Heteroatom Chemistry
Volume 13, Number 6, 2002

Organometallic Chemistry of Silver and Copper *N*-Heterocyclic Carbene Complexes

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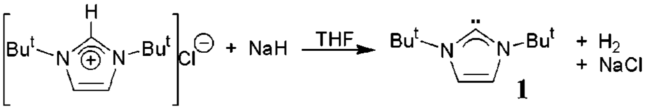
Received 23 April 2002

ABSTRACT: *The only stable organometallic carbene complexes of silver and copper are those of* N-*heterocyclic carbenes, since formally these robust divalent carbon ligands bind only by a σ donor interaction to the metal. A survey of the range of complexes that have now been reported is presented.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:534–539, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10098

INTRODUCTION

Since the time it was proven that stable, "bottleable" carbenes such as **1** can indeed be isolated by deprotonation of dialkyl imidazolium salts, Eq. (1) [1], *N*-heterocyclic carbenes (NHCs) have rejuvenated the field of organometallic carbene chemistry. It is of interest that although the organometallic silver–carbene and copper–carbene fragment is a widely accepted intermediate in a wide range of reactions catalyzed by these metals [2], no complexes containing a simple silver or copper Fischer or Schrock-type carbene have ever been isolated. This paper discusses the new imidazol-2-ylidene-based carbene chemistry of silver and copper, which has been made possible by the advent of the *N*-heterocyclic carbenes.



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NATURE OF THE METAL–CARBENE BOND

The predominance of electronic factors over steric factors in determining the kinetic stability of the nucleophilic, singlet, free carbene is now understood, and the spectroscopic consequences of the anisotropy of the carbenoid carbon atom have been both measured and modeled [3]. In contrast to d-block Fischer carbene complexes, in which the formally electrophilic carbene carbon atom is stabilized by an adjacent p-block heteroatom, and significant backbonding from the metal, these metal carbene complexes bond predominantly through donation to the metal from the filled orbital of the carbene that has a high proportion of s-character, with minimal, if any, evidence for backbonding [4]. Vapor-phase photoelectron spectroscopy experiments on the volatile *N*,*N'*-di-*tert*-butyl carbene (**1**) and its homoleptic palladium and platinum bis(carbene) adducts [5] show no significant change in the π-system of the carbene upon binding [6].

Thus, metal carbene adducts do not have to be considered as containing a true metal carbon double bond; a dative, σ-type bond can be invoked, and ligands based on **1** have provided a number of new opportunities in synthetic organometallic chemistry.

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Contract grant sponsor: EPSRC.
Contract grant sponsor: Royal Society.
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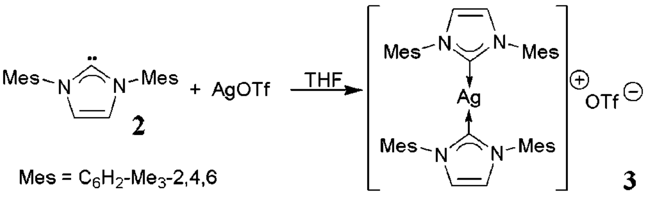
Possibly the most notable consequence of the absence of any requirement for backbonding has meant that metal–NHC complexes for most elements in the periodic table have been made, including adducts of Li [7], Be [8,9], and now hexavalent U [10].

PREPARATION OF SILVER AND COPPER CARBENE ADDUCTS

By Direct Reaction with the Free NHC

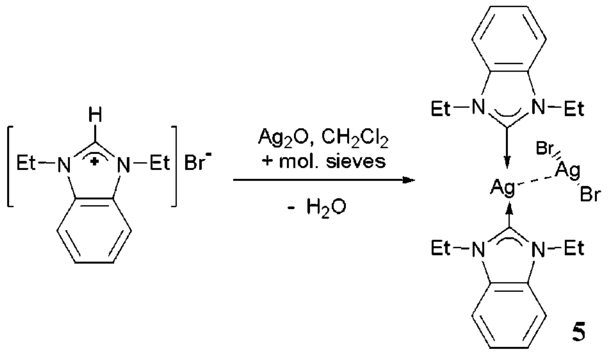


(2)

