Stabilization of Organometallic Species Achieved by the Use of N-Heterocyclic Carbene (NHC) Ligands

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This review describes the stabilization of various coordinatively unsaturated metal centers through the incorporation of N-heterocyclic carbene (NHC) ligands. Such species are more thermally stable compared to the more ubiquitous tertiary phosphane systems. Although NHCs can be considered as phosphane mimics it has become apparent that there are substantial differences between the two ligand families. In general, NHC ligands are much more electron-donating and sterically demanding than bulky phosphane ligands. We also discuss the various thermochemical and infrared studies of metal carbene species that have provided insight into NHC ligands properties, and at last allowed meaningful comparison to tertiary phosphane ligands. While NHCs are generally viewed as strong binding low reactive ligands, in some instances they have been found to be not so innocent and can undergo facile intramolecular C–H activation as well as abnormal ligand binding [C-5(4) vs. C-2]. Here we highlight such reactions with late-transition metal centers that have allowed the isolation of various unsaturated LTM species. These have so far eluded isolation in analogous phosphane-based systems.

Introductions

Since the first speculation on the existence of transient carbene intermediates in the early 1900s,[1,2] carbenes have evolved from real intermediates whose existence could be demonstrated by kinetic and trapping studies in the 1960s[3–5] to stabilized forms currently being studied in many research groups.[6–8] For the last 6 years we have been interested in the coordination of N-heterocyclic carbenes (NHCs) (imidazol-2-ylidenes, **1**; Scheme 1) to various metal centers and, like many other research groups, have found that NHCs stabilize highly reactive organometallic species.[9–13] Many of these carbene species show high catalytic activity in many metal-mediated organic transformations, e.g. ruthenium-mediated olefin metathesis,[14–19] iridium-catalyzed hydrogenation and hydrogen transfer[20–23] plati-

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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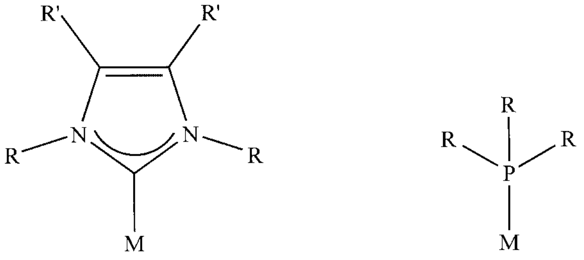
num-catalyzed hydrosilylation,[24] and palladium C–C coupling reactions;[25–28] however, the strong σ-donor nature of the ligands often results in more stable catalysts than analogous phosphane-based systems.



R = alkyl, aryl, amine, ether...

Scheme 1.

A number of studies have suggested that as ligands, nucleophilic carbenes have similar properties to electron rich trialkylphosphanes (strong σ donors with negligible π-accepting ability) (Scheme 1).[17,29–36] Yet phosphane ligands suffer from significant P–C bond degradation at elevated temperatures,[29] while NHCs have been shown to possess greater thermal stability in addition to stronger donating ability.[37] Already, the easily modified NHC ligands are highly acclaimed affording more stable, yet highly reactive, metal catalysts where phosphane analogues have been found less effective or ineffective.[15,24,28,38–44] In addition, they have allowed the stabilization of many reactive organometallic intermediates that have never been fully characterized in analogous phosphane chemistry despite the use of sterically demanding ligands.[45–47] The pioneering studies of Tolman on phosphanes have had a major impact on the development of new and improved phosphane ligands for catalysis,[48] binding studies involving carbene ligands have only just begun to shed light on this ligand class.[36,45,49–53] In this report we describe efforts directed toward the understanding of the NHC ancillary system and their ability to stabilize unsaturated late-transition metal species.

Ruthenium NHC Metathesis Catalysts

The use of more thermally stable NHC-ruthenium catalysts (**1**,[16] **2**[54] Figure 1) in olefin metathesis has resulted in the preparation of new functionalized carbocycles and heterocycles from acyclic diene precursors unattainable using Grubbs catalyst **3**[55–57] or the alkoxy imido molybdenum catalyst **4** developed by Schrock.[58] The differences in reactivity between ruthenium and molybdenum arise from the fact that carbene ruthenium complexes have a greater functional group tolerance and higher moisture and atmospheric oxygen stability relative to those of the extremely sensitive molybdenum system.[59–61]

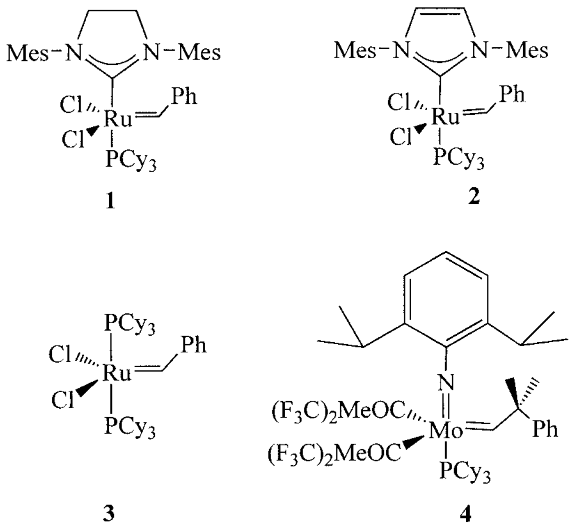


Figure 1. Olefin metathesis catalysts

We have been involved in the catalyst development efforts aimed at improving catalyst activity, functional group tolerance, and versatility for many years. In 1999 we examined electronic and steric properties of bulky NHC ligands with an unsaturated ruthenium complex and compared those results to a PCy$_3$-containing system.[15,36] The unsaturated tetrameric species [Cp*RuCl]$_4$ (Cp* = η^5-C$_5$Me$_5$)[62] rapidly reacts with sterically demanding phosphanes and various NHC ligands [Equation (1)] in THF to afford deep blue coordinatively unsaturated [Cp*Ru(PR$_3$)Cl] (R = cyclohexyl or isopropyl)[63] and [Cp*Ru(NHC)Cl] complexes. The reactions were exothermic and quantitative; facts that allowed for the determination of enthalpies of reaction by anaerobic solution calorimetry. In general, the results showed that the examined NHCs, with the exception of the sterically demanding IAd, are better donors than the best phosphane donor ligands.

$$[\mathrm{Cp^*RuCl}]_4 + 4\mathbf{L} \xrightarrow[\mathrm{r.t.}]{\mathrm{THF}} \mathrm{Cp^*Ru}(\mathbf{L})\mathrm{Cl} \qquad (1)$$

L	R		$-\Delta H_{rxn}$ (kcal/mol)	relative BDE (kcal/mol)
	cyclohexyl	ICy:	85.0(0.2)	21.2
	4-methylphenyl	ITol:	75.3(0.4)	18.8
	4-chlorophenyl	IpCl:	74.3(0.3)	18.6
	2,4,6-trimethylphenyl	IMes:	62.6(0.2)	15.6
	adamantyl	IAd:	27.4(0.4)	6.8
PCy$_3$:			41.9(0.2)	10.5
P*i*Pr$_3$:			37.4(0.3)	9.4

These enthalpy values can be converted into relative bond dissociation enthalpies (BDE) on the basis of a mol of product and clearly indicate that NHCs are better donor ligands than PCy$_3$ in the [Cp*Ru(L)Cl] system. To further verify the thermochemical results, ligand exchange reactions between [Cp*Ru(PCy$_3$)Cl] and IMes or ICy were examined and indeed the formation of free PCy$_3$ and [Cp*Ru(PCy$_3$)Cl] was observed [Equation (2)].

$$\mathrm{Cp^{*}Ru(PCy_3)Cl} + \mathrm{NHC} \xrightarrow[\text{r.t.}]{\text{THF}} \mathrm{Cp^{*}Ru(NHC)Cl} + \mathrm{PCy_3} \qquad (2)$$

NHC = IMes, ICy

The next step in our physicochemical studies was to examine whether this ligand substitution pattern was also valid for a catalytically related system: Ruthenium-based olefin metathesis. This did indeed proved feasible. The better donor ability of the NHC ligands (not including IAd) in supporting activity in metathesis-active ruthenium systems is thought to have a steric and an electronic component.

