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Review

NHC ligands versus cyclopentadienyls and phosphines as spectator ligands in organometallic catalysis

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Abstract

N-heterocyclic carbenes are compared with cyclopentadienyls and phosphines in terms of bonding and reactivity. Synthetic difficulties that currently prevent the general incorporation of NHCs into chelate, pincer and tripod ligand architectures are related to the inability of the NHC to reversibly decoordinate to correct binding 'errors' in the initial kinetic products of NHC complex formation. The strengths and weaknesses of current synthetic approaches, such as Lin's Ag_2O transmetallation route, are discussed. Linker dependent reactivity patterns are related to azole ring orientation effects and some aspects of cyclometalation are considered.

Contents

1. Introduction

Until recently, only two classes of ligand that are both sterically and electronically tunable could be said to have become spectator ligands of broad utility in organometallic catalysis: phosphines, PR_3, and cyclopentadienyls, C_5R_5.[1] Phosphines are the most widely used, in part thanks to the work of Tolman [1]. By documenting the trends in their electronic and steric effects, his work allowed both factors to be predictably tuned for optimization of catalytic properties. Cyclopentadienyls can also be modified sterically and electronically by incorporation of various substituents, but no equivalent of the Tolman approach has yet achieved broad acceptance, so trends are less predictable. In both series, changes in the substituents cause both electronic and steric changes and these two factors are hard to vary independently.

Both ligand classes much more commonly adopt the role of spectator, rather than actor ligands, in that they rarely undergo modification during a reaction sequence. To be sure, phosphines can give cyclometalation and P–R bond cleavage [2,3], and cyclopentadienyl ligands

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[1] Such ligands as H, Me, aryl, alkenes and CO are omitted from this list because they are not reliable spectators but are often actively incorporated into a catalytic cycle, nor are they predictably tunable electronically and sterically. Numerous N-donor ligands are useful spectators in catalysis but no one class dominates the scene – one cannot count porphyrins because these rarely give organometallic catalysis. Halides are often effective spectators, but lack the steric tunability of phosphines.

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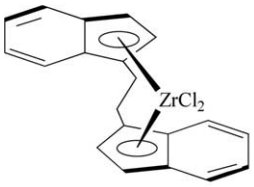
can undergo cyclometalation and alkyl migration [4,5], but these are rare enough to be counted as exceptions.

Multidentate ligands are possible in both series, but phosphines again provide a far richer range of chelate, pincer, tripod and other ligand architectures to choose from. Strapping two cyclopentadienyls together with an *ansa* bridge has been a very important strategy in the design of catalytic sites of specific symmetry, as in the case of **1**, adapted to the formation of isotactic polypropylene in the most important catalytic application of cyclopentadienyls, olefin polymerization [6].



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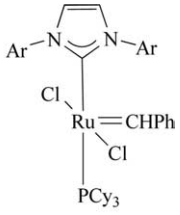


2

Free phosphines are not particularly easy to synthesize, but the commercial availability of a wide range of these mitigates this problem. Decades of work on phosphine coordination chemistry has provided relatively easy synthetic routes to a dazzling array of different complexes, giving the phosphine series a big advantage for routine application. Cyclopentadiene precursors to cyclopentadienyls are not particularly easy to synthesize and conversion to the cyclopentadienyl anion can require strong bases that are often incompatible with the presence of reactive functionality on the substituents. Conversion of a cyclopentadiene to the thallium salt, TlCp, with Tl_2CO_3, followed by transmetallation to the transition metal is a mild procedure but thallium salts are less acceptable in the current green chemistry climate and this route is falling into disuse [7].

In the last decade, the rise of *N*-heterocyclic carbenes (NHCs) has been so strongly-marked, that this ligand class can now be considered as having joined the small, privileged group of broadly catalytically useful ligands comparable with cyclopentadienyls and phosphines. Perhaps the best example of the beneficial effect that NHCs can have comes from the later generation Grubbs alkene metathesis catalysts (**2**), where an NHC replaces a PCy_3 (Cy = cyclohexyl) of the classic bis-phosphine ruthenium catalyst with a great improvement in activity [8].

