Available online at www.sciencedirect.com
SCIENCE DIRECT®
Coordination Chemistry Reviews 248 (2004) 2239–2246
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Recent homogeneous catalytic applications of chelate and pincer *N*-heterocyclic carbenes

Eduardo Peris[a,∗,1], Robert H Crabtree[b,∗,2]

[a] *Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, Av. Vicente Sos Baynat,*
s/n 12071 Castellón, Spain
[b] *Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT 06520-8107, USA*

Received 22 August 2003; accepted 20 April 2004

Contents

Abstract

During the last decade, the use of *N*-heterocyclic carbene ligands (NHCs) based on imidazolium ions and related heterocycles has emerged as an alternative to phosphines in the design of new organometallic catalysts. We review catalysts with chelate and pincer NHC ligands, including complexes of palladium, ruthenium, rhodium and iridium. Transfer hydrogenation and Heck chemistry are given special attention. Also discussed are Suzuki and Sonogashira coupling and immobilization on clay supports. Synthetic aspects are covered as well as a discussion of structural features, catalytic properties and catalyst recovery and recycling.

Keywords: Carbenes; NHC; Catalytic properties; Catalyst homogeneity; Supported catalyst

1. Introduction and synthesis of complexes

There are relatively few homogeneous transition metal catalysts where both steric and electronic effects can be finely controlled by small changes of ligand structure within the series. Phosphines have been the most widely used in this connection, aided by the availability of the Tolman map of electronic and steric effects [1]. *N*-heterocyclic carbenes (NHCs), derived from the replacement of the proton at C-2 in an imidazolium salt by a metal, have been known for many years [2], but interest was dormant until Arduengo et al. [3], isolation of the free imidazol-2-ylidene carbene in 1991. Their potential as genuinely useful ligands for catalysis is a relatively recent development springing from Herrmann et al. [4]. Spectroscopic studies suggested NHCs were principally sigma-donors and only poor pi-acceptors, like phosphines, so an analogy between the two classes of ligands developed [5].

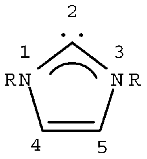
∗ Corresponding authors.

E-mail addresses: eperis@qio.uji.es (E. Peris), robert.crabtree@yale.edu (R.H. Crabtree).

[1] Fax: 34 964 728214.

[2] Fax: +1 203 432 6144.

0010-8545/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2004.04.014



Further work has shown that the two ligand classes are distinct in electronic properties, NHCs being more strongly donor than even the most basic phosphines. [4,6,7] The fan shaped steric profile of NHCs is also different from the cone shape of PR_3 but this has yet to be fully exploited. Certainly, it is easy to incorporate very bulky groups such as mesityl on the nitrogen atoms at positions 1 and 3 [7], and to vary the steric size of these groups in a stepwise fashion.

Chelate carbenes, a focus of this review, require the use of linkers between the imidazole rings, which presents potential complications in that these sites may be deprotonated by relatively strong bases such as the BuLi sometimes used to form the carbene from the precursor imidazolium salt. Milder bases than BuLi, such as $K[N(TMS)_2]$, KH or KO*t*Bu were therefore introduced to resolve this problem; liquid ammonia or THF were the preferred solvents for generating the carbene [8].

Pincer carbenes are a more recent development [6], and in this case direct metallation of the imidazolium salt with $Pd(OAc)_2$ proved successful, although the temperature required was high (170 °C). Subsequent pincers used an oxidative addition of the imidazolium salt to $Pd_2(dba)_3$ under very mild conditions [9]. In an unexpected development, displacement of the central pyridine ring of the CNC pincer proved easy, even occurring during conformational fluxionality of the CNC ring, when an outer sphere halide coordinates to the metal to convert the pincer to a chelating bis-carbene ligand.

A potentially severe drawback of the metallation procedure only became apparent with the discovery that imidazolium salts can sometimes metallate at C-4 or C-5, in the backbone part of the ring, a region normally considered inert [10]. This in turn means that catalysts that are made in situ by treatment of the imidazolium salt with say $Pd_2(dba)_3$ may need to be considered as having uncertain structures until they can be isolated and characterized. The reactions that give abnormal C-4 or C-5 metallation prove to be very sensitive to conditions and even to counter ion [11].