After first proving that NHCs could be isolated as crystalline products from the reaction shown in Eq. (1), Arduengo then proceeded to employ the free NHC (**2**) explicitly to isolate the first silver and copper carbene complexes, Eq. (2) [11]. Since then, the reaction of Ag^+ with the free NHC has rarely been used; one notable recent example being the use of AgOTf to stabilise a tridentate pyridyl dicarbene at temperatures above 0°C. Though a tridentate pyridyl dicarbene that is stable only at 0°C in THF has been recently reported; here AgOTf is used to form the stable silver triflate adduct **4**, Fig. 1 [12].

By in situ Deprotonation of an Imidazolium Salt

More recently, Lin *et al.* discovered that, along with many other basic metal acetates and alkoxides, silver oxide is capable of deprotonating an imidazolium halide to form a silver carbene adduct such as **5**, as shown in in Eq. (3) [13]. The reaction is driven to completion by the addition of activated 4 Å molecular sieves, which absorb the eliminated water.



(3)

Lin et al. point out that in their system, the reaction of silver chloride with this imidazolium chloride under basic phase transfer catalysis conditions also yields the silver carbene complex. Thus, formally the silver chloride, both formed in this reaction and eliminated in subsequent transfer of the carbene to other metals, can be recycled. While the use of Ag_2O is now widespread in the synthesis of NHCs (some syntheses also use Ag_2CO_3 as an alternative, but this is considerably less common), so far only these authors have proven this potential recyclability. It has been noted that if stoichiometric silver oxide is used, the conversion of the black suspension into a more mobile grey precipitate allows a crude but effective monitoring of the extent of the reaction [14].

Silver–silver interactions in the low-coordination number products can give rise to some interesting structural variations in complexes such as **6**, which contain both linear and trigonal planar Ag(I) in different structural motifs, depending on the size of the *N*-alkyl substituents [15], Fig. 2.

Tessier and Youngs have also observed silver–silver interactions in **7**, an $[Ag_4L_2]PF_6]_4$ cyclophane structure, which contains a central planar core of four Ag cations; the four ions form a lozenge from two $Ag^+{}_2$ ion pairs in a conformation enforced by the macrocyclic nature of the polydentate NHC ligand [16], Eq. (4). This complex is also the first to

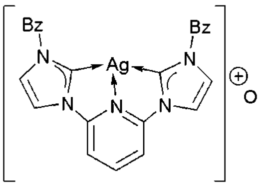


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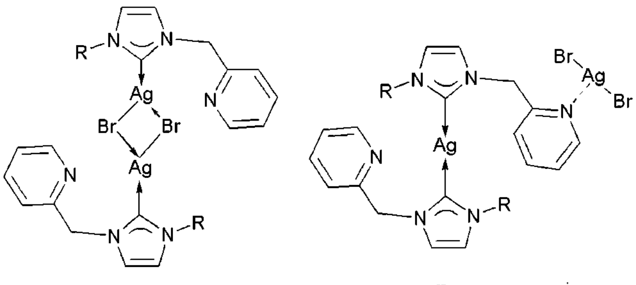
FIGURE 1 Mononuclear silver adduct of a dicarbene pyridyl ligand.



6a R = C_6H_2-Me_3-2,4,6 **6b** R = C_6H_3-$Pr^i{}_2$-2,6

FIGURE 2 Structural variations in related silver adducts.

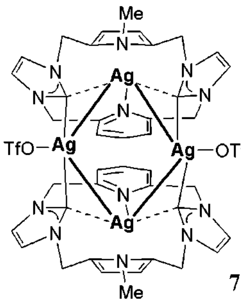


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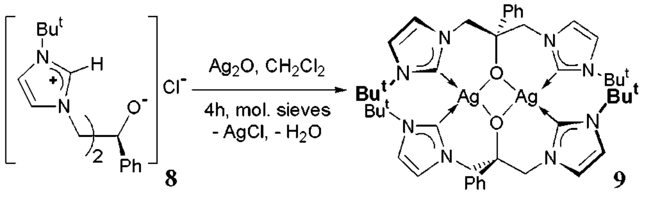
FIGURE 3 A tetranuclear Ag^+ complex, which displays both s and p interactions with the NHC carbene.

display a π-type bonding interaction to an NHC; an η^1 Ag—$C_{carbene}$ bond is suggested from the two different C—Ag coupling constants seen for the carbenoid carbon (a larger, conventional 220 Hz $^1J_{C-Ag}\sigma$ coupling and an unprecedented 47 Hz $^1J_{C-Ag}\pi$-carbene coupling), and confirmed in the solid state by a single crystal X-ray diffraction study (see Fig 3).