After our initial studies had been reported, Fürstner and Hermann[64] studied substitution effects on catalytic behavior (Figure 2). They observed that **7** and **8** bearing benzylic residues on the carbene ligands exhibit the lowest activity, whereas high activity was displayed for **5** and **6**. This result is in contrast to the behavior of **1**, in which replacement of PCy_3 by $P\mathit{i}Pr_3$ results in a noticeable loss of catalytic activity. As we had observed, complexes bearing only one NHC ligand (**10**, **11**) showed significantly higher activity compared to bis-NHC systems. Mechanistically, since the Ru–NHC is a stronger bond than the Ru–PCy_3 bond, the mixed PR_3/NHC ligand system would proceed by phosphane ligand displacement if a dissociative-type pathway, leading to the active catalyst, is at play.[15,36] Another interesting result is that despite changing halogens in complexes **6** and **9** no difference in catalytic activity was observed. This result contrasts reactivity pattern for **1** where a decrease in activity from chloride to bromide to iodide was observed.[56]

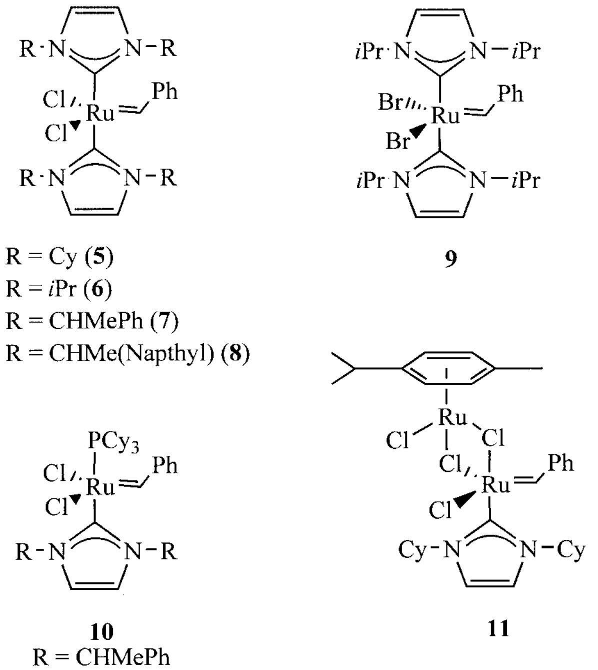
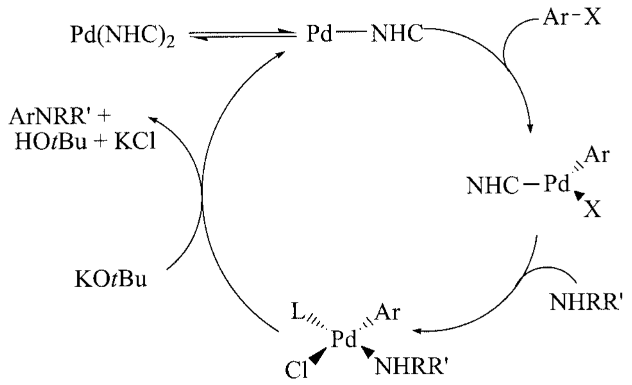


Figure 2. Substitution effects in Ru–NHC metathesis systems

Much work has been and continues to be published in the area of ruthenium-based olefin metathesis since our initial observation of the beneficial use of NHC as supporting ligand. A fundamental understanding of the sterics and electronic properties of the ligands themselves proved invaluable. To say that these results provided a systematic ligand design approach would be incorrect but surely assisted our ligand exploration.

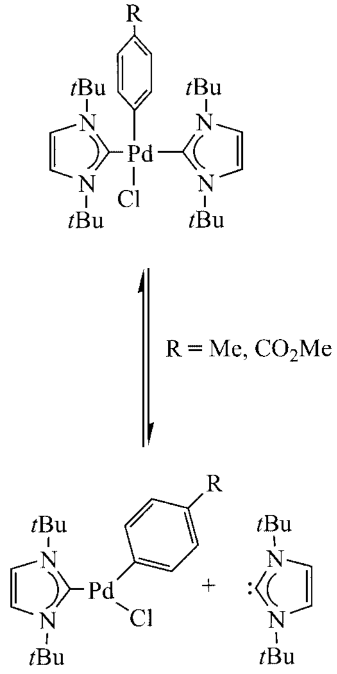
Palladium(0) NHC Complexes

The stability imparted by the NHC ligands to metal centers is further observed in palladium chemistry with the preparation of efficient catalysts that have been shown to possess considerable potential in many C–C bond forming reactions, which have included the Heck reaction,[65–69] the telomerization of alkenes[43,70,71] and the Suzuki–Miyaura cross-coupling reaction.[72–75] These Pd-mediated processes have been shown to proceed through a d^{10}-Pd^0 center. In particular, recent work by Hartwig,[76,77] Cloke[78] and Nolan[79] on reactions involving Ar–X with the precatalyst $[Pd(NHC)_2]$ suggest dissociation of one NHC to generate a PdL fragment, which then undergoes oxidative addition of aryl halide (Scheme 2), a reaction pathway similar to that proposed in analogous phosphane systems.[76,80,81]



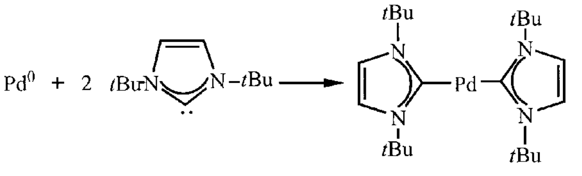
Scheme 2. Proposed mechanism for aryl amination.

While Amatore and Jutand[82] proposed an alternative route for phosphane palladium-catalyzed systems through an anionic three-coordinate complex of the type $[Pd^0L_2Cl]^-$ or $[Pd^0L_2(OAc^-)]$ as the active intermediate, detailed kinetic studies by Cloke suggest that oxidative addition reactions occur via a two-coordinate 14-electron $[Pd^0$-NHC] complex.[83] Furthermore, the ability of the oxidative addition products $[Pd(I\mathit{t}Bu)_2(R\text{-}4\text{-}C_6H_4)Cl]$ (R = Me, CO_2Me, OMe) to reversibly dissociate free carbene according to Scheme 3 was demonstrated. The Pd–NHC dissociation enthalpy value of 25.57 $kcal/mol^{-1}$ for $[Pd(I\mathit{t}Bu)_2(Me\text{-}4\text{-}C_6H_4)Cl]$ was determined suggesting that the three-coordinate arylpalladium chloride product was the most likely intermediate in amination reactions.

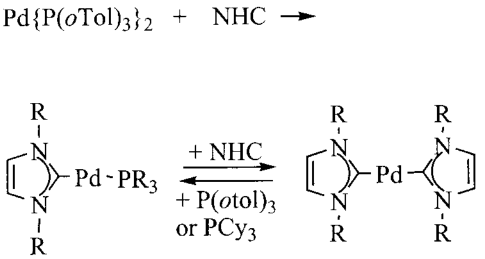


Scheme 3.

Studies by Hermann on the Heck reaction with [$Pd(NHC)_2$] also suggest the intermediacy of this same Pd–L complex.[66] Hermann noticed short induction periods for Pd^{II} complexes on addition of a reducing agent. However, when Pd^0 was used no induction period was observed suggesting Pd^0 complexes enter in the catalytic cycle faster. Despite an increasing interest in this area over the last 5 years, there are only a few examples of fully characterized Pd^0-carbene complexes.[67,68,70,74,84–86] The isolation of two-coordinate unsaturated NHC Pd^0 complexes was first achieved by Cloke and co-workers.[84] While they prepared a homoleptic [$Pd(ItBu)_2$] (ItBu = 1,3-di-*N*-*tert*-butylimidazol-2-ylidene) complex by co-condensation palladium vapor with *N*,*N*′-di-*tert*-butylimidazol-2-ylidene (I*t*Bu). This route was low yielding and limited to NHC ligands that could be sublimed [Equation (3)]. A ligand exchange reaction between [$Pd(PR_3)_2$] (R = *o*-tolyl) and two equivalents of free NHC afforded [$Pd(NHC)_2$] in higher yields. Furthermore addition of only one NHC equivalent to [$Pd(PR_3)_2$] (R = *o*-tolyl) resulted in a mixed [$Pd(PR_3)(NHC)$] species [Equation (4)]. Alternatively, the synthesis of mixed species can also be generated by mixing the [$Pd(NHC)_2$] complex with free phosphane [$P(o\text{-tolyl})_3$, PCy_3], suggesting some reversibility is associated with the reaction.[87,88]

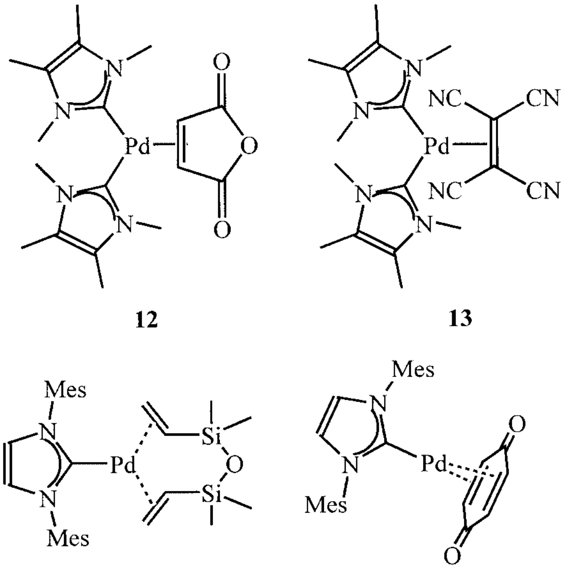


(3)



(4)

The derivatives are readily prepared from reaction of [Pd(COD)(alkene)] (COD = cyclooctadiene) with the NHCs [1,3,4,5-tetramethylimidazol-2-ylidene (IMe) and IMes] to afford the complexes [$Pd(IMe)_2$(alkene)] [alkene = maleic anhydride (MAH) (**12**), tetracyanoethylene (TCNE) (**13**)] (Figure 3).[67] Spectroscopic studies showed significant back-bonding of the olefin on the Pd center suggesting that the carbene ligands are strongly donating. Although **12** and **13** are envisaged as approaching Pd^{II} these complexes readily undergo oxidation reactions typical of Pd^0.