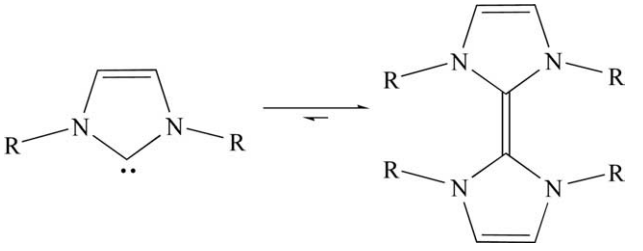
At first, it seems, considered as mere phosphine mimics, it is now clear that NHCs have a chemistry that is original, novel, useful and much more complex than was originally supposed.

The purpose of this review is to examine the analogies and differences between the three classes of ligand, Cp, PR_3 and NHC, to note some instances where our knowledge of NHC chemistry is deficient and how it might be remedied. The general developments in the field have been reviewed extensively [9], including the historically important first NHC complexes [10], the isolation of the first free carbene [11], and the first free NHC carbene [12]. Cyclopentadienyls, as 5 electron ligands (6e on the ionic model), are less closely related to NHCs than are phosphines, which share with NHCs the property of being monodentate 2 electron ligands, so the NHC – phosphine comparison will be emphasized here.

Synthesis: The synthesis of imidazoles and imidazolium ions has been so extensively developed over many decades that this part of the problem, at least, can be considered as largely solved [13]. The starting imidazole can be alkylated or the whole imidazolium ring can be built up, typically from an arylamine, formaldehyde and glyoxal. The vast array of functionality that can be appended to the imidazole ring leads to the possibility of incorporation of functionalized substituent groups on the azole core. This should allow molecular recognition [14], cooperative acid/base, metal-binding or redox effects to enhance catalyst properties by applying enzyme-like strategies in which the catalytic site is not simply the metal but a designed ensemble of cooperative functionality. Such a program is difficult to imagine in the phosphine or cyclopentadienyl area, not only because of synthetic difficulties, but also because the N1 and N3 substituents of NHCs point towards the metal, while the substituents of a Cp point away from the C_5 centroid and, even less favorable, those of PR_3 point away from the metal. This makes the NHC substituents more available to interact productively with the metal site.

With the *N*,*N*′-dialkyl or -diaryl imidazolium salt in hand, a problem does arise in the paucity and lack of generality of means available to metallate it. A detailed review of 20th century synthetic routes is available [15]. The imidazolium salt, being an NHC complex of the proton, deprotonation is an obvious step to reveal the free NHC. Much early work used strong bases to do this and in many cases this free NHC then successfully binds to the metal salt to yield the desired NHC complex [9]. Such methods are less easy to apply to chelate bis-imidazolium salts because free NHCs tend to dimerize by the Wanzlick equilibrium (Eq. (1)) [16]. Perhaps because the equilibrium very much favors the dimer, this dimer has not proved generally useful for synthesis of NHC complexes, although notable exceptions exist [17]. The Kuhn route from a thiourea precursor (Eq. (2)) also requires a harsh reagent, metallic K in THF at 80° [18]. Strong bases or reductants are not expected to be compatible with the full range of desired substituent functionality, however, so improved methods are needed. For example, with phase-transfer catalysts like tetrabutylammonium bromide it is possible to generate NHC complexes with a milder bases such as aqueous sodium hydroxide solution – benzimidazolium bromides and $(Me_2S)AuCl$ react in CH_2Cl_2/H_2O at room

temperature to give $[(NHC)_2Au]Br$ [19]. For the more acidic triazolium salts, triethylamine in THF can be used as the external base for deprotonation, but in cases where deprotonation takes place in the presence of a metal complex or salt, the NHC may bind to the metal in an agostic mode or even oxidatively add to the metal first, so that the deprotonation is greatly facilitated [20]. For imidazolines, the alcohol adduct is a useful precursor [8b].