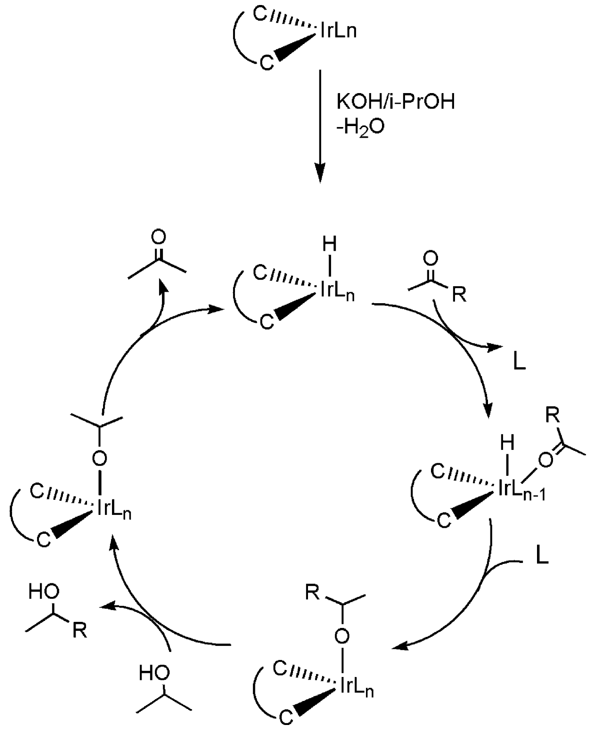
Additional mild procedures are welcome in this area because it may be desirable to add even more sensitive functionality in future. One promising procedure is treatment of the imidazolium salt with Ag_2O to form the silver–NHC complex followed by transmetallation to the metal of interest. This promising transmetalation method was introduced in 1998 by Wang and Lin [12]. A variety of silver–NHC complexes have been made [13], and many of them have been successfully transferred to Pd, Au, Rh and Ir [14,15]. Failure to form a stable silver carbene complex, or more commonly, failure of the silver carbene to *trans*-metallate to the precursor can be problems with this method, however.

2. Transfer hydrogenation

So many different catalytic applications of NHCs have now been described that we limit our discussion to cases in which a chelating or pincer carbene has been used. An early catalytic application was transfer hydrogenation from iPrOH to a ketone with KOH as co-catalyst. The accepted mechanism is deprotonation of metal-bound iPrOH to give an iPrO–M species. This can beta-eliminate to give a hydride that can attack the substrate ketone $R_2C=O$ to give $R_2CH–O–M$. Alkoxide exchange with iPrOH liberates the product and re-forms the iPrO-M species. It is sometimes hard to eliminate the alternative Meerwein–Ponndorf–Verley (MPV) mechanism, however, which involves direct hydride transfer between alkoxide and carbonyl compound. In the context of carbene ligands, the presence of an intermediate metal hydride is a potential source of problems. If the carbene reductively eliminates with the hydride, the ligand is lost with formation of an imidazolium salt. Fortunately, there is no indication that such a reductive elimination is easy because the catalysts described in this section are capable of catalyzing up to 5×10^4 turnovers before deactivation. The chelating character of the carbenes may help prevent decomposition, in part simply by chelation, but also by holding the carbene ring in a conformation that disfavors reductive elimination, a reaction that is expected to require the empty p_z orbital on the carbene carbon to be colinear with the adjacent M–H bond.

The first reported example was the $[Rh^{III}(bis\text{-}carbene)I_2(OAc)]$ catalyzed reduction of a variety of ketones and imines [16]. The synthesis of this Rh(III) species from the bis-imidazolium salt and $[(cod)Rh^{I}Cl]_2$ using NaOAc/KI is unusual in taking place under inert atmosphere without apparent oxidant in the system; presumably trace air takes this role. The usual *n*-Bu wingtip groups gave adequate catalytic results but relatively rapid deactivation is seen. A great improvement was obtained by moving to iridium and to neopentyl wingtip groups [17]. The latter groups lack beta hydrogen atoms and so may resist Hofmann type elimination under the basic conditions used. These systems had good functional group tolerance in the substrate (e.g. NO_2, Br, pyridine ring) and conjugated enones were reduced to the saturated alcohol. Alkenes were isomerized, consistent with the presence of hydride intermediates, but not reduced; this makes the MPV mechanism unlikely. The catalytic systems were completely insensitive to air so that they could be run on the open bench without any special precautions. On the mechanistic side, it was shown that in d_1-cyclohexanol, the D on the carbinol carbon was essentially quantitatively transferred to the product carbinol carbon, as expected for a monohydride mechanism (Schemes 1 and 2).

Danopoulos, Winston, and Motherwell showed that deprotonation of 2,6-bis(arylimidazolium) pyridine dibromide with $KN(SiMe_3)_2$ gave thermally stable 2,6-bis(arylimidazol-2-ylidene) pyridine, which was further used to prepare ruthenium ‘pincer’ complexes. The latter showed catalytic



Scheme 1. Proposed schematic catalytic cycle for the hydrogen transfer catalyzed by iridium(bis-carbene) complexes involving a monohydride active species.