However, some deprotonation reactions of this type have proven more difficult and the CH_2Cl_2 solvent is replaced with a chlorinated solvent such as dichloroethane, allowing a higher reflux temperature. Also, instead of forming AgCl as a by-product, polyhalide counterions, such as $[AgCl_2]^-$ or $[AgI_2]^-$, often form [13,15,17]. In some instances these can complicate subsequent transmetallation reactions. Many people, including Wang and Lin, have used the PF_6^- counterion instead of halide to avoid ion-pair formation (mentioned earlier), while Cavell has shown that the $[AgBr_2]^-$ can be substituted by BF_4^- by a subsequent treatment of the salt with $AgBF_4$ in hot acetonitrile solution [18].

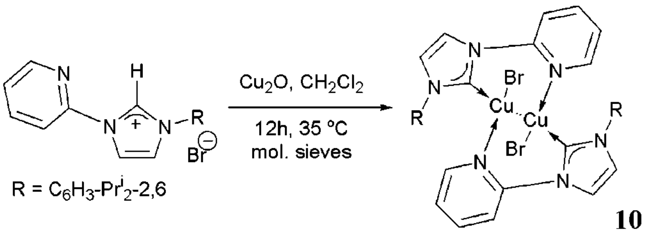
We have recently developed a tridentate NHC proligand **8** with a pendant anionic group, derived from the ring opening of epichlorohydrin derivatives [19]. The monoalkoxide di-imidazolium chloride formed is particularly readily deprotonated by Ag_2O, Eq. (4), with the elimination of H_2O and AgCl, but because the ligand possesses an overall uninegative charge, the molecular silver alkoxide **9** does not retain any silver halide anion.



(4)

This provides a greater driving force for any subsequent metathesis chemistry with metal halides by the conversion of a silver alkoxide to a silver halide by-product. The stability of the complex is interesting in its own right, since to the best of our knowledge it is the first isolated example of a simple silver alkoxide [20].

In solution some complexes exhibit lability of the silver–carbene bond, so although it is easy to identify the characteristic high-frequency carbenoid carbon resonance NMR (generally $\delta = 170–190$ ppm), the one-bond ^{13}C-^{107,109}Ag coupling constants cannot always be identified.

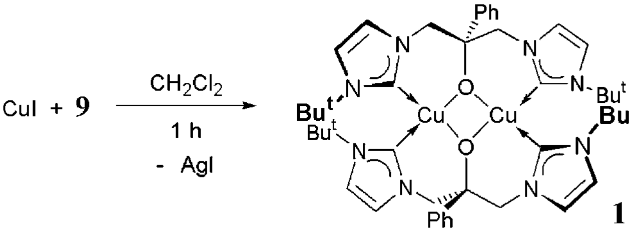


(5)