12 **13**

14 **15**

Figure 3. NHC–Pd^0 complexes

Reports of monocarbenepalladium(0) complexes without additional phosphane donors are scarce. Beller et al. recently synthesized a number of monocarbene(diolefin)palladium(0) complexes.[68,69] The addition of IMes to either palladium(0)–diallyl ether complex [$Pd_2(dae)_3$] (dae = diallyl ether) in 1,1,3,3-tetramethyl-1,3-divinyldisiloxane or [(COD)Pd(quinone)] [quinone = *p*-benzoquinone (BQ), 1,4-naphthoquinone (NQ)] at low temperatures afforded the complexes [(IMes)Pd(dae)] (**14**), [(COD)Pd(BQ)] (**15**) and [(COD)Pd(NQ)] (**16**), respectively. Complexes **14**–**16** showed remarkable productivities and selectivity in a number of telomerization and Heck reactions, again concluding that the active species in carbene Pd-mediated organic transformations appears to be a Pd^0-carbene center.

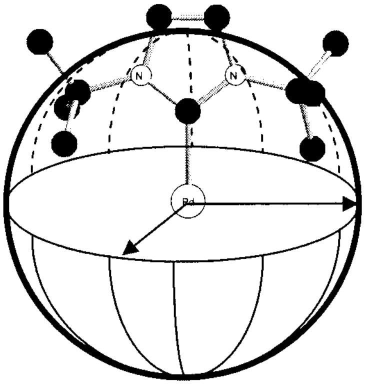
Steric Factors of NHC in Palladium(II) Complexes

Recently we reported the synthesis and cross-coupling catalytic reactivity of a family of [(NHC)Pd(allyl)Cl] complexes (Scheme 4).[50] These were synthesized either through addition of two equivalents of free carbene to [Pd(allyl)-Cl]$_2$ under inert atmosphere (an adapted procedure from a protocol employed in the preparation of [(PCy$_3$)Pd(allyl)-Cl][89]) or by an in situ liberation of the imidazolium salts, followed by slow addition of [Pd(allyl)Cl]$_2$. The catalytic reactivity of these [(NHC)Pd(allyl)Cl] complexes varied substantially as a function of the identity of the NHC. While electronic differences were ruled out after crystallographic evidence showed little to no difference in the Pd–C$_{carbenic}$ bond lengths, this suggested that steric factors associated with the saturated and unsaturated imidazole backbone and side arm groups on the NHC were involved.

Prompted by this, we undertook a detailed investigation focusing on the steric factors of NHC ligands. The use of the classical "cone angle" steric factor described by Tolman for phosphane ligands[48] cannot be applied to the "fence"- or "fan"-type NHCs. Instead a wing-span model was conceptualized taking into account the wing-span angle (closest carbon substituent on the NHC) to the palladium center. This intial model was recently refined by imposing a sphere of radius (3 Å) centered around the palladium atom and the volume occupied by the ligand determined (Table 1) was then taken as the steric factor associated with any given NHC. Recently, a similar method was used to estimate the steric factor for a series of ruthenium-NHC complexes.[90]

By quantifying the steric demand of each NHC in these complexes, this has allowed a realistic comparison, not only between NHCs but also to tertiary phosphane ligands. The most sterically demanding I*t*Bu, IAd and SIPr ligands resulted in a decreased activity in the studied amination reaction. Furthermore IPr and IMes showed marked differences in reactivity compared to their saturated analoges SIPr and SIMes in spite of having almost identical structures. We associated this difference to the presence of two sp^3 carbon atoms inducing deformation of the dihydroimidazol-2-ylidene ring resulting in supplementary rotation of the aryl moieties around the N–C$_{aryl}$ bond. As a consequence, the Pd center is more sterically protected, thereby presumably facilitating reductive elimination in Scheme 2.

Table 1. Buried volume calculated for [(NHC)Pd(allyl)Cl] complexes.

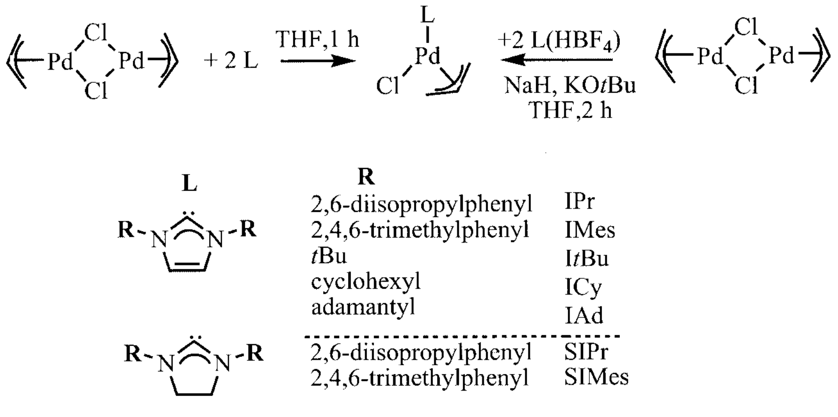


Complex	Buried volume[a] (%)	Buried volume[b] (%)
[(IPr)Pd(allyl)Cl]	26.10	24.99
[(IMes)Pd(allyl)Cl]	26.50	25.87
[(I*t*Bu)Pd(allyl)Cl]	33.37	32.25
[(ICy)Pd(allyl)Cl]	25.17	23.90
[(IAd)Pd(allyl)Cl]	33.56	32.20
[(SIPr)Pd(allyl)Cl]	33.03	32.27
[(SIMes)Pd(allyl)Cl]	27.49	26.91

[a] Calculated buried volume for a fixed distance Pd–C$_{carbenic}$ of 2 Å. [b] Buried volume calculated based on crystallographic distances.

Carbonyl NHC Nickel Complexes

The importance of quantifying steric and electronic effects of ligands have had a major impact in the development of new and improved phosphane ligands for catalysis.[48] In the case of the NHC ligands surprising differences in catalytic activities of the corresponding metal catalysts have already been observed, but could not be rationalized or explained experimentally. Although many spectroscopic studies have indicated the similarities between NHCs and phos-



R	
2,6-diisopropylphenyl	IPr
2,4,6-trimethylphenyl	IMes
*t*Bu	I*t*Bu
cyclohexyl	ICy
adamantyl	IAd
2,6-diisopropylphenyl	SIPr
2,4,6-trimethylphenyl	SIMes

Scheme 4.

phane, we felt that it was important to experimentally determine properties associated with the most widely used NHCs (depicted in Scheme 5). This would then allow for the direct comparison of NHC and phosphane steric/electronic properties.

The substitution reaction involving [Ni(CO)$_4$] and NHC ligands (IMes, SIMes, IPr, SIPr, ICy) gave rise to the expected, saturated complexes [Ni(CO)$_3$(IMes)], [Ni(CO)$_3$(SIMes)], [Ni(CO)$_3$(IPr)], [Ni(CO)$_3$(SIPr)], [Ni(CO)$_3$(ICy)] (Scheme 5), [Equation (5)].[49] However, the most bulky NHC ligands, I*t*Bu and IAd, led to the isolation of novel, unsaturated three-coordinate carbonyl nickel compounds [Ni(CO)$_2$(I*t*Bu)] and [Ni(CO)$_2$(IAd)].[91]

$$\mathrm{Ni(CO)_4 + NHC \xrightarrow[-CO]{} (NHC)Ni(CO)_3 \text{ or } (NHC)Ni(CO)_2} \qquad (5)$$

X-ray characterization was obtained for most of the [Ni(CO)$_3$(NHC)] series and for both [Ni(CO)$_2$(NHC)] complexes (see below for discussion). Ball-and-stick diagrams of [Ni(CO)$_3$(IMes)] and [Ni(CO)$_3$(SIMes)] are presented in Figure 4 and [Ni(CO)$_3$(IPr)] and [Ni(CO)$_3$(SIPr)] in Figure 5. All complexes show the expected tetrahedral geometry around the metal center, with the Ni–C(NHC) bond lengths lying within the range of 1.96–1.98 Å {[(Ni(CO)$_3$(IMes)] 1.971(3) Å; [Ni(CO)$_3$(SIMes)] 1.960(2) Å; [Ni(CO)$_3$(IPr)] 1.979(2) Å; [Ni(CO)$_3$(SIPr)] 1.962(4) Å}. The saturated NHC ligands SIMes and SIPr showed slightly shorter bond lengths than their corresponding analogues containing the unsaturated NHC ligands. However, all the Ni–NHC distances are in good accordance with their exclusive σ donor characteristics.[67,92] As observed in other crystallographic studies on saturated NHC species, the presence of two sp^3 carbon atoms in the heterocyclic ring imidazole backbone, results in torsion angles of 6.4° {for [Ni(CO)$_3$(SIMes)]} and 2.6° {for [Ni(CO)$_3$(SIPr)]}. Surprisingly, the former value is significantly lower than the one for free SIMes (13.4°). The unsaturated NHCs have the aryl substituents disposed at an angle of 90° (+/–10°) with respect to the imidazole backbone plane.