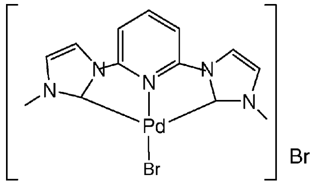
activity in transfer hydrogenation of carbonyl compounds [18]. Ru(CNC)(CO)Br_2 (CNC = 2,6-bis(butylimidazol-2-ylidene)pyridine, compound **7** in Section 4) gave similar chemistry, with TONs as high as 2×10^5 [19].

3. Heck and related C–C bond formation reactions

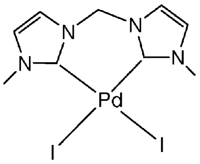
Many of the most widely used C–C bond formation reactions, such as the Heck reaction, for example, require the use of any of a wide variety of Pd as catalysts. Pd(0) readily undergoes oxidative addition with various C–*X* bonds, and the easy addition of unsaturated bonds to the RPd*X* intermediate so formed, followed by beta elimination, completes the reaction. The reaction can be catalyzed by palladium complexes with or without phosphine ligands (phosphine assisted versus phosphine-free catalysts). The phosphine-containing catalysts, sometimes regarded as classical [20], often give good results in the Heck reaction. The primary role of the phosphine is to support Pd in its zero oxidation state, as PdL_4 or PdL_3 species. The search for new phosphine-free Pd catalysts is driven by both economic and academic reasons: phosphine ligands are expensive, toxic and unrecoverable. Besides, one of the most important challenges in the search for good catalysts for the Heck reaction is the activation of traditionally more inert bonds, such as C–Cl (aryl chlorides are often cheaper and more readily available than other aryl halides), for which high temperatures are needed where P–C bond cleavage reactions of phosphine complexes may deactivate the catalyst.

Herrmann and co-workers [21–23] and McGuinness and Cavell [14], have recently performed Heck reactions with aryl chlorides using carbene-containing Pd complexes with reasonably high TON values. The strongly electron donating character of the NHC ligand may facilitate oxidative addition. In the context of this review, it seemed useful to see whether pincer-carbene ligands instead of phosphines, would form palladium catalysts with enhanced or, at least, different catalytic properties.

Preliminary work [24] involved the bis-carbene-pincer complex **1**, whose synthesis at high temperature (DMSO, 170 °C) revealed its exceptional high thermal stability. A related bis-carbene palladium complex such as **2** [23,25], results a very efficient Heck catalyst under nitrogen at 140 °C, but it deposits Pd black after 8 h in refluxing DMA in air, while **1** is unchanged after 24 h under the same harsh conditions.

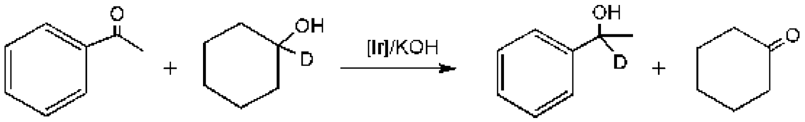


1

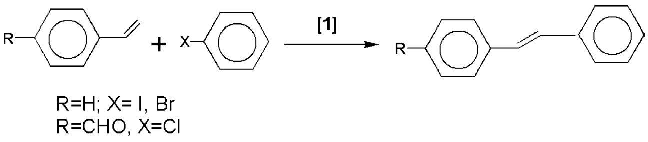


2

Compound **1** was tested in standard Heck conditions (Scheme 3), and showed good activities in the coupling of iodobenzene and styrene to give *trans*-stilbene in diethylacetamide (DEA, bp 184 °C) in the presence of NaOAc as base with catalyst loading as low as 0.2%. Bromobenzene and styrene are also quantitatively converted to *trans*-stilbene with catalyst loadings of 5%. Activated aryl chlorides reacted moderately (75% conversion, 5% catalyst) and required the addition of n-Bu_4NBr as co-catalyst. Although these results did not differ much from those for other catalysts which can be even more efficient for certain substrates, the main lesson from this work is that Heck reactions can be carried out in the presence of air, so Heck coupling need not be an air sensitive process.

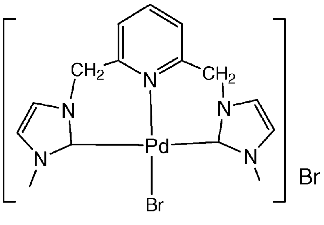


Scheme 2. Hydrogen transfer between acetophenone and d_1-cyclohexanol.



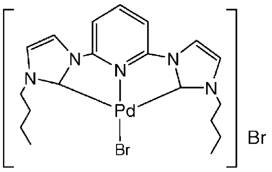
Scheme 3. Standard Heck reactions studied.