Interestingly, Danopoulos et al. have shown that copper(I) oxide could be used in the same manner as silver oxide to deprotonate an acidic imidazolium salt. In a broad study of NHCs N-functionalized with pendant, neutral pyridyl groups, they reported that although a variety of donor-ligand solvated Cu(I) halide starting materials fail to react with the *in situ* generated NHC, a heated mixture of Cu_2O, pyridyl-imidazolium halide, and 4 Å molecular sieves in dichloromethane at 35°C or in dichloroethane at 90°C afforded around 65% yields of the copper carbene complex depicted in Eq. (5). This complex could be isolated as a dinuclear or polymeric [Cu-ligand] chain, although only the former exhibits a Cu–Cu interaction (2.655 Å). In contrast, our alkoxy-imidazolium complexes based on **8** only react with Cu_2O under forcing conditions, to give poor yields of copper complexes. This could be due to a reduced acidity of the imidazolium group because of H-bonding interactions with the alkoxide group in the chlorinated solvents chosen so far [21]. We note that Bildstein had also encountered the problem of reduced acidity in *N*,*N*′-diferrocenyl substituted imidazolium salts [22]; no simple deprotonation by Ag_2O was possible unless the imidazolium was converted to its tetraphenylborate salt, this then yielded the desired silver bis(ferrocenyl-NHC) complex in 63% yield. In the first Raman study of an NHC complex, the spectrum of a linear silver complex displays an L—Ag—L stretch at 70 cm^{-1}. Bertrand has made use of a dicationic triazole ring to generate the first carbene coordination polymer which incorporates silver triflate [23].

By Metathesis Routes

Calculations by Boehme and Frenking have predicted that although all these bonds should be considered as strong, the copper–carbene bond strength is calculated to be 319 kJ mol^{-1}, a silver–carbene bond should be weaker than the analogous copper–carbene bond by approximately 63 kJ mol^{-1} [24]. This is borne out in a number of reactions that show the facile transmetalation reaction to generate copper–carbene adducts. For example, the silver alkoxide **9** reacts smoothly with copper iodide to form a copper alkoxide–carbene **11**, Eq. (6).



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(6)

Although the ligand is flexible and **11** can also be made in a donor solvent such as acetonitrile, surprisingly **11** displays a nearly square-planar geometry at each Cu(I) center—unprecedented in non-macrocylic Cu(I) chemistry, Fig. 4.

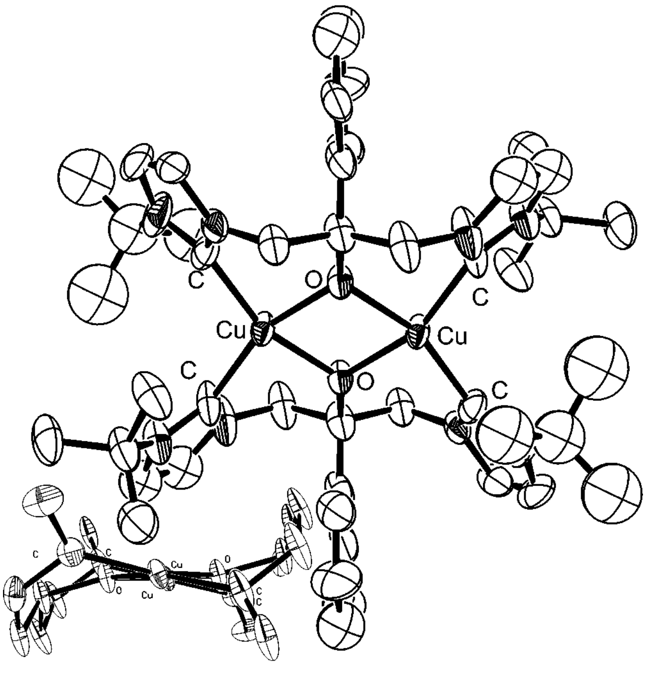
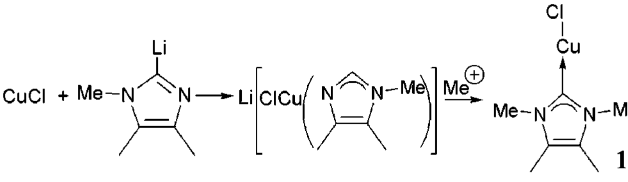


FIGURE 4 Thermal ellipsoid plot of 11 and side view of $Cu_2O_2C_4$ core, 50% probability.

By Alternative Reactions

The first copper(I) mono(carbene) complexes were synthesized by the alkylation of thiazolyl or imidazolyl-cuprates, after their formation from the reaction between CuCl or CuI and a lithiated 4-methylthiazole-, benzothiazole, 1-methylimidazole (Eq. (7)), or 1-methylbenzoimidazole [25].