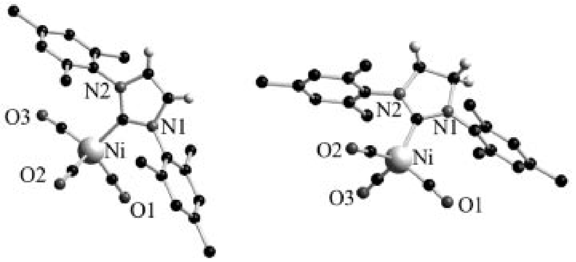


Figure 4. Ball-and-stick representation of [Ni(CO)$_3$(IMes)] (left) and [Ni(CO)$_3$(SIMes)] (right).

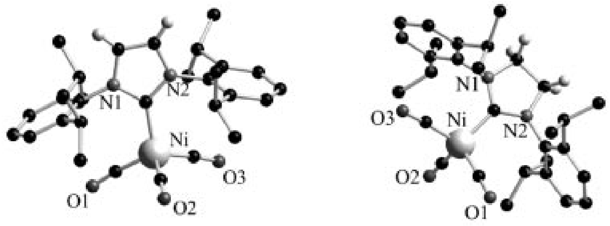
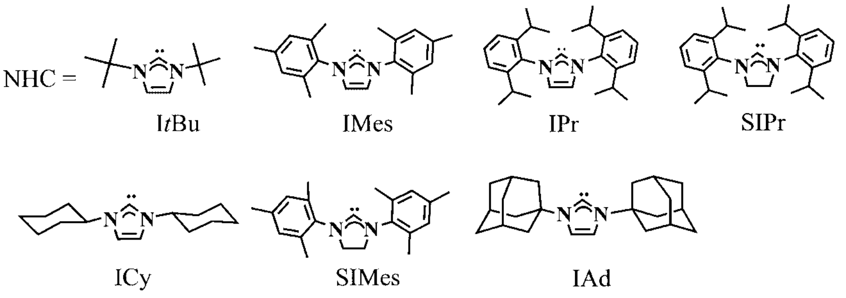


Figure 5. Ball-and-stick representation of [Ni(IPr)(CO)$_3$] (left) and [Ni(SIPr)(CO)$_3$] (right).

The CO infrared frequencies obtained for the [Ni(CO)$_3$(NHC)] complexes confirmed that N-heterocyclic carbenes are better σ donors than tertiary phosphanes (Table 2). Unlike the substantial electronic differences seen in phosphane ligands when moving from ary- to alkyl-substituted P ligands, the overall electronic difference in NHC data was relatively small. Expectably the NHC data showed that ICy was the most basic ligand due to its alkyl substitution. Furthermore, the saturated NHC ligands, SIMes and SIPr, were found to be slightly less electron-donating than their unsaturated analogues IMes and IPr. This supports our recently observed trends in the relative bond disruption enthalpies of ruthenium complexes involving the aforementioned ligands.[90] These experimental results clearly contradict the common assumption that saturated NHC ligands are more electron-donating and that metal complexes incorporating them perform better in catalysis for this reason. Our experimental data suggest that electronic factors are unlikely to play a major role in the differences in catalytic activity, or if this is indeed the case, substantial differences



Scheme 5.

take origin in extremely small electronic differences within the NHC ligand class.

Table 2. CO infrared frequencies in $[Ni(CO)_3(L)]$ complexes.

Complex	ν_{CO} [A_1 (cm^{-1})]; CH_2Cl_2	ν_{CO} [E (cm^{-1})], CH_2Cl_2
$[Ni(CO)_3(IMes)]$	2050.7	1969.8
$[Ni(CO)_3(SIMes)]$	2051.5	1970.6
$[Ni(CO)_3(IPr)]$	2051.5	1970.0
$[Ni(CO)_3(SIPr)]$	2052.2	1971.3
$[Ni(CO)_3(ICy)]$	2049.6	1964.6
$[Ni(CO)_3(PtBu_3)]$[a]	2056.1	1971
$[Ni(CO)_3(PiPr_3)]$(a)	2059.2	1977
$[Ni(CO)_3(PPh_3)]$[a]	2068.9	1990

[a] Taken from ref.[48]

As previously mentioned the most bulky NHC ligands, I*t*Bu and IAd, led to the isolation of novel, unsaturated 16-electron three-coordinate carbonyl nickel compounds $[Ni(CO)_2(ItBu)]$ and $[Ni(CO)_2(IAd)]$ (Figure 6).[91] While carbonyl-free, three-coordinate Ni^0 complexes are not uncommon,[93–95] such unsaturated carbonyl nickel systems are exceedingly rare and the only example known in literature has been isolated as a mixture of $[Ni(CO)_3(L)]$ and $[Ni(CO)_2(L)]$ compounds.[96–102] The closest carbon atom on one of the side-arm R groups in $[Ni(CO)_2(NHC)]$ appears to approach the metal center. However, the distances lie outside the range seen for agostic interactions.[103,104] In fact, within the series of NHCs studied these two ligands are the only ones to contain α-carbon atoms in the side chains that are bound to three additional C atoms. While the aromatic IMes, SIMes, IPr and SIPr as well as ICy can minimize steric interactions with the metal center by orientation of their R-groups perpendicularly to the imidazole plane, such an arrangement cannot be reached for IAd and I*t*Bu.

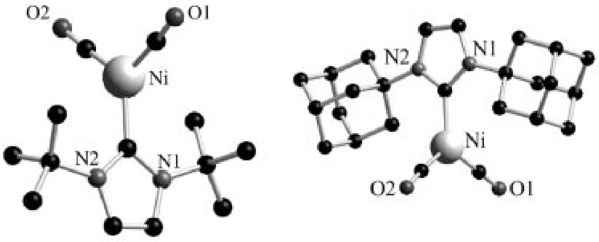


Figure 6. Ball-and-stick representation of $[Ni(CO)_2(ItBu)]$ (left) and $[Ni(CO)_2(IAd)]$ (right). Hydrogen atoms are omitted for clarity.

According to Equation (5), Ni–NHC bond energies could be determined if the reaction was reversible. For saturated complexes $[Ni(CO)_3(NHC)]$ no reactivity was observed, despite applying high CO pressures, showing these complexes to be inert towards displacement of NHC and carbonyl ligands. In contrast, the unsaturated analogues were highly reactive towards ligand substitution and oxidative addition of substrates. Reacting $[Ni(CO)_2(ItBu)]$ and $[Ni(CO)_2(IAd)]$ with 1 atm of CO resulted in the quantitative formation of $[Ni(CO)_4]$,[105] without any formation of $[Ni(CO)_3(NHC)]$ (NHC = I*t*Bu, IAd) complex and thus, allowed the determination of Ni–NHC bond dissociation energies (Table 3).

Table 3. CO and L BDE values, in kcal/mol, in the $[Ni(CO)_2(L)]$ and $[Ni(CO)_3(L)]$ complexes, L = NHC ligand or phosphane, and calculated $\%V_{Bur}$ of the free NHC and PR_3 ligands.

			BDE of L in $Ni(CO)_2(L)$	$\%V_{Bur}$
I*t*Bu	13.3 (15.6)[a]	24.0	44.3	37
SI*t*Bu	10.3 (13.1)[a]	21.8	45.1	38
IAd	7.6 (14.1)[a]	20.4	46.5	37
IMes	28.3 (27.2)[a]	41.1	46.5	26
SIMes	26.8 (26.4)[a]	40.2	47.2	27
IPr	26.7 (27.2)[a]	38.5	45.4	29
SIPr	25.6 (25.8)[a]	38.0	46.1	30
ICy	27.0 (26.1)[a]	39.6	46.3	23
PH_3	30.7	22.7	25.7	17
PPh_3	30.4	26.7	30.0	22
$PtBu_3$	27.4	28.0	34.3	30

[a] Values in brackets obtained with the QM/MM technique.

DFT-calculated BDE values indicated that CO is weakly bound to the SI*t*Bu-, Si*t*Bu- and IAd-based complexes (BDE around 10 kcal/mol). However, CO is much more strongly bound to the IPr, SIPr, ICy, IMes and SIMes complexes (BDE greater than 25 kcal/mol). These results are in good qualitative agreement with the experimental fact that $[Ni(CO)_2(NHC)]$ complexes are observed for NHC = IAd and I*t*Bu, while $[Ni(CO)_3(NHC)]$ complexes are observed for the other NHC ligands. Calculated BDE of the NHC ligands showed a similar pattern, with BDE of NHC ligands in the SI*t*Bu-, Si*t*Bu- and IAd-based $[Ni(CO)_3(NHC)]$ complexes roughly 20 kcal/mol lower than the BDEs of the NHC ligand in the IMes, SIMes, IPr, SIPr and ICy complexes. Furthermore, the calculated BDE of the NHC ligand in $[Ni(CO)_2(ItBu)]$ and $[Ni(CO)_2(IAd)]$ (46.5 and 44.3 kcal/mol, respectively) are in excellent agreement with the experimental values (43 ± 3 and 39 ± 3 kcal/mol, respectively). The BDE values were experimentally tested by treatment of $[Ni(CO)_2(ItBu)]$ with one equivalent of IAd [Equation (6)]. Quantitative formation of $[Ni(CO)_2(IAd)]$ was observed with no detection of the saturated, but sterically disfavored, $[Ni(CO)_2(IAd)(ItBu)]$ species.

