5-a]pyridine iodide, an abnormal Ir(I)–NHC but not the Rh(I)–NHC was formed (Scheme 39ii) [51].

In view of the stability of organometallic complexes with NHC ligands, Peris utilized the Ag2O technique to obtain stable Cp*-Ir(III)–NHCs (Scheme 40) [60]. Cyclometallated products were obtained when salts (a–e) were used. However, the reactions of the salts (f and g) produced only the stable noncyclometallated complexes.

Reaction of an imidazolium cyclophane with excess Ag2O gave a tetranuclear Ag(I)–NHC in DMSO and a dinuclear Ag(I)–NHC in water. The reaction of 2-methyl or 2-benzyl imidazolium salts with excess of Ag2O led to the oxidative cleavage of the C–C bond at C2-position and formed the normal Ag(I)–NHCs in good yields. Addition of Ag(I) to the preformed Ag(I)–NHCs also directed the formation of Ag(I)–NHCs with diverse structures. Ag(I)–NHCs played an important role asNHCtransfer agents in the development of many metal–NHCs. So far transfers of NHC from Ag(I) to Ni(II), Pt(II), Pd(II), Cu(I), Cu(II), Au(I), Rh(I), Rh(III), Ir(I), Ir(III), Ru(II), Ru(III) and Ru(IV) have been reported. Some of the metal–NHCs can be prepared only by the transmetallation technique. The occurrence of transmetallation and nature of the transmetallated product depended not only on the Ag(I)–NHCs but also on the receiving metal-precursors and the reaction conditions. During the transfer of NHC to Ru (II) and Rh(I), oxidation of the metal ions was sometimes observed due to the high oxidation power of the Ag(I) or the halogenated solvents. In certain examples, the failure of transmetallation was proposed to be due to the strong Ag–C bond, bulky Nsubstituents or non-fluxional behavior. However, with similar features, examples of successful transfer of NHC were reported.

The failure of NHC transfer from [Ag(NHC)halide] to group 4 metals was attributed to the high chlorophilicity of group 4 metal ions together with the large solvation/lattice enthalpy of the ionic products. The use of 2,4-blocked imidazolium salts with certain substituents resulted in the formation of either normal metal–NHCs or abnormal metal–NHCs.

Other than transmetallation, The use of Ag(I)–NHCswas also realized in homogeneous catalysis such as in the preparation of 1,2-bis(boronate) esters [16,97] and ring opening polymerization of lactides [85,98b], olefin polymerization [21], and as a source of free NHC in the copper catalyzed conjugate addition of diethylzinc to a variety of Michael acceptors [65]. More efforts are to be encouraged in this area to discover more applications.

The liquid crystal properties of Ag(I)–NHCs may have material science application. Furthermore, the use of Ag(I)–NHCs as precursors for silver nanoparticles will certainly have an impact in medicinal, and applied sciences. The nature of these AgNPs, however, remains to be answered.

It is also interesting to mention theoretical calculations dealing with Ag(I)–NHCs, which provide insights into the nature of metal–NHC. The calculations reported by Mayer and coworkers [14] on the N–Me substituted tripodal Ag(I)–NHC and by Frenking and co-workers on unfunctionalized Ag(I)–NHC [129] showed non-negligible _-back bonding. However, calculations reported recently by Ghosh and co-workers concluded that functionalized NHCs are effective _-donors [98].

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.

[40] (a) J.A. Mata, A.R. Chianese, J.R. Miecznikowski, M. Poyatos, E. Peris, J.W. Faller, R.H. Crabtree, Organometallics 23 (2004) 1253;

(b) A.R. Chianese, B.M. Zeglis, R.H. Crabtree, Chem. Commun. (2004) 2176;

(c) A.R. Chianese, X. Li, M.C. Janzen, J.W. Faller, R.H. Crabtree, Organometallics. 22 (2003) 1663;

(d) G. Rivera, R.H. Crabtree, J. Mol. Catal. A: Chem. 222 (2004) 59.

[41] (a) E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, Inorg. Chem. 43 (2004) 2213;

(b) E. Mas-Marza, M. Sanau, E. Peris, Inorg. Chem. 44 (2005) 9961.

[42] Y.A. Wanniarachchi, M.A. Khan, L.M. Slaughter, Organometallics 23 (2004) 5881.

[43] T. Fujihara, Y. Obora, M. Tokunaga, H. Sato, Y. Tsuji, Chem. Commun. (2005) 4526.

[44] C.-Y. Wang, Y.-H. Liu, S.-M. Peng, S.-T. Liu, J. Organomet. Chem. 691 (2006) 4012.