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(7)

STRUCTURAL PROPERTIES OF THE METAL-NHC ADDUCTS

One structural consequence of the σ-only dative bond is that the metal carbon distance is close to that expected for a M—C bond, particularly for the more electropositive metals. A survey of the NHC complexes reported to date shows Ag—C distances in the range between 2.058 (for the benzimidazole-derived NHC) and 2.099 Å, with a mean of 2.078 Å. Impressively, the NHC—AgCl distance calculated by Boehme and Frenking is 2.076 Å [24]. Single Ag—C bonds in the few simple complexes (containing sp^2 and sp^3 carbon) in the literature fall within the range 2.14–2.23 Å.

Structurally characterized copper–NHC complexes so far displayed Cu—C distances in the range 1.88–1.97 Å, with shorter distances (ca. 1.88 Å) exhibited by the "carbene" complexes in which one NR is replaced by S. The reported Cu—C single bond range for sp^2 and sp^3 carbon is 1.90–1.96 Å, while the distance calculated by Boehme and Frenking for NHC—CuCl is 1.848 Å [24]. The fact that the experimental values are longer than the calculated value may be in part due to the formation of additional bonding interactions with adjacent Cu and halide ions in the dinuclear structures that are so often observed in the experiments.

Upon deprotonation to a free NHC, the NCN angle invariably narrows from 109° to ca. 102–104°, and the NC bonds lengthen, concomitant with the increase in p-character of the N—C σ-bonds as the carbene lone-pair becomes stabilized by a higher percent s-character; binding to a metal through the σ lone pair then results in an slight opening up of the NCN angle and shortening of the NC bonds in the planar NHC ring.

Another consequence of the dative bond is that the torsion angle between the metal and the plane of the bound heterocyclic carbene ring has no geometrical significance, since there is formally no barrier to rotation about the dative bond.

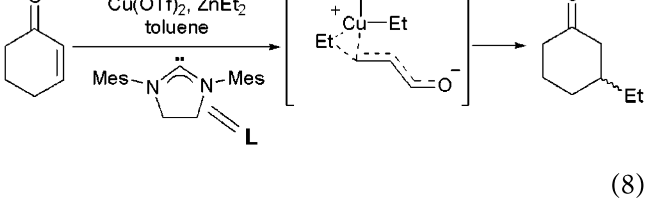
REACTIVITY OF SILVER AND COPPER NHC COMPLEXES

Transmetallation Reactions

The most common reaction reported to date for silver NHC complexes is the transmetallation reaction with $PdCl_2(MeCN)_2$ or other bis(solvate)s to form new divalent Pd complexes as potential homogeneous catalysts [18]. This is generally because the silver oxide deprotonation provides a mild and effective method of both deprotonating a functionalized imidazolium salt that might be decomposed by other reagents such as potassium hexamethyldisilazide or dissolved metal–liquid ammonia, and the silver adducts are generally less air sensitive than the free carbene. Other than the formation of Group 10 and 11 derivatives, remarkably a few other metathesis reactions have been reported to date.

Catalysis by Metal Complexes Supported by NHC Ligands

There are clearly fundamental reasons why the metal NHC adducts and the transient metal carbenes formed as catalytic intermediates cannot be compared under this heading. However, ligand-accelerated catalysis (LAC) effects have now been reported in copper-catalyzed conjugate addition reactions of dialkyl zinc to conjugated ketones (Eq. (8)) [26].



(8)

The introduction of the free NHC into the mixture has been used successfully, but combining an iodo-silver NHC adduct with the divalent copper triflate in the reaction vessel, which presumably makes the system more tolerant to air or moisture, also gives excellent results.

CONCLUSIONS

So far, silver and copper NHC complexes has provided new mild routes to functionalized, homogeneous Group 10 catalysts, relatively stable sources of the reactive σ-donor NHC in catalysis, an opportunity to characterize the first simple silver alkoxide and the first nonmacrocyclic square-planar Cu(I). No isolated divalent copper NHC complexes have been reported, although the opportunities for NHCs to stabilize such a species and form active catalysts have begun to be explored.

ACKNOWLEDGMENT

The author thanks the EPSRC for an Advanced Fellowship.