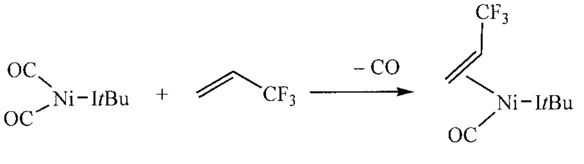
$$Ni(ItBu)(CO)_2 + IAd \rightleftharpoons Ni(IAd)(CO)_2 + ItBu \quad (6)$$

In view of the wing-span model seen to describe the steric influence of NHC ligands for palladium (see above), we have now used DFT-optimized geometry studies to extend this model for a greater number of free NHC ligands and again positioned a putative metal atom at 2 Å from the coordinating C atom. The volume as a sphere centered on the metal was measured, buried by overlap with atoms of the various NHC ligands, $\%V_{Bur}$. The volume of this sphere represented the space around the metal atom that must be shared by the different ligands upon coordination. For example bulkier NHC ligands require a larger occupied sphere volume ($\%V_{Bur}$). A list of $\%V_{Bur}$ values is presented in Table 3. The rather different values of $\%V_{Bur}$ between the

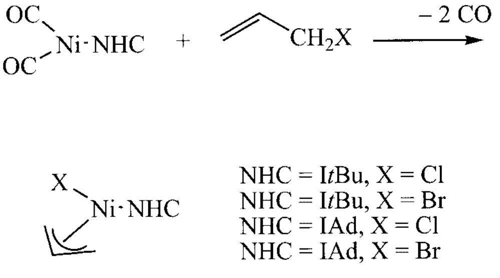
NHC ligands is in qualitative agreement with the different BDEs we calculated.

Unlike data obtained for NHC, the similar carbonyl values for the phosphane-based systems (Table 3) clearly indicated that the steric factor's influence is insignificant in determining the stability of the $[Ni(CO)_3(PR_3)]$ systems. Furthermore, comparison of the BDE of the CO values between the less bulkier NHC systems and the phosphane systems suggest a high stability of the phosphane-based tricarbonyl complexes. The remarkably higher BDE of the NHC–Ni systems vs. the BDE of the PR_3-Ni complexes is in good agreement that NHC ligands bind more tightly to transition metals.

Since the difference between $[Ni(CO)_3(NHC)]$ and $[Ni(CO)_2(NHC)]$ complexes was attributed to steric factors alone, a substitution reaction between $[Ni(CO)_2(NHC)]$ (I*t*Bu, IAd) and two equivalents of smaller NHC ligands, IMes and ICy, afforded the saturated complexes of general composition $[Ni(CO)_2(NHC)_2]$.[53] Other reactions showed that substitution of one carbonyl ligand when reacting $[Ni(CO)_2(NHC)]$ with trifluoropropene was possible and selectively afforded the unsaturated $[Ni(NHC)(CO)(C_3H_3F_3)]$ compound [Equation (7)]. Furthermore both CO ligands were displaced when $[Ni(CO)_2(NHC)]$ was treated with either allyl chloride or allyl bromide [Equation (8)]. The resulting allyl halide complexes of general formula $[NiX(C_3H_5)(NHC)]$ were obtained through oxidative addition of these substrates to the Ni^0 center.[49]



(7)

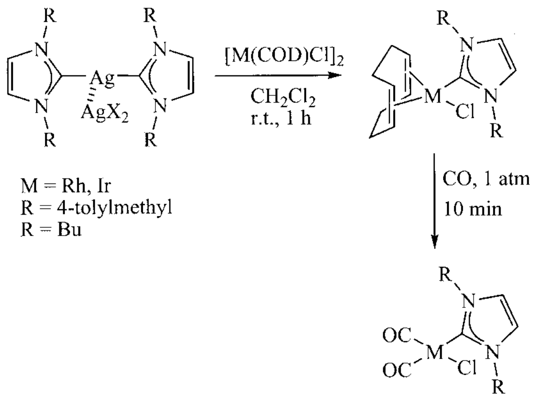


(8)

Overall, the performed DFT calculations on the series of $[Ni(L)(CO)_2]$ and $[Ni(L)(CO)_3]$ compounds (L = NHC, PR_3) are supported by experimental results, with the calculations showing that both $[Ni(IAd)(CO)_3]$ and $[Ni(ItBu)(CO)_3]$ are inherently unstable as seen in the BDE values for both the CO and NHC ligands. The lower PR_3–Ni BDE values compared to NHC–Ni are in agreement with the common assumption that NHC ligands bind more tightly to metals. The establishment of a method to quantify the steric factors characterizing NHCs and phosphanes has at last been realized, finally enabling a direct comparison between these ligand classes. The values for the different ligands are measured as buried volume ($\%V_{bur}$). All of these values obtained are in perfect agreement with experimental data, showing that IAd and I*t*Bu are more bulky than $P(tBu)_3$ and other PR_3 and NHC ligands.

NHC Late-Transition Metal (LTM) Carbonyl Complexes

A recent study by Crabtree et al. also confirmed the stronger electron-donor properties of NHC ligands.[52] In lieu of using the synthetic approach of direct complexation of the free NHC to rhodium or iridium centers, a transmetalation reaction from the corresponding silver NHC salt to $[M(COD)Cl]_2$ (M = Rh, Ir) afforded the complexes [(TMIY)Rh(COD)Cl] [TMIY = 1,3-bis(4-tolylmethylimidazolin-2-ylidene], [(TMIY)Ir(COD)Cl] and [(IBu)Ir(COD)Cl] (IBu = 1,3-dibutylimidazolin-2-ylidene) in high yield (Scheme 6). COD was easily displaced from these complexes by CO (1 atm) to give the corresponding dicarbonyl compounds $[(TMIY)RhCl(CO)_2]$ (**18**), $[(TMIY)IrCl(CO)_2]$ (**19**) and $[(IBu)IrCl(CO)_2]$ (**20**) with CO (atm).



18, M = Rh, R = 4-tolylmethyl
19, M = Ir, R = 4-tolylmethyl
20, M = Ir, R = Bu

Scheme 6.

A mutually *cis* geometry of the carbonyl groups for complexes **18**–**20** was proposed despite ^{13}C NMR spectroscopy revealing two inequivalent CO carbon atoms. ^1H NMR spectroscopy supported the *cis* geometry with diastereotopic N–CH_2 protons. Low-temperature NMR studies on **18** and **19** showed that the metal–carbon bond had restricted rotation. The activation free energies for metal–carbene bond rotation in **18** and **19** [$\Delta G^‡$(kcal·mol) 16.7 and 15.7, respectively] closely agreed to those of Doyle and Lappert[106] on **21** ($\Delta G^‡$ = 16 kcal/mol) (Figure 7). Previous studies have strongly indicated that no electronic rotation barrier exists for NHCs. For the sterically crowded systems (**22**,[107] **23**[108] and **24**[109]) no M–C rotation at room temperature was evident. However, studies by Ender and Gielen[110] on **25** and **26** directly supported a steric origin to the rotation barrier, with **25** showing no rotation at room temperature, whereas a lower rotational barrier was observed for **26**.

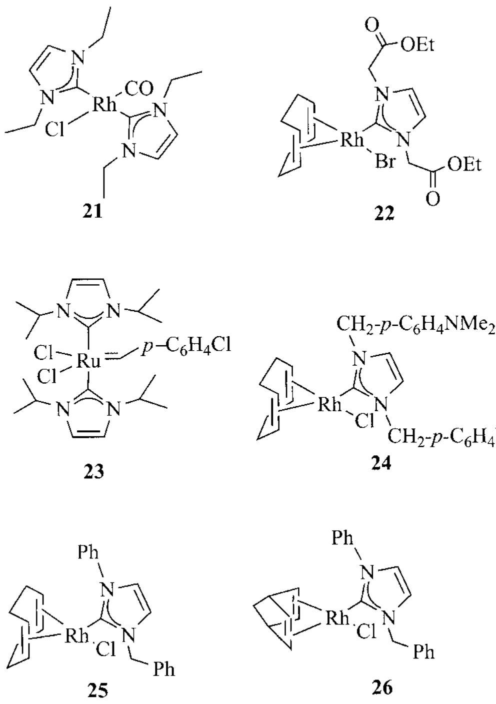


Figure 7. NHC complexes containing a low-energy rotational barrier.

Compounds **19** and **20** were investigated using FT-IR spectroscopy. A plot (Figure 8) of the average ν(CO) values for **19** and **20** together with the ν(CO) data for structurally analogous phosphane compounds $[Ir(PR_3)Cl(CO)_2]$[111,112] were plotted vs. the Tolman electronic parameter (TEP). Also included are the ν(CO) frequencies obtained for the $[Ni(CO)_3(NHC)]$ system described above. The plot shows a good linear correlation on exclusion of phosphite ligands. The IR data indicate that the NHCs listed are more electron donating than even the most basic phosphane ligand. This correlates well to other studies by Crabtree,[113] and with our own studies on $[Ni(CO)_x(NHC)]$ (x = 2,3) systems, in addition to the already discussed calorimetric investigation on ruthenium–NHC compounds.[90] Furthermore, a qualitative comparison of IR data obtained with our rhodium–NHC compound also supports this conclusion.[114]

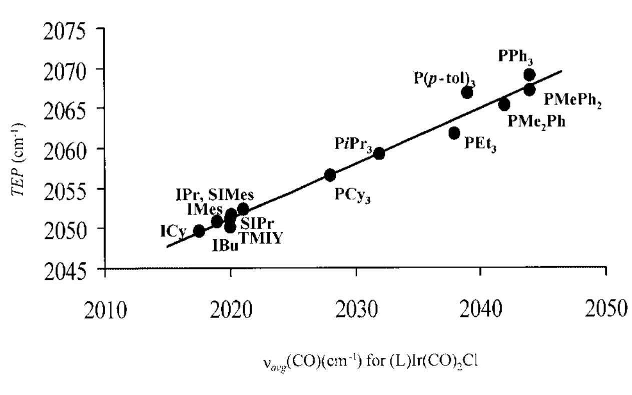


Figure 8. Plot of average ν_{CO} for $LIr(CO)_2Cl$ (L = NHC, PR_3) vs. ν_{CO} for $LNi(CO)_3$, the Tolman electronic parameter (TEP).