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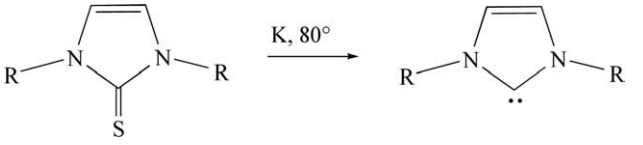
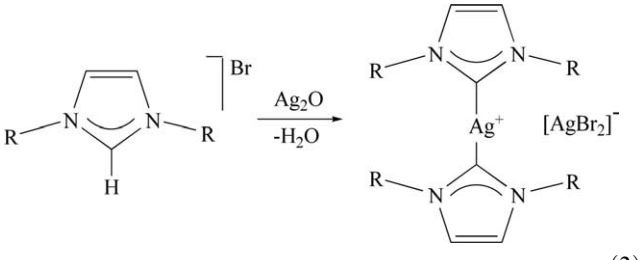


(2)

A great advance was made by Lin in the use of Ag_2O as a metallating agent [21]. The oxide is capable of deprotonating the protonic C2 hydrogen of the imidazolium salt while the Ag^+ ion metallates the C2 position. Free NHC is avoided because the synthesis not only works well even in the presence of air and moisture, but even in water as solvent. The Ag–NHC complex so formed can then react with a variety of metal salts and organometallic precursors to give a very wide series of NHC complexes. Occasionally, the method can run into trouble such as a failure to metallate or in metallation being accompanied by oxidative CC bond cleavage (Eq. (4)) [22]. Another characteristic problem is the failure of the intermediate silver complex of a potentially chelating NHC to chelate after transfer to the second metal. Instead, complexes are typically obtained in which each arm of the NHC acts as a monodentate ligand (Eq. (5)) [23], sometimes, the chelate and the non-chelate form are both obtained [24]. The Ag_2O or transmetallation reactions can sometimes go in only very low yield or not at all [24–26].



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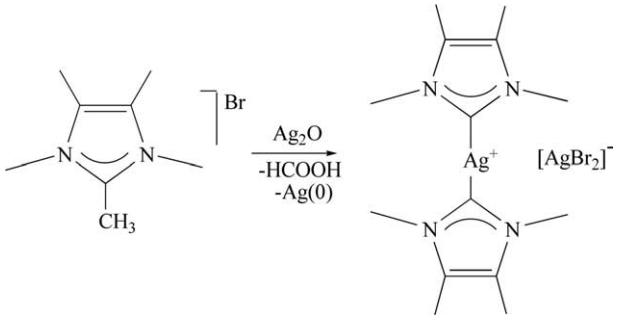

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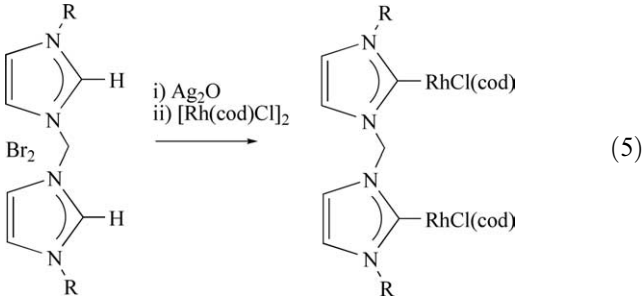
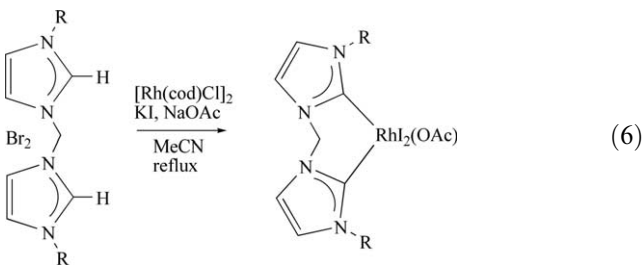


(5)

The common failure to chelate in potentially chelating bis-NHC ligands, mentioned above, shows up another important difference between phosphines and NHCs. Phosphine binding is reversible and so initial errors in binding mode can be corrected and the thermodynamic chelate product be formed in the end. NHCs tend to bind irreversibly so the initial kinetic binding mode is usually retained in the product. This is particularly frustrating because it prevents the development of chelate, pincer and tripod NHC ligands that have been so useful in phosphine chemistry. This must be counted as one of the most serious deficiencies in our current understanding. To be sure, irreversibility can be advantageous, as in covalent grafting onto a solid support.