[45] A. Kascatan-Nebioglu, M.J. Panzner, J.C. Garrison, C.A. Tessier, W.J. Youngs, Organometallics 23 (2004) 1928.

[46] J.Y. Zeng, M.-H. Hsieh, H.M. Lee, J. Organomet. Chem. 690 (2005) 5662.

[47] (a) S. McGrandle, G.C. Saunders, J. Fluor. Chem. 126 (2005) 449; (b) S. Burling, M.F. Mahon, S.P. Reade, M.K. Whittlesey, Organometallics 25 (2006) 3761.

[48] A.J. Boydston, C.W. Bielawski, Dalton Trans. (2006) 4073.

[49] W.A. Herrmann, D. Baskakov, E. Herdtweck, S.D. Hoffmann, T. Bunlaksananusorn, F. Rampf, L. Rodefeld, Organometallics 25 (2006) 2499.

[50] S.I. Lee, S.Y. Park, J.H. Park, I.G. Jung, S.Y. Choi, Y.K. Chung, B.Y. Lee, J. Org. Chem. 71 (2006) 91.

[51] M. Alcarazo, S.J. Roseblade, A.R. Cowley, R. Fernandez, J.M. Brown, J.M. Lassaletta, J. Am. Chem. Soc. 127 (2005) 3290.

[52] X.-Y. Yu, B.O. Patrick, B.R. James, Organometallics 25 (2006) 2359.

[53] P.A. Evans, E.W. Baum, A.N. Fazal, M. Pink, Chem. Commun. (2005) 63.

[54] S. Saravanakumar, M.K. Kindermann, J. Heinicke, M.K¨ockerling, Chem. Commun. (2006) 640.

[55] (a) E. Bappert, G. Helmchen, Synlett (2004) 1789;

(b) J.-M. Becht, E. Bappert, G. Helmchen, Adv. Syn. Catal. 347 (2005) 1495.

[56] G. Xu, S.R. Gilbertson, Org. Lett. 7 (2005) 4605.

[57] C.A. Quezada, J.C. Garrison, M.J. Panzner, C.A. Tessier, W.J. Youngs, Organometallics 23 (2004) 4846.

[58] A.R. Chianese, A. Kovacevic, B.M. Zeglis, J.W. Faller, R.H. Crabtree, Organometallics 23 (2004) 2461.

[59] (a) M. Viciano, M. Poyatos, M. Sanau, E. Peris, A. Rossin, G. Ujaque, A. Lledos, Organometallics 25 (2006) 1120;

(b) C. Vicent, M. Viciano, E. Mas-Marza, M. Sanau, E. Peris, Organometallics 25 (2006) 3713.

[60] (a) R. Corberan, M. Sanau, E. Peris, J. Am. Chem. Soc. 128 (2006) 3974;

(b) R. Corberan, M. Sanau, E. Peris, Organometallics 25 (2006) 4002.

[61] T. Sajoto, P.I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M.E. Thompson, R.J. Holmes, S.R. Forrest, Inorg. Chem. 44 (2005) 7992.

[62] P.L. Arnold, A.C. Scarisbrick, A.J. Blake, C. Wilson, Chem. Commun. (2001) 2340.

[63] X.-J. Wan, F.-B. Xu, Q.-S. Li, H.-B. Song, Z.-Z. Zhang, Inorg. Chem. Commun. 8 (2005) 1053.

[64] X. Hu, I. Castro-Rodriguez, K. Meyer, J. Am. Chem. Soc. 125 (2003) 12237.

[65] (a) J. Pytkowicz, S. Roland, P. Mangeney, Tetrahedron: Asymmetry 12 (2001) 2087;

(b) C.L.Winn, F. Guillen, J. Pytkowicz, S. Roland, P. Mangeney, A. Alexakis, J. Organomet. Chem. 690 (2005) 5672;

(c) A. Alexakis, C.L. Winn, F. Guillen, J. Pytkowicz, S. Roland, P. Mangeney, Adv. Syn. Catal. 345 (2003) 345.

[66] (a) J.J. Van Veldhuizen, J.E. Campbell, R.E. Giudici, A.H. Hoveyda, J. Am. Chem. Soc. 127 (2005) 6877;

(b) A.O.W. Leu, C.N. Oberhuber, J.E. Campbell, A.H. Hoveyda, J. Am. Chem. Soc. 126 (2004) 11130;

(c) K.-S. Lee, M.K. Brown, A.W. Hird, A.H. Hoveyda, J. Am. Chem. Soc. 128 (2006) 7182.