This preliminary result prompted the design of new pincer-carbene palladium complexes with improved catalytic activities. Disadvantages of **1** are its low solubility in nonpolar solvents and its high reaction temperatures. Fortunately, pincer-carbene ligand precursors are easy to prepare and versatile, so they can be readily modified in order to promote changes that can affect to the physical and chemical properties of their complexes. The introduction of a CH_2 spacer between the rings enhances solubility, presumably by avoiding the flat geometry of **1**, which may allow metal-metal and aromatic stacking interactions in the solid state. The resulting catalyst, **3** [26], is soluble in $CHCl_3$, and resulted a much better activity than **1**.



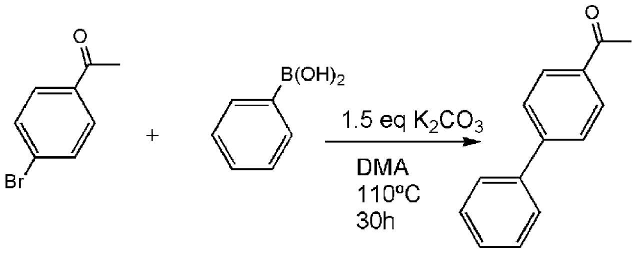
3

The chemical and physical properties of **1** can also be modified by changing the wingtip N-alkyl groups. Substitution of the methyl group in **1** by an *n*-butyl substituent, improved the solubility of the catalyst, probably by disturbing the intermolecular interactions of the compound in the solid state (compound **4**) [27].



4

Compound **4** showed a better Heck reactivity than **1** giving good coupling activities even for aryl chlorides. For the olefination of chlorobenzaldehyde yields remain high, even at catalyst loading of $2 \times 10^{-3}\%$. The TONs of 47,500–75,000 obtained with catalyst loading of $2 \times 10^{-4}\%$ are among the highest yet reported for aryl chlorides, although the temperatures previously used were lower [28,29]. Previous aryl chloride olefinations generally required high catalyst loadings or long reaction times for comparable conversions [14,21–23,25,29–31]. In addition, our yields are almost the same even in the absence of n-Bu_4NBr, but the reaction time is longer. A key mechanistic problem in Pd chemistry is the potential for precipitation of colloidal Pd which can itself be an excellent catalyst. The catalysts described above retained activity in the presence of Hg(0), however, arguing against the presence of heterogeneous Pd.



Scheme 4. Generalized Suzuki reaction.

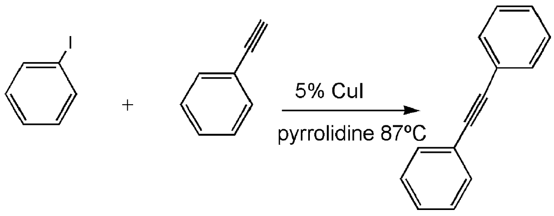
3.1. Catalyst re-use

One of the most interesting challenges in the Heck reaction is the search for recyclable catalysts. In order to find whether the catalyst would be stable enough to be recycled, suitable experiments were designed and carried out with 4-bromoanisole and styrene. On completion of the coupling reactions, if the mixture is cooled and additional aliquots of substrate and base added, the reaction is found to continue without loss of activity. Six cycles were carried out, each time without addition of more catalyst or solvent. The fact that the reaction mixture retains full activity for several cycles provides evidence for the stability of the system and shows its potential for re-use.

3.2. Suzuki and Sonogashira catalysis

The Suzuki reaction between the activated aryl bromide 4-bromoacetophenone and phenyl boronic acid yielded the substituted biphenyl in 88% yield when 1 mol% of **4** was used, and 70% for a 0.2 mol % loading (Scheme 4, 30 h both reactions) [32]. Traditionally, solvents as THF, dioxane, and toluene are used in the Suzuki reaction, but the solubility of **4** constrained us to use DMA. Again, these reactions were unaffected by air.