REFERENCES

[1] Arduengo, A. J.; Harlow, R. L.; Kline, M. J Am Chem Soc 1991, 113, 361–363.
[2] (a) Rovis, T.; Evans, D. A. Prog Inorg Chem 2001, 50, 1; (b) Doyle, M. P.; Forbes, D. C. Chem Rev 1998, 98, 911; (c) Buhl, M.; Terstegen, F.; Loffler, F.; Meynhardt, B.; Kierse, S.; Muller, M.; Nathe, C.; Luning, U. Eur J Org Chem 2001, 2151; (d) Straub, B. F.; Hofmann, P. Angew Chem Int Ed Engl 2001, 40, 1288.
[3] (a) Arduengo, A. J.; Krafczyk, R. Chem Unserer Zeit 1998, 32, 6–14; (b) Dixon, D. A.; Arduengo, A. J. J Phys Chem 1991, 95, 4180–4182.
[4] Arduengo, A. J. Accounts Chem Res 1999, 32, 913–921.
[5] Arnold, P. L.; Cloke, F. G. N.; Geldbach, T.; Hitchcock, P. B. Organometallics 1999, 18, 3228–3233.
[6] Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N. Chem Commun 1997, 1963–1964.
[7] (a) Arduengo, A. J.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. Chem Lett 1999, 1021; (b) Frankel, R.; Kniczek, J.; Ponikwar, W.; Noth, H.; Polborn, K.; Fehlhammer, W. P. Inorg Chim Acta 2001, 312, 23–39.
[8] Herrmann, W. A.; Runte, O.; Artus, G. R. J. J Organomet Chem 1995, 501, C1.
[9] Arduengo, A. J.; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. J Am Chem Soc 1994, 116, 7927–7928.
[10] Oldham, W. J. , Jr.; Oldham, S. M.; Scott, B. L.; Abney, K. D.; Smith, W. H.; Costa, D. A. Chem Commun 2001, 1348.
[11] Arduengo, A. J.; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. Organometallics 1993, 12, 3405–3409.
[12] Caballero, A.; Diez-Barra, E.; Jalon, F. A.; Merino, S.; Tejeda, J. J Organomet Chem 2001, 617, 395–398.
[13] Wang, H. M. J.; Lin, I. J. B. Organometallics 1998, 17, 972.
[14] Pytkowicz, J.; Roland, S.; Mangeney, P. J Organomet Chem 2001, 631, 157–163.
[15] Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. J Chem Soc, Dalton Trans 2000, 4499–4506.

[16] (a) Garrison, J. C.; Simons, R. S.; Kofron, W. G.; Tessier, C. A.; Youngs, W. J. Chem Commun 2001, 1780–1781; (b) Garrison, J. C.; Simons, R. S.; Talley, J. M.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. Organometallics 2001, 20, 1276–1278.

[17] Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. J Organomet Chem 2001, 617, 546–560.

[18] Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. Inorg Chim Acta 2002, 327, 116–125.

[19] Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. Chem Commun 2001, 2340–2341.

[20] The most closely related silver complexes that have been reported are silver acetylacetonate and carboxylate derivatives. Silver nitrate is traditionally used in silver sol–gel chemistry in the absence of silver alkoxides.

[21] Scarisbrick, A. C.; Arnold, P. L. Unpublished results.

[22] Bildstein, B.; Malaun, M.; Kopacka, H.; Wurst, K.; Mitterbock, M.; Ongania, K. H.; Opromolla, G.; Zanello, P. Organometallics 1999, 18, 4325–4336.

[23] Guerret, O.; Solé, S. P.; Gornitzka, H.; Teichert, M.; Trinquier, G.; Bertrand, G. J Am Chem Soc 1997, 119, 6668–6669.

[24] Boehme, C.; Frenking, G. Organometallics 1998, 17, 5801–5809.

[25] Raubenheimer, H. G.; Cronje, S. J Organomet Chem 2001, 617, 170–181.

[26] (a) Fraser, P. K.; Woodward, S. Tetrahedron Lett 2001, 42, 2747–2749; (b) Pytkowicz, J.; Roland, S.; Mangeney, P. Tetrahedron: Asymmetry 2001, 12, 2087–2089.