Abnormal Binding Modes for NHC Ligands

There have been an increasing number of reports of unexpected late-transition metal products with NHC ligands ranging from unusual binding modes to oxidative addition through C–H bond activation of alkyl side-arm substituents suggesting that these spectator ligands are much less innocent than originally thought. While previous examples in this review show normal metal binding at C-2 (Figure 9, **I**), abnormal C-5(4) (Figure 9, **II**) binding has now been reported.[115–118] The C-5(4) binding mode was previously considered as an unlikely binding possibility because free carbenes isolated by Arduengo et al.[119] always adopted a C-2 binding mode (Figure 9, **III**) with adjacent nitrogen atoms considered as stabilizing both the free carbene (Figure 9, **I**) and the M–C bond.

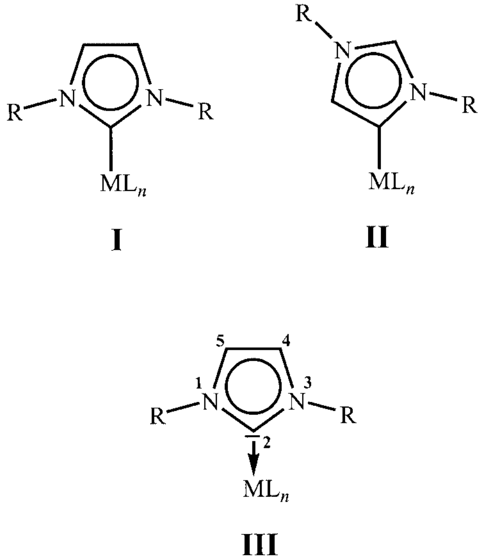
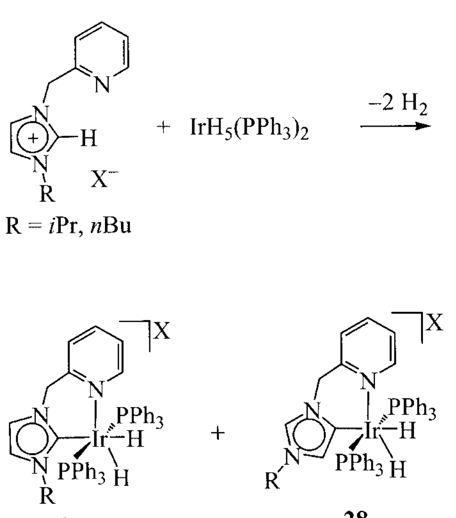


Figure 9. Alternative binding modes of NHC.

Nonclassical carbene formation has been obtained initially from mixing pyridine-substituted imidazolium salts (py-NHC) with $[IrH_5(PPh_3)_2]$ in refluxing C_6H_6. Subsequent loss of H_2 afforded complexes of general composition $[(py\text{-}NHC)IrH_3(PPh_3)_2]$ in moderate yield [Equation (9)].[115] The isolation of these first examples of C-4(5)-bound carbenes was surprising since not only **II** is more stable than **III**, but theoretical and density functional calculations[120] predict that binding at the C-4(5) position can be thermodynamically less favored (23.3 kcal/mol) than C-2 coordination.

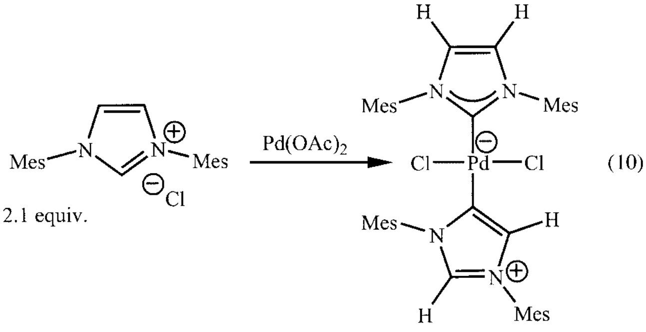
In general, it is thought that C-4(5) binding is favored as a result of lower steric congestion around the metal center. Since the C-4(5) binding mode has only been isolated to date using limited variation in the imidazolium salts, the nature of the counterion (X = Br, BF_4, PF_6, SbF_6; R = Me, *i*Pr) was studied and indicated that it has a pronounced effect on the kinetic activity of C-2 vs. C-5(4) binding switching the kinetic product between **27** and **28** [Equation (9)]. The use of bromide afforded almost quantitative yields of C-2-bound iridium(III) NHC product **27**, while SbF_6 re-



27 **28**

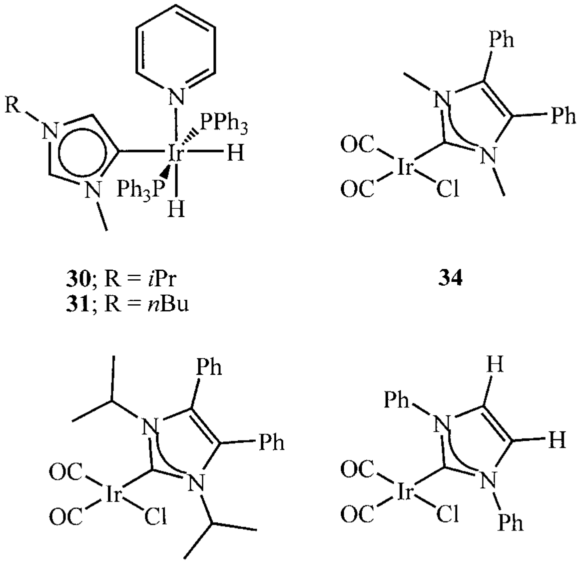
sulted in the formation of the abnormal C-4(5)-bound **28** as the major product.[121]

Until recently C-4(5) binding was only linked to chelating N-heterocyclic carbenes, and as a result it was reasoned to be mainly due to steric effects.[116] Lebel et al. recently isolated a [(IMes)(IMes′)PdCl$_2$] complex containing both C-2 and C-4(5) NHC ligands in high yield by reaction of palladium(II) acetate and the imidazolium salt IMes·HCl [Equation (10)] under standard reaction conditions (dioxane, 80 °C, 6 h).[118] In comparison, the C-2 ligated [(IMes)$_2$PdCl$_2$] could be obtained from PdCl$_2$, Cs$_2$CO$_3$, and 2 equivalents of IMes·HCl in high yield. However, complex **29** was found to have greater catalytic activity for Suzuki–Miyaura and Heck coupling reactions suggesting that this binding mode results in complexes with enhanced reactivity.



29

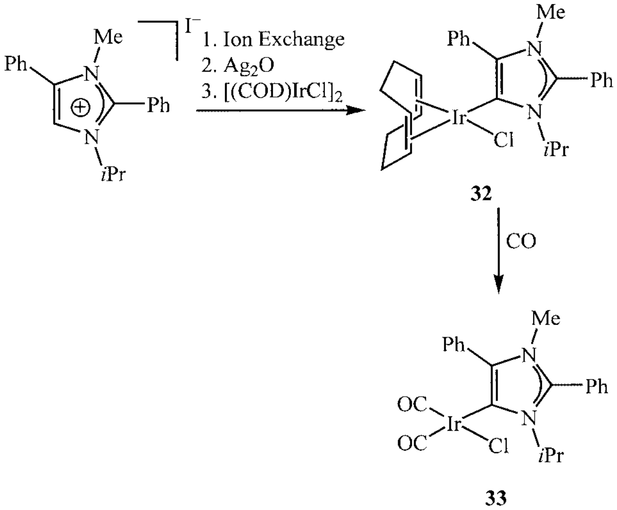
Recent studies by Crabtree et al.[117] on the electronic and steric properties of this abnormal C-4(5) coordination mode for a series of NHCs (in which the C-2 position has been blocked in one case) have allowed a useful comparison between the abnormal to the normal binding modes. Monodentate abnormal NHC iridium(III) complexes **30** and **31** were synthesized by refluxing their corresponding simple unsymmetrical imidazolium salts, pyridine and [IrH$_5$(PPh$_3$)$_2$] in tetrahydrofuran (Figure 10).



30; R = *i*Pr
31; R = *n*Bu
34
35
36

Figure 10. Monodentate abnormal (**30**, **31**) and normal (**34**–**36**) iridium complexes.

A more sophisticated route was developed by blocking the C-2 and C-4(5) positions with a phenyl group [NHC = 1-isopropyl-3-methyl-4,5-diphenylimidazolin-2-ylidene (PMINHC)] to generate the C-4(5) metal complex.[117] A transmetalation reaction between the silver salt of PMINHC and [(COD)IrCl]$_2$ resulted in the C-4(5)-bound complex [(PMINHC)Ir(COD)Cl] (**32**). Reaction of **32** with CO yielded [(NHC)Ir(CO)$_2$Cl] (**33**) (Scheme 7).