The Sonogashira reaction was also evaluated with **4** (Scheme 5). Iodobenzene and phenylacetylene can be coupled in pyrrolidine (bp 87 °C) with CuI as co-catalyst in 99% yield. Yields are as low as 10% even after 19 h with 4-bromoacetophenone. We interpreted this low yield as resulting from an undesired oxidative homocoupling of the alkyne (Glaser reaction) to the corresponding symmet-



Scheme 5. Generalized Sonogashira reaction.

rical diyne [33]. When the reaction is performed under nitrogen atmosphere and by slow addition of the alkyne, keeping its concentration low, **4** proved to be highly efficient affording the desired products in very short reaction times. Under these reaction conditions, the coupling was almost complete within 0.5 h for *p*-nitrobromobenzene, and quantitative within 2.5 h for *p*-bromobenzaldehyde and *p*-bromoacetophenone**.**

3.3. Clay immobilization

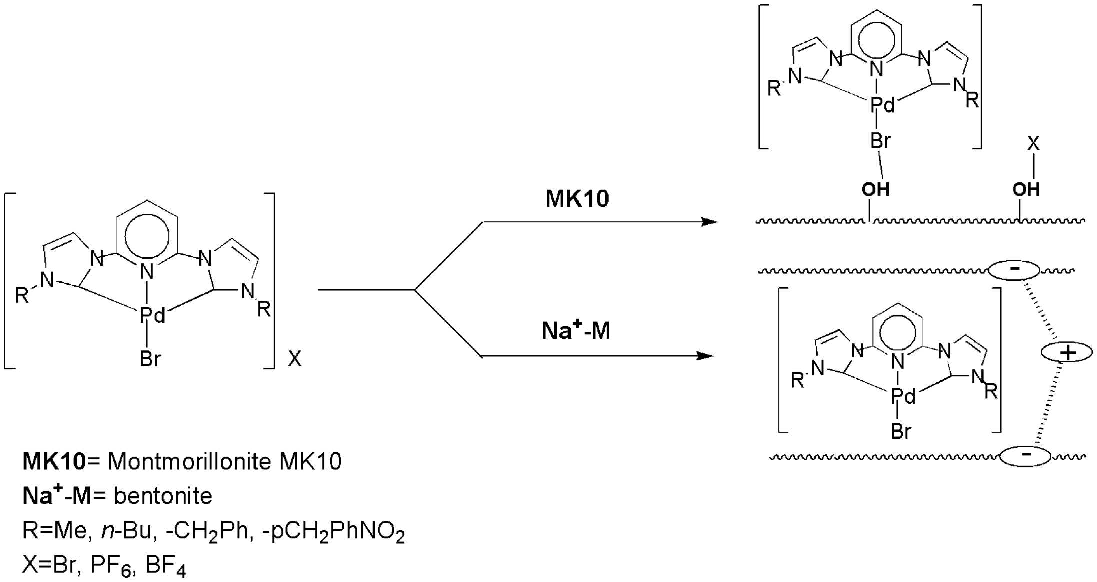
Heck reactions present a tough challenge for the design of highly recyclable systems. The reaction needs at least three reagents (halide, olefin, base) besides the catalyst itself. The salt generated by neutralisation of HX and base in the last step of the catalytic cycle accumulates in the reaction medium, leading to an unpredictable influence on the catalyst [20] including possible promotion of the reaction rate [34]. Despite all these problems, some approaches to support [35] and heterogenize Pd catalytic systems involve immobilization of Pd catalysts on polymers, modified mesoporous silica gel [22,36], or modified silica gel [37]. However, although some of these preformed heterogenized catalytic systems, such as the bis-carbene complex immobilized by Herrmann and co-workers [22], can be efficiently recycled in a Heck reaction, they suffer from the disadvantage that they require multistep syntheses.

Taking into account the good Heck reactivity of compound **4** and its great stability, this and related compounds seemed excellent candidates for new recyclable C–C coupling catalysts. Scheme 6 shows the general procedure for the immobilization of the palladium catalysts onto the clays montmorillonite K-10 (MK-10) and bentonite (Na^+-M), carried out by the solvent impregnation method. The immobilized compounds are shown in Scheme 6; all are similar to **4** with slight modifications such as change of the *N*-alkyl wingtips (R = CH_3, *n*-Bu, -CH_2Ph, *p*-CH_2-Ph-NO_2; *X* = Br, PF_6, BF_4).

The Heck reactivities of the heterogenized catalysts compare well with their homogeneous counterparts, indeed, a perfect correlation of activities is observed with NaOAc as base; the reactivity of the catalyst is therefore preserved upon immobilization. Removal of the supported catalyst by filtration and repeated C–C coupling reaction with recycling showed that good conversion is retained over several cycles, but a significant loss of activity is seen. Leaching of the palladium complex was not involved because the amount of Pd(II), as determined by elemental analysis (AAS) and XPS in the solid before and after the catalytic consecutive experiments was essentially unchanged. It is important to point out that no Pd(0) was found by XPS on the surface of the solids after being used in catalytic reactions.