Direct metallation of the imidazolium salt by a metal precursor is not so widely applicable but a case is known where this procedure gives good yields of a chelating NHC of M(III), where the silver method gave the non-chelating M_2L complex of M(I). Oxidative addition of the CH bond to Rh(I) is the probable mechanism. Because the reaction works equally well even in the strict absence of air, H_2 evolution is believed to provide redox balance in this case (Eq. (6)) [23].



(6)

The intermediate hydride formed on CH oxidative addition of an imidazolium salt may be isolable [27] or may undergo reaction with a second equivalent of the imidazolium salt to yield H_2 and a bis-carbene complex [28].

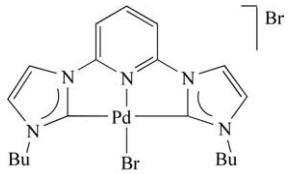
Improved synthetic methods are undoubtedly needed for future expansion of the NHC field, particularly in the case of chelate, pincer and tripod NHCs [29].

Degradation pathways: Little work has been reported, at least in the open literature, concerning the degradation pathways of classical organometallic catalysts. Yet development of catalysts efficient enough for practical application requires an understanding of degradation in order to develop means of blocking such undesired pathways.

Several relevant results have been obtained in which an NHC was cleaved relatively easily from the metal. In contrast with phosphine chemistry, such a reaction is generally irreversible. Crudden documented cleavage of the Rh–carbene bond in the reaction of Rh–*N*-heterocyclic carbene complexes with triphenylphosphine in dichloroethane to give the parent imidazolium salt [30]. Reductive elimination of the NHC with a methyl group can give the 2-methyl imidazolium salt by M–C bond cleavage and the mechanism was studied for the methyl–Pd(II) complex, $[(cod)PdMe(tmiy)]BF_4$ (tmiy = 1,3,4,5-tetramethyl imidazole-2-ylidene) [31]. Interestingly, phosphines are not generally subject to either degradation reaction, so in this respect at least, phosphines maintain an advantage over NHCs.

The C2 carbon of the NHC system shows a strong preference to remain sp^2, presumably to allow π-donation from the N1 and N3 p-orbitals and to maintain aromaticity. This preference is expected to lead to a greater reluctance to cleave from the metal, relative to M–CH_3 or M–Ph, since the transition state for such a process would normally require the intermediacy of an sp^3 carbon at C2. For the same reason, NHCs do not tend to form bridged structures where the NHC carbon at C2 is bound to two metals, although this is very common – and can even be considered the preferred binding mode – for the parent CH_2 carbene. The NHC degradation pathways noted above may, therefore, be slow enough not to be fatal to catalysis as long as the catalytic steps are sufficiently faster than degradation.

Some NHC catalysts are extremely stable, however, for example, a Pd(II) NHC pincer complex with a CNC donor set (**3**) is stable and catalytically active even in boiling diethylacetamide (184°) in air. The activity for the Heck reaction is not poisoned by Hg(0) as would be the case if the catalytic activity of the complex had originated from Pd(0) coming from decomposition [32].



3

A useful recent review of NHC chemistry considers decomposition pathways of metal-NHC complexes in some detail [33].