[67] C.Y. Legault, C. Kendall, A.B. Charette, Chem. Commun. (2005) 3826.

[68] P. Csabai, F. Joo, Organometallics 23 (2004) 5640.

[69] P.L. Arnold, A.C.S. carisbrick, Organometallics 23 (2004) 2519.

[70] P.L. Chiu, H.M. Lee, Organometallics 24 (2005) 1692.

[71] (a) T.J. Geldbach, G. Laurenczy, R. Scopelliti, P.J. Dyson, Organometallics 25 (2006) 733;

(b) M.-E. Moret, A.B. Chaplin, A.K. Lawrence, R. Scopelliti, P.J. Dyson, Organometallics 24 (2005) 4039.

[72] M. Poyatos, A. Maisse-Franc¸ois, S. Bellemin-Laponnaz, E. Peris, L.H. Gade, J. Organomet. Chem. 691 (2006) 2713.

[73] J.J. VanVeldhuizen, S.B. Garber, J.S. Kingsbury, A.H. Hoveyda, J. Am. Chem. Soc. 124 (2002) 4954.

[74] X. Wang, S. Liu, G.-X. Jin, Organometallics 23 (2004) 6002.

[75] S.Winston, N. Stylianides, A.A.D. Tulloch, J.A. Wright, A.A. Danopoulos, Polyhedron 23 (2004) 2813.

[76] E.M. Prokopchuk, R.J. Puddephatt, Organometallics 22 (2003) 563.

[77] I.J.B. Lin, C.S. Vasam, Comment. Inorg. Chem. 25 (2004) 75.

[78] P.L. Arnold, Heteroatom Chem. 13 (2002) 534.

[79] J.C. Garrison, W.J. Youngs, Chem. Rev. 105 (2005) 3978.

[80] A.J. Arduengo, H.V.R. Dias, J.C. Calabrese, F. Davidson, Organometallics 12 (1993) 3405.

[81] (a) O. Guerret, S. Sol´e, H. Gornitzka, G. Trinquier, G. Bertrand, J. Organomet. Chem. 600 (2000) 112;

(b) O. Guerret, S. Sol´e, H. Gornitzka, M. Teichert, G. Trinquier, G. Bertrand, J. Am. Chem. Soc. 119 (1997) 6668.

[82] (a) K.M. Lee, H.M.J. Wang, I.J.B. Lin, Dalton Trans. (2002) 2852;

(b) C.K. Lee, C.S. Vasam, T.W. Huang, H.M.J. Wang, R.Y. Yang, C.S.

Lee, I.J.B. Lin, Organometallics 25 (2006) 3768.

[83] T. Ramnial, C.D. Abernethy, M.D. Spicer, I.D. McKenzie, I.D. Gay,

J.A.C. Clyburne, Inorg. Chem. 42 (2003) 1391.

[84] P. de Fremont, N.M. Scott, E.D. Stevens, T. Ramnial, O.C. Lightbody, C.L.B. Macdonald, J.A.C. Clyburne, C.D. Abernethy, S.P. Nolan, Organometallics 24 (2005) 6301.

[85] (a) A.C. Sentman, S. Csihony, R.M. Waymouth, J.L. Hedrick, J. Org. Chem. 70 (2005) 2391;

(b) A.C. Sentman, S. Csihony, G.W. Nyce, R.M.Waymouth, J.L. Hedrick, Polym. Prepr. 45 (2004) 299.

[86] S.P. Downing, A.A. Danopoulos, Organometallics 25 (2006) 1337.

[87] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advance Inorganic Chemistry, 6th ed., Wiley, New York, 1999.

[88] W. Chen, F. Liu, J. Organomet. Chem. 673 (2003) 5.

[89] Q.X. Liu, F.B. Xu, Q.S. Li, X.S. Zeng, X.B. Leng,Y.L. Chou, Z.Z. Zhang, Organometallics 22 (2003) 309.

[90] Un published Results of I.J.B. Lin’s Research Group.

[91] J. Pytkowicz, S. Roland, P. Mangeney, J. Organomet. Chem. 631 (2001) 157.

[92] M. Paas, B.Wibbeling, R. Fr¨ohlich, F.E. Hahn, Eur. J. Inorg. Chem. 2006 (2006) 158.

[93] K. Weigl, K. Kohler, S. Dechert, F. Meyer, Organometallics 24 (2005) 4049.

[94] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterbock, K.- H. Ongania, G. Opromolla, P. Zanello, Organometallics 18 (1999) 4325.