Since montmorillonite K-10 readily absorbs ionic species from solutions, we suspected that NaOAc, used as the base on each consecutive C–C coupling run, could be adsorbed onto the solid surface, hence saturating or blocking the catalytic active sites. Indeed, elemental and XPS analysis of the solids before and after recycling, showed that the amount of Na and C adsorbed considerably increased after consecutive runs. In order to recover the catalytic activity after catalyst recycling we decided to use NEt_3 as non ionic base instead of NaOAc. Indeed, NEt_3 yields quantitative conversions for the coupling of iodobenzene and styrene, even after ten consecutive runs. As expected, this base does not show any significant affinity for surface adsorption, allowing the catalytic sites to remain active on reuse (Fig. 1).

Once optimised for the Heck coupling of iodobenzene with styrene, we decided to extend the study to other substrates, in order to determine whether our catalysts could also be useful for C–C coupling of the less reac-



Scheme 6. Immobilization of the Pd-catalyst on montmorillonite MK-10 and bentonite.

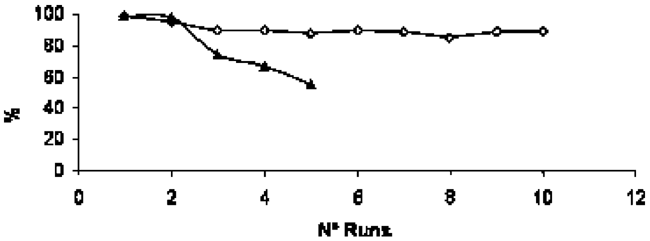


Fig. 1. Conversions for the consecutive couplings (runs) of iodobenzene and styrene. Reactions in diethylacetamide (DEA) at 180 °C with 0.1 mol% catalyst used (4). (◇) NEt_3 as base. (▲) NaOAc as base.

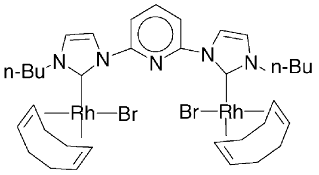
tive C–Br and C–Cl bonds. After optimising the reaction conditions, we were able to activate C–Br, for five consecutive runs without detectable catalytic decay. However, the activation of C–Cl bonds was achieved in 15% yield at best.

Mechanisms in Pd chemistry raise particularly difficult issues. Mechanisms other than the traditional Pd(0)/Pd(II) cycle have been invoked in order to explain how pincer phosphapalladacyclic Pd(II) could achieve high activity in the Heck reaction [25,28,30,38]. In particular, a Pd(II)/Pd(IV) cycle may be operating for some types of compounds. In many cases, the reduction of Pd catalysts leads to the formation of Pd-black, that is itself reactive for the Heck reaction in a heterogeneous fashion. In our case, we find that elemental mercury, which selectively poisons heterogeneous catalysts, leaves the Heck activity of **4** entirely unaffected so precipitated or colloidal Pd is not the active catalyst.

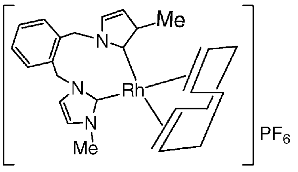
4. Other reactions

The coordination of pincer ligands to Pt-group metals has afforded a wide range of compounds whose properties are still far from fully explored. Along with the reactions mentioned in the previous chapters, several other homogeneous catalyzed reactions have attracted preliminary study, showing the chemical versatility of this type of ligands. For example, the synthesis of Rh(I)–carbene complexes prompted the study of reactions typically catalyzed by phosphine complexes of Rh(I), such as hydroformylation and hydrosilation of terminal alkynes; the preparation of Ru–(CNC) pincer complexes suggested the study of reactions such as oxidation of olefins.

In this regard, the dinuclear Rh(I) compound **5**, showed high activity in the hydroformylation of a variety of terminal alkenes. However, although conversions were high and **5** proved to be a good hydroformylation catalyst, the most remarkable feature of this catalyst is that it remains dimetallic under the harsh conditions used in the reaction [39]. High pressure NMR (HPNMR) spectroscopy reveals that the carbene ligand remains bound to Rh under 30 atm of CO/H_2, retaining the dinuclear character of the complex. Although it is very difficult to identify the catalytically active species, the high stability of the dimetallic compound and the absence of HPNMR signals due to monometallic species, suggest that the catalytic active species may be dimetallic.



5

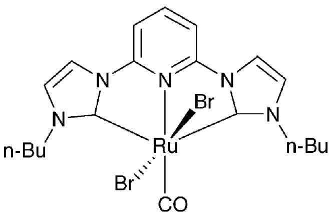


6

The cationic bis-carbene Rh(I) complex **6** was also tested in the catalytic hydroformylation of alkenes, but proved to be completely ineffective. In this regard, severe differences in the catalytic behavior of **5** and **6** were also found for the hydrosilylation of terminal alkynes. While compound **5**, and the analogue complex with methyl wingtip groups, were found to be effective catalysts for this reaction, **6** resulted in a very ineffective catalyst, affording good conversions of the alkynes to the corresponding silyl alkenes only after very long reaction times (>72 h) [40].