Steric and electronic effects: In phosphines and cyclopentadienyls, a change of substituent causes a change, not only in the steric, but also in the electronic effect of the ligand, because the R group that is varied is directly attached to the donor atom (Fig. 1). For example going from PPh_3 to PCy_3 causes a change in both factors, and each factor cannot be varied independently. In NHCs, the substituents are attached to atoms one or two bonds away from the donor atom, so that the donor atom itself retains the same immediate environment throughout. Although this is not yet adequately studied experimentally [34], a change of substituent seems to cause a steric change in an NHC with only a minor perturbation of the electronic effect. If a significant change in electronic effect is desired, a change in the nature of the azole ring may be the best strategy. For example, the electron donor effect should vary as benzimidazole < imidazole < imidazoline with a change of azole. Some computational data is available on (NHC)Ni-$(CO)_3$ that is consistent with this idea [35a].

Phosphines and cyclopentadienyls are typically cone-shaped, so rotation about the M–L bond should not have major consequences for either steric or electronic effects. NHCs are fan-shaped and so rotation can in principle have big effects. This is mitigated in the case of monodentate NHCs in that the NHC will tend to rotate so as to minimize any steric clash with the other ligands. In the case of chelate NHCs, however, the orientation of the azole rings is not completely free but fixed within a relatively narrow range by the constraints of the linker. The linker in a chelate NHC causes the azole rings to be closer to coplanar for

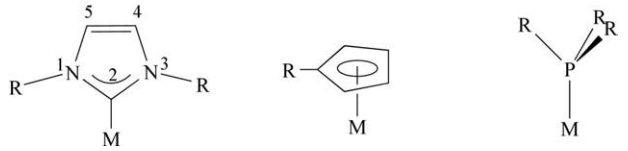
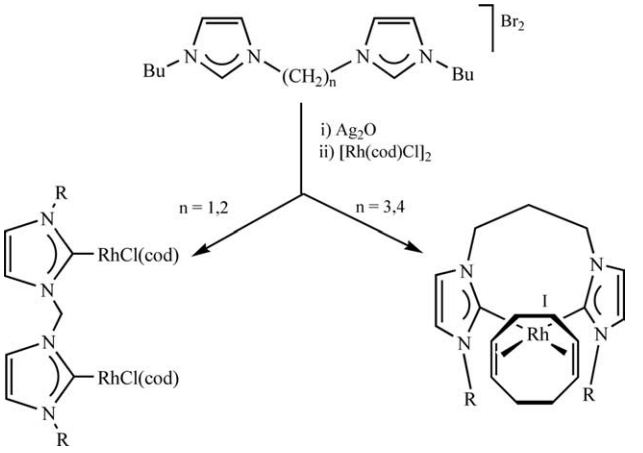


Fig. 1. The N1 and N3 substituents of NHCs point towards the metal, while the substituents of a Cp point away from the C_5 centroid and those of PR_3 point away from the metal. This makes the NHC substituents more available to interact productively with the metal site [14] in ways described in the text.

a short linker but close to mutually parallel for a three or four carbon linker. In one case, a change of linker length was shown to have dramatic effects on the outcome of metallation (Eq. (7)). A short linker favors the non-chelated bis-M(I) product, while a long linker favors the chelate M(I) product. Only for the long linker are the azole rings able to align with the *z*-direction and so minimize steric interactions with the cod ligand in the *xy*-plane. For the short linker, the favored orientation can only be adopted in the bis-M(I) product, where each azole ring is free to align along the *z*-axis of each separate metal center without being subject to the constraints of chelation that models show would have confined the azole ring in an unfavorable orientation close to the *xy*-plane. This effect has some analogy with the use of an ansa strap to fix the rotational orientation of indenyl ligands in olefin polymerization catalysis.