Scheme 7.

A plot of the IR ν(CO) measurements on the abnormal C-4(5)-bound derivative **33** (Figure 11) indicated that the NHC is substantially more electron donating than C-2-bound analogues (**34**–**36**, Figure 12) in addition to ν(CO) data for the [(NHC)Ni(CO)$_3$] system described above.[49] However, more data is clearly warranted to quantify the stronger donor properties of this C-4(5)-bound carbene.

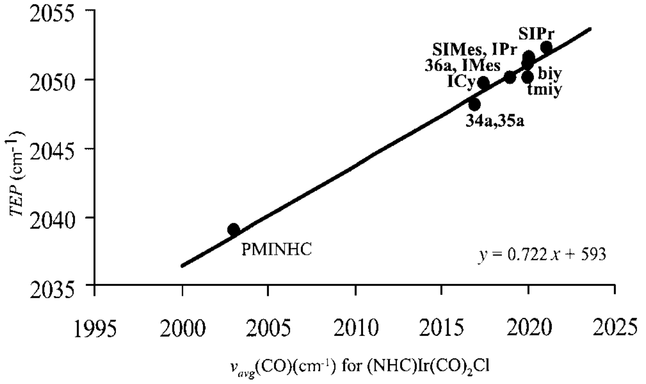
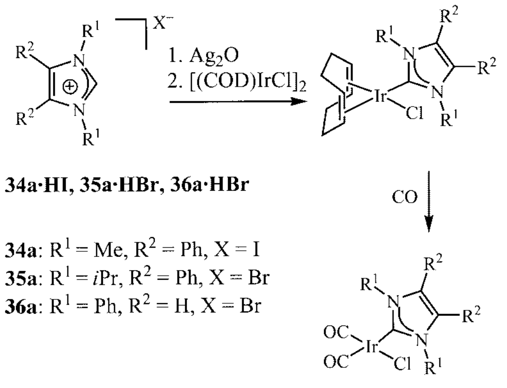


Figure 11. Plot of average ν_{CO} for $(NHC)Ir(CO)_2Cl$ vs ν_{CO} for $(NHC)Ni(CO)_3$, the Tolman electronic parameter (TEP).



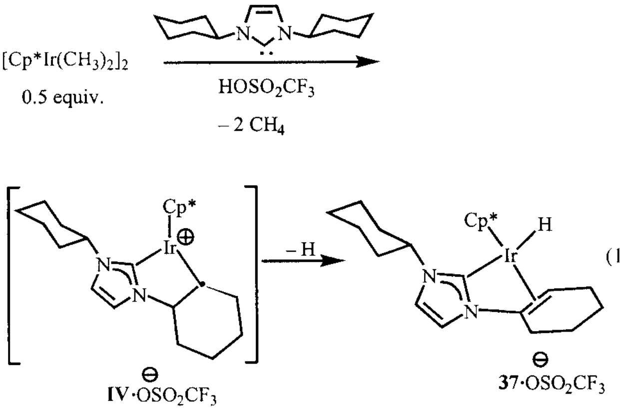
34a·HI, 35a·HBr, 36a·HBr

34a: R^1 = Me, R^2 = Ph, X = I
35a: R^1 = *i*Pr, R^2 = Ph, X = Br
36a: R^1 = Ph, R^2 = H, X = Br

34, 35, 36

Figure 12. Preparation of (NHC)Ir(I) dicarbonyl complexes.

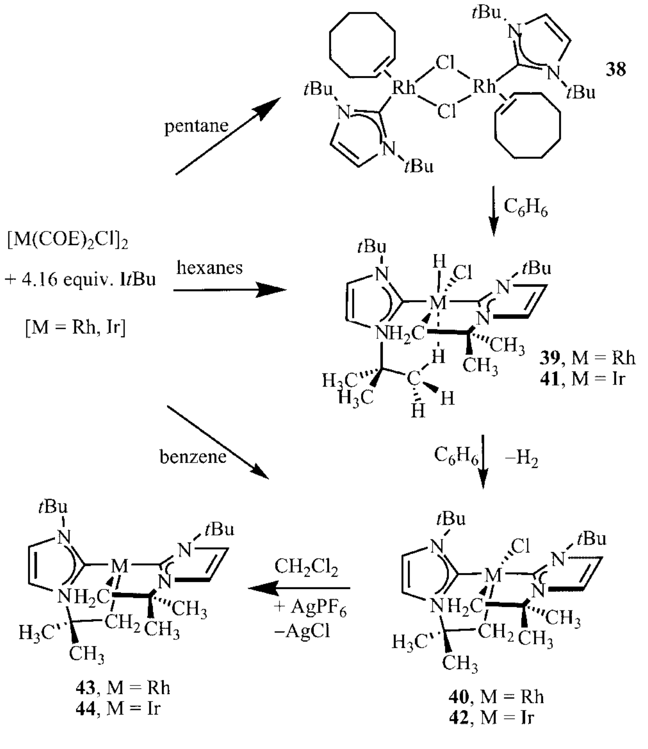
NHCs with late-transition metals have been found to undergo facile intramolecular C–H bond activation,[114,122–130] and in one example reported by Whittlesey et al. under more forcing conditions C–C bond activation.[131] In all but three of these cases, *N*-substituted phenyl and mesityl groups were present. Herrmann[132] has reported that ICy undergoes C–H bond cleavage by $[(Cp^*)IrCl_2]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) [β-hydride elimination resulted in the rapid formation of 1-(2-cyclohexenyl)-3-cyclohexylimidazol-2-ylidene (L′) with no direct activation product observed (**IV**)] affording $[Cp^*(L')IrH]^+(OSO_2CF_3^-)$ (**37**) [Equation (11)].



(11)

IV·OSO_2CF_3 **37**·OSO_2CF_3

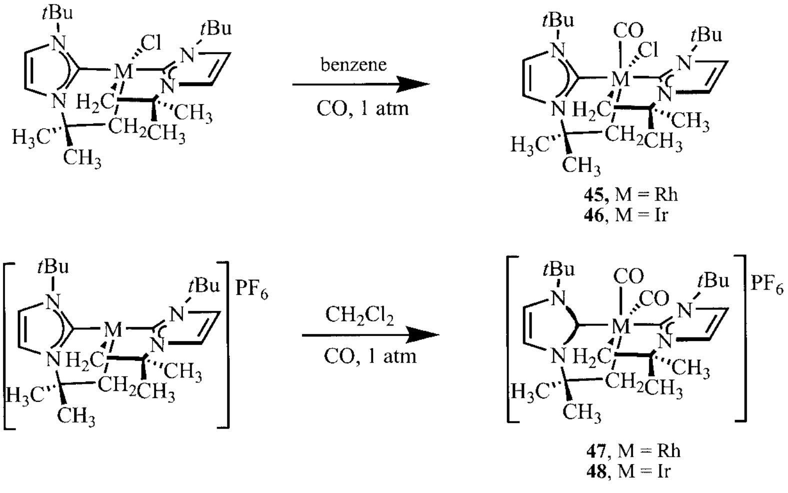
We have very recently described[45] the solvent-selective interaction of I*t*Bu [I*t*Bu = *N*,*N*-di(*tert*-butyl)imidazol-2-ylidene] with $[Rh(COE)Cl]_2$ (COE = *cis*-cyclooctene), which resulted in the isolation of [Rh(COE)(I*t*Bu)Cl] (**38**) as well as two precursors, [Rh(H)Cl(I*t*Bu′)(I*t*Bu)] (**39**) and [Rh(I*t*Bu′)$_2$Cl] (**40**), en route to a unique product by a double cyclometalation process. Analogous reactions with $[Ir(COE)Cl]_2$ led exclusively to the two *en route* precursors [Ir(H)Cl(I*t*Bu′)(I*t*Bu)] (**41**) and [Ir(I*t*Bu′)$_2$Cl] (**42**) with no observation of a [Ir(COE)(I*t*Bu)Cl]$_2$ species using hydrocarbon solvents (Scheme 8).[47] Abstraction of the chloride ion from [M(I*t*Bu′)$_2$Cl] (**40**, **42**) allowed the preparation of the unprecedented "naked" *cis*-divacant four coordinate 14-electron d^6-ML_4 Rh^{III} and Ir^{III} complexes of the type [M(I*t*Bu′)$_2$](PF_6) [M = Rh (**43**), Ir (**44**)]. These compounds are neither stabilized by agostic interactions, nor by a change in spin state as observed very recently by Caulton et al. for a Ru^{II} compound.[133] Interestingly, the chloride containing 16-electron precursors (**40**, **42**) give complexes that are stabilized by agostic interactions.



Scheme 8.

Further examination of the coordinatively unsaturated cationic 14-electron complexes [Rh(I*t*Bu′)$_2$]PF_6 (**43**) and [Ir(I*t*Bu′)$_2$]PF_6 (**44**) and of their neutral 16-electron analogues RhCl(I*t*Bu′)$_2$ (**40**) and IrCl(I*t*Bu′)$_2$ (**42**) by the small linear CO ligand generated the six-coordinate saturated complexes and as a result confirmed the unsaturated nature of the "precursor" complexes **40, 42–44** (Scheme 9).