We believe that the difference in the catalytic behavior of **5** and **6** arises from their different susceptibility for oxidation. For reasons to be discussed elsewhere, oxidation to a Rh(III) analogue is favored for **5** but is clearly disfavored for **6** which remains Rh(I) even under oxidizing conditions. In this sense, those catalytic reactions for which an oxidative addition is required in any of the reactions steps (hydroformylation, hydrosilylation), is clearly disfavored for compound **6** and not for **5** or analogue dinuclear species.

The Ru(CNC)–pincer complex **7**, gave an efficient catalyst for the oxidation of simple olefins to aldehydes. Remarkably, no side products were observed from overoxidation, epoxidation or diol formation [19].



7

5. Future prospects

In view of the increasing success of monodentate NHCs in catalysis, we can expect a rise in the use of chelating NHCs. The advantages seem to be enhanced stability and a more rigid conformation. The latter could become more important in asymmetric catalysis, for example. Extension to triazole analogues and other heterocyclic carbenes have already shown initial promise and may be advantageous for altering electronic effects. Open chain analogues may afford additional ligand flexibility. The NHCs are more donor than any traditional phosphine ligands, so we now have access to a long unexplored part of the Tolman ligand map.

Acknowledgements

EP thanks the DGESIC(MAT2002-04421-C02-01) and RHC thanks the US DOE, BP Chemicals and Johnson Matthey for funding in this area.

References

[1] C.A. Tolman, Chem. Rev. 77 (1977) 313.

[2] K. Ofele, J. Organomet. Chem. 12 (1968) P42;
H.W. Wanzlick, H.J. Schonher, Angew. Chem. Int. Edit. 7 (1968) 141;
D.J. Cardin, B. Cetinkay, E. Cetinkay, M.F. Lappert, E.W. Randall, E. Rosenber, J. Chem. Soc. Dalton Trans. (1973) 1982.

[3] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[4] W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, G.R.J. Artus, Chem. Eur. J. 2 (1996) 772;
W.A. Herrmann, Angew. Chem. Int. Edit. 41 (2002) 1291.

[5] W.A. Herrmann, D. Mihalios, K. Ofele, P. Kiprof, F. Belmedjahed, Chem. Ber. Recl. 125 (1992) 1795.

[6] L. Perrin, E. Clot, O. Eisenstein, J. Loch, R.H. Crabtree, Inorg. Chem. 40 (2001) 5806.

[7] J.K. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674.

[8] W.A. Herrmann, C. Kocher, L.J. Goossen, G.R.J. Artus, Chem. Eur. J. 2 (1996) 1627.

[9] J.R. Miecznikowski, S. Grundemann, M. Albrecht, C. Megret, E. Clot, J.W. Faller, O. Eisenstein, R.H. Crabtree, Dalton Trans. (2003) 831.

[10] S. Grundemann, A. Kovacevic, M. Albrecht, J.W. Faller, R.H. Crabtree, J. Am. Chem. Soc. 124 (2002) 10473.

[11] A. Kovacevic, S. Grundemann, J.R. Miecznikowski, E. Clot, O. Eisenstein, R.H. Crabtree, Chem. Commun. (2002) 2580.

[12] H.M.J. Wang, I.J.B. Lin, Organometallics 17 (1998) 972.

[13] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterbock, K.H. Ongania, G. Opromolla, P. Zanello, Organometallics 18 (1999) 4325;
P.L. Arnold, A.C. Scarisbrick, A.J. Blake, C. Wilson, Chem. Commun. (2001) 2340;
A. Caballero, E. Diez-Barra, F.A. Jalon, S. Merino, A.M. Rodriguez, J. Tejeda, J. Organomet. Chem. 627 (2001) 263;
J.C. Garrison, R.S. Simons, J.M. Talley, C. Wesdemiotis, C.A. Tessier, W.J. Youngs, Organometallics 20 (2001) 1276;
J.C. Garrison, R.S. Simons, W.G. Kofron, C.A. Tessier, W.J. Youngs, Chem. Commun. (2001) 1780;
J. Pytkowicz, S. Roland, P. Mangeney, J. Organomet. Chem. 631 (2001) 157;
C.K. Lee, K.M. Lee, I.J.B. Lin, Organometallics 21 (2002) 10;
K.M. Lee, H.M.J. Wang, I.J.B. Lin, J. Chem. Soc. Dalton Trans. (2002) 2852.