(7)

The electronic effects of NHCs have been estimated by a Tolman type method [1] in a metal carbonyl complex using either experimental or computational values of the ν(CO) as indicator [35]. The results show that NHCs are typically much stronger net donors than phosphines. Since the NHC carbene protonates so much more readily than PR_3, the σ-donor power of the NHC lone pair is undoubtedly much stronger than for PR_3. It is not yet clear how strong is the π-acceptor power of the NHC series. Calculations have been reported that argue for stronger and for weaker π-acceptor power [36a,36b–38], but this is clearly a substituent-, coligand-, and metal-dependent property so more work is needed. It is also unclear how much the π-acceptor power will vary if the orientation of the azole ring is varied. The potentially π-acceptor orbitals (Fig. 2), the two C–N σ^* orbitals and the azole ring π^*, are both fixed in space relative to the azole ring plane and so the degree of back donation may well depend on orientation, particularly in a d^2 case, where only one d-orbital is available for

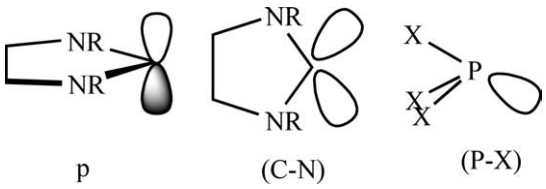


Fig. 2. The potentially π-accepting orbitals of the NHC are the carbon p_π (left) and the two C–N σ^* orbitals (center). There is some analogy with PX_3 (X = alkyl, aryl, alkoxy, halide) in that the three P–X σ^* orbitals (right, one only shown) of PX_3 are the π-acceptor orbitals. The NHC could even be a π-donor via its filled π-orbitals.

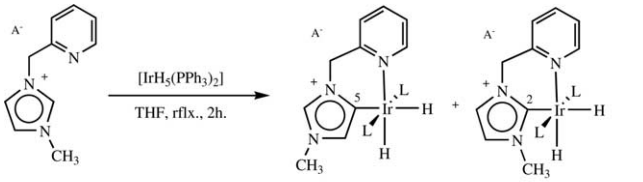
back donation. If the two C–N σ^* orbitals are the predominant π-acceptor functions of the NHC, then the situation is reminiscent of that for PX_3, where the P–X σ^* orbitals perform this function [36c]. In principle, the NHC could even be a π-donor via its filled π-orbitals.

Meyer and coworkers [37] have argued that NHCs are 'fair π-acceptors' even with such relatively weakly π-basic metals as Cu(I), Ag(I) and Au(I), although Lammertsma and coworkers [38] have argued that the NHC is a weak π-acceptor even for a much more π-basic Ir(I) fragment. The difference may only be one of rhetorical emphasis but further work is clearly needed.

NHCs are well accepted as being both higher field and higher trans effect ligands than PR_3, with the result that the characteristics of the metal's substrate binding site are altered. In going from the Grubbs phosphine to the Grubbs NHC metathesis catalyst, for example, the higher activity seems to be related to the increased tendency of the metal site to bind substrate olefin over binding phosphine, the latter also being present in the medium as a result of prior dissociation from the metal [39].

Abnormal versus normal NHCs: The vast majority of NHCs have the metal attached at C2, but in a growing class this attachment occurs at C4(5). This has most often been an unintended result, but abnormal NHCs (aNHC) have also been deliberately synthesized. Although they are more electron donor than the nNHCs, the aNHCs tend to cleave from the metal more easily so this may limit their utility in catalysis [40–42]. The existence of aNHCs means that it is no longer possible to carry out in situ metallations, as can be found in catalytic applications, with the expectation that the structure of the product will contain *n*NHCs only. In one case (Eq. (8)), the formation of aNHC versus *n*NHC was even dependent upon the counterion present in the precursor imidazolium salt: bromide favors the *n*NHC and hexafluoroantimoniate the *a*NHC [43].

These examples show that the chemistry of NHCs is more complicated than at first suspected and much more complicated than in Cp or PR_3: for example, there is no analogue of an abnormal NHC in cyclopentadienyl or PR_3 chemistry.