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

[15] 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;
D.J. Nielsen, K.J. Cavell, B.W. Skelton, A.H. White, Inorg. Chim. Acta 327 (2002) 116;
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 (2001) 546;
A.R. Chianese, X.W. Li, M.C. Janzen, J.W. Faller, R.H. Crabtree, Organometallics 22 (2003) 1663.

[16] M. Albrecht, R.H. Crabtree, J. Mata, E. Peris, Chem. Commun. (2002) 32.

[17] M. Albrecht, J.R. Miecznikowski, A. Samuel, J.W. Faller, R.H. Crabtree, Organometallics 21 (2002) 3596.

[18] A.A. Danopoulos, S. Winston, W.B. Motherwell, Chem. Commun. (2002) 1376.

[19] M. Poyatos, J.A. Mata, E. Falomir, R.H. Crabtree, E. Peris, Organometallics 22 (2003) 1110.

[20] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.

[21] W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, G.R.J. Artus, Angew. Chem. Int. Edit. Engl. 34 (1995) 2371.

[22] J. Schwarz, V.P.W. Bohm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, Chem. Eur. J. 6 (2000) 1773.

[23] W.A. Herrmann, C.P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93.

[24] E. Peris, J.A. Loch, J. Mata, R.H. Crabtree, Chem. Commun. (2001) 201.

[25] W.A. Herrmann, C. Brossmer, K. Ofele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem. Int. Edit. Engl. 34 (1995) 1844.

[26] S. Grundemann, M. Albrecht, J.A. Loch, J.W. Faller, R.H. Crabtree, Organometallics 20 (2001) 5485.

[27] J.A. Loch, M. Albrecht, E. Peris, J. Mata, J.W. Faller, R.H. Crabtree, Organometallics 21 (2002) 700.

[28] W.A. Herrmann, C. Brossmer, C.P. Reisinger, T.H. Riermeier, K. Ofele, M. Beller, Chem. Eur. J. 3 (1997) 1357.

[29] S. Iyer, C. Ramesh, Tetrahedron Lett. 41 (2000) 8981.

[30] D. Morales-Morales, R. Redon, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619.

[31] A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, J. Dupont, Org. Lett. 2 (2000) 1287;
M. Beller, A. Zapf, Synlett (1998) 792;
M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem. Int. Edit. 37 (1998) 481;
M. Portnoy, Y. Bendavid, D. Milstein, Organometallics 12 (1993) 4734;
Y. Bendavid, M. Portnoy, M. Gozin, D. Milstein, Organometallics 11 (1992) 1995;
A.F. Littke, G.C. Fu, J. Am. Chem. Soc. 123 (2001) 6989;
S. Iyer, C. Ramesh, Tetrahedron Lett. 40 (1999) 4719.

[32] E. Mas-Marza, A.M. Segarra, C. Claver, E. Peris, E. Fernandez, Tetrahedron Lett. 44 (2003) 6595.

[33] H.F. Chow, C.W. Wan, K.H. Low, Y.Y. Yeung, J. Org. Chem. 66 (2001) 1910;
S. Thorand, N. Krause, J. Org. Chem. 63 (1998) 8551;
C.L. Yang, S.P. Nolan, Organometallics 21 (2002) 1020.

[34] S. Fujita, T. Yoshida, B.M. Bhanage, M. Shirai, M. Arai, J. Mol. Catal. A Chem. 180 (2002) 277.

[35] K. Kohler, R.G. Heidenreich, J.G.E. Krauter, M. Pietsch, Chem. Eur. J. 8 (2002) 622;
M. Wagner, K. Kohler, L. Djakovitch, S. Weinkauf, V. Hagen, M. Muhler, Top. Catal. 13 (2000) 319.

[36] A. Biffis, M. Zecca, M. Basato, Eur. J. Inorg. Chem. (5) (2001) 1131;

A. Biffis, M. Zecca, M. Basato, J. Mol. Catal. A Chem. 173 (2001) 249;
J. Silberg, T. Schareina, R. Kempe, K. Wurst, M.R. Buchmeiser, J. Organomet. Chem. 622 (2001) 6.
[37] J.H. Clark, D.J. Macquarrie, E.B. Mubofu, Green Chem. 2 (2000) 53.
[38] B.L. Shaw, New. J. Chem. 22 (1998) 649.
[39] M. Poyatos, P. Uriz, J.A. Mata, C. Claver, E. Fernandez, E. Peris, Organometallics 22 (2003) 440.
[40] M. Poyatos, E. Mas-Marza, J.A. Mata, M. Sanau, E. Peris, Eur. J. Inorg. Chem. (6) (2003) 1215.