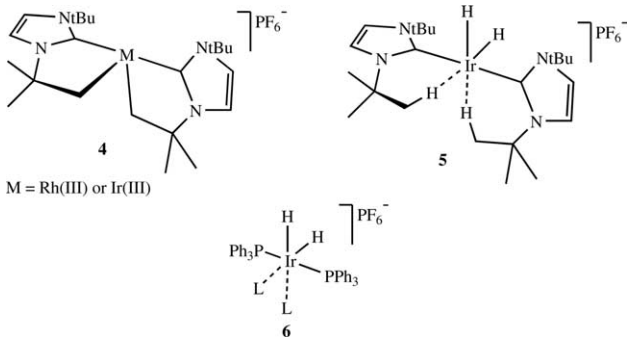


(8)

Cyclometalation: Cyclometalation, limited here to the oxidative addition of a CH bond of an R substituent on a ligand, is relatively common for phosphines and alkyl cyclopentadienes. It is normally undesired in the context of catalysis because the ligand is then no longer acting as a pure spectator. NHCs may be somewhat resistant to cyclometalation because, other than cases where a bis-imidazolium precursor was deliberately designed to chelate [23], few examples of NHC cyclometalation appears to have been reported [44]. This apparent near-immunity may be an artefact based in part on the very wide application of IMes, where the mesityl groups at N1 and N3 are stereoelectronically ill-adapted to cyclometalate. To the extent that at least partial immunity from cyclometalation proves to hold, a possible reason is that few NHC hydride complexes are known, relative to the situation for Cp and PR_3. Although the reasons for this instability are unclear, it could disfavor cyclometalation because cyclometalation products are often hydrides, as are cyclometalation intermediates in cases where some subsequent rearrangement leads to loss of the MH bond.

In a rare case of NHC cyclometalation [44a], a pyridine group attached to N3 cyclometalates at Ir(I) to give an Ir(III) hydride. This is significant because in phosphine chemistry, a benzyl substituent is specially prone to cyclometalation, presumably because a stable 5-membered ring is formed. In the NHC case, a stable 5-membered ring is formed with an aryl group at N3 because the aryl substituent is attached not to the donor atom itself, C2, but to the adjacent N3. Another probable factor favoring cyclometalation in this case is the nature of the group at N1. In phosphine chemistry, bulky groups favor cyclometalation, probably as a manifestation of the Thorpe-Ingold effect [45]. In the present case, the very bulky mesityl group located at N1 may favor cyclization via the N3 aryl.

Whittlesey et al. found that $[RuH_2(PPh_3)_3(CO)]$ reacts with free IMes at 80 °C over 14 days to cleave the *ortho*-C–Me bond and give a cyclometalation product. These conditions are probably not relevant to catalysis, however.



Nolan and coworkers [44b] have an interesting example of the bis-cyclometalation of an *N*,*N*′-bis-*tert* butyl imidazole-2-ylidene on Rh(I) and Ir(I) to give a 14e complex (**4**). The high trans effect of the alkyl–metal bonds must help keep the trans sites empty, but π donation by the NHC ligands is also invoked on the basis of DFT calculations. Reaction with H_2 [44c] cleaves the Ir–alkyl bonds to give the agostic $[IrH_2(NHC)_2]^+$ (**5**). Complex **5** is of interest as an unusual case of an NHC-hydride. In the spirit of this review, **4** and **5** also invites comparison with the analogous phosphine series: Caulton and Eisenstein's [46] agostic $[IrH_2(PR_3)_2]^+$ and our own $[IrH_2(L)_2(PR_3)_2]^+$ (**6**), where L can be a broad range of weakly binding ligands (H_2, agostic CH, acetone, IMe, etc.) [47].

2. Conclusion

As the complexity of their chemistry has become apparent, NHCs are no longer considered phosphine analogues. Nevertheless, comparison with the much better understood chemistry of phosphines can still be helpful. It can show us where deficiencies in our understanding of NHCs might most usefully be remedied. Can a Tolman-like picture of electronic and steric effects be usefully developed, for example? The multiplicity of useful ligand architectures in phosphine chemistry – chelates, pincers and tripods – gives us a range of targets. Deficiencies in our synthetic methods are obvious: potentially chelating ligands often do not in fact chelate.

Acknowledgements

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