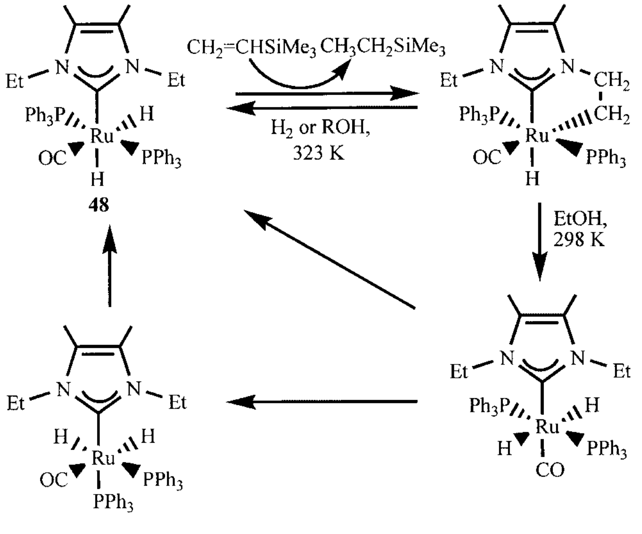
The unusual stability of the unsaturated [M(I*t*Bu′)$_2$Cl] and [M(I*t*Bu′)$_2$](PF_6) compounds was attributed to the elec-



Scheme 9.

tron-donating nature of the all carbon-based NHC ligands surrounding the metals. Detailed DFT studies suggested that not only NHC ligands are simple σ donors but the π orbitals on the NHC ring can be deeply involved in the bonding of the metal. A similar finding was recently published by Meyer,[134] where NHCs were found to accept electron density from electron-rich metals through a d-π* back-donation scheme. Conversely, our study indicates that NHCs can also donate electron density to electron-poor metal atoms through a π-d donation scheme. The stabilization offered through this flexibility might certainly have important implications in catalysis explaining perhaps slower decomposition of catalytically active highly unsaturated species and increased thermal stability in comparison to analogous LTM-PR$_3$ systems.

Whittlesey and co-workers recently described a rare example of C–H bond activation of an alkyl-substituted N-heterocyclic carbene by thermolysis of [Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)H$_2$] [IEt$_2$Me$_2$ = 1,3-bis(ethyl)-4,5-dimethylimidazol-2-ylidene] (**48**) in the presence of CH$_2$=CHSiMe$_3$ (Scheme 10).[135] The process interestingly proved to be reversible by H$_2$ or alcohols to afford different isomers of the starting dihydride complex.



Scheme 10.

Conclusions

The unique stabilization of coordinatively unsaturated metal centers by N-heterocyclic carbene ligands has now become well recognized. Many of these complexes have been shown to catalyze a variety of organic transformations through the stabilization of low-valent metal species. It is now evident from thermochemical, structural and infrared studies studies that NHCs are more electron donating and sterically more demanding than the most basic/bulky phosphane ligands. As a result, the stabilization of many reactive intermediates, which have been elusive so far in phosphane chemistry, has helped elucidate the precise effects of the NHC ligand in catalytic systems. Furthermore the versatility of NHCs has only begun to be realized with C-2 vs. abnormal C-4(5) binding modes possible in addition to facile intramolecular C–H activation of the nitrogen substituents with LTM. In this report, we have presented a short illustration of a selected number of important observations dealing with NHCs, it is our belief that this ligand family will continue to surprise.

Acknowledgments

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[1] H. Staudinger, O. Kupfer, *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 501.
[2] J. Wallach, *Ber. Dtsch. Chem. Ges.* **1925**, 15, 645.
[3] H. W. Wanzlick, H. J. Kleiner, *Angew. Chem.* **1961**, *73*, 493.
[4] H. W. Wanzlick, H. J. Kleiner, *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75–80.
[5] H. W. Wanzlick, F. Esser, H. J. Kleiner, *Chem. Ber.* **1963**, *96*, 1208.
[6] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[7] W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.

[8] A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 985–1009.

[9] M. Regitz, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*,725–728.

[10] A. J. Arduengo III, R. Krafczyk, *Chem. Ztg.* **1998**, *32*, 6–14.

[11] T. Weskamp, V. P. W. Böcher, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12–22.

[12] L. Jafarpour, S. P. Nolan, *Adv. Organomet. Chem.* **2001**, *46*, 181–222.

[13] C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247–2273.

[14] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2493.

[15] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.

[16] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.

[17] L. Jafarpour, S. P. Nolan, *J. Organomet. Chem.* **2001**, *617*, 17–27.

[18] T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29.

[19] A. Fürstner, *Angew. Chem. Int. Ed.* **2000**, *39*, 3013–3043.

[20] L. D. Vasquez-Serrano, B. T. Owens, J. M. Buriak, *Chem. Commun.* **2002**, 2518–2519.

[21] H. M. Lee, T. Jiang, E. D. Stevens, S. P. Nolan, *Organometallics* **2001**, *20*, 1255–1258.

[22] A. C Hillier,H. M. Lee, E. D. Stevens, S. P. Nolan, *Organometallics* **2001**, *20*, 4246–4252.

[23] L. D.Vasquez-Serrano, B. T. Owens, J. M. Buriak, *Chem. Commun.* **2002**, 2518–2519.

[24] I. E. Markò, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declerq, *Science* **2002**, *298*, 204–207.

[25] G. A. Grasa, M. S. Viciu, J. Huang, S. P. Nolan, *J. Org. Chem.* **2001**, *66*, 7729–7737·

[26] G. A. Grasa, M. S. Viciu, J. Huang, C. Zhang, M. L. Trudell, S. P. Nolan, *Organometallics* **2002**, *21*, 2866–2873·

[27] M. S. Viciu, R. F. Germaneau, S. P. Nolan, *Org. Lett.* **2002**, *4*, 4053–4056.

[28] O. Navarro, R. A. Kelly III, S. P. Nolan, *J. Am. Chem. Soc.* **2003**, *125*, 16194–16195.

[29] J. P. Collman, L. S. Hedegus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed; University Science: Mill Valley, CA, **1987**.

[30] K. Denk, P. Sirsch, W. A. Herrmann, *J. Organomet. Chem.* **2002**, *649*, 219–224.

[31] L. H. Pignolet (Ed.), *Homogeneous Catalysis with Metal Phosphine Complexes*, Plenum: New York, **1983**.

[32] G. W. Parshall, S. Ittel, *Homogeneous catalysis*; John Wiley & Sons: New York, **1992**.

[33] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1999**, *38*, 2416–2419.

[34] J. Huang, L. Jafarpour, A. C. Hillier, E. D. Stevens, S. P. Nolan, *Organometallics* **2001**, *20*, 2878–2882.

[35] A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabree, *Organometallics* **2003**, *22*, 1663–1667.

[36] J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 2370–2375.

[37] S. T. Liu, R. Z. Ku, L. Y. Liu, F. M. Kiang, *J. Organomet. Chem.* **1997**, *543*, 249.

[38] D. S. Clyne, J. Jin, E. Genest, J. C. Gallucci, T. V. RajanBabu, *Org. Lett* **2000**, *2*, 1125–1128.

[39] M. T. Powell, D, R. Hou, M. C. Perry, X. H. Cui, K. Burgess, *J. Am. Chem. Soc.* **2001**, *123*, 8878–8879.

[40] M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 3596–3604.

[41] I. E. Mehlhofer, T. Stressner, W. A. Herrmann, *Angew. Chem. Int. Ed* **2002**, *41*, 1745–1747.

[42] J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700–706.

[43] M. S. Vicui, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2003**, *22*, 3175–3177.

[44] M. Poyatos, E. Mas-Marza, J. A. Mata, M. Sanau, E. Peris, *Eur. J. Inorg. Chem.* **2003**, 1215–1221.

[45] R. Dorta, E. D. Stevens, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 5054–5055.

[46] R. Dorta, E. D. Stevens, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2003**, *125*, 10490–10491.

[47] N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516–3526.

[48] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–324.

[49] R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, in press.

[50] M. S. Viciu, O. Navarro, R. F. Germaneau, R. A. Kelly III, W. Sommer, N. Marion, E. D. Stevens, L. Cavallo, S. P. Nolan, *Organometallics* **2004**, *23*, 1629–1635.

[51] R. A. Diggle, S. A. Macgregor, M. K. Whittlesey, *Organometallics* **2004**, *23*, 1857–1865.

[52] A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663–1667.

[53] P. Mahjoor, N. M. Scott, E. D. Stevens, S. P. Nolan, manuscript in preparation.

[54] L. Jafarpour, S. P. Nolan, *Organometallics* **2000**, *19*, 2055–2057.

[55] P. Schwab, M. B. France, J. W. Ziller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041.

[56] P. Schwab, R. H. Grubbs, R. H. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

[57] E. L. Diaz, S. T. Nyugen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897.

[58] R. R. Schrock, J. Murdzeck, G. C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.

[59] A. Briot, M. Bujard, V. Gouverneur, S. P. Nolan, C. Mioskowski, *Org. Lett.* **2000**, *2*, 1517–1519.

[60] L. Jafarour, S. P. Nolan, *Org. Lett.* **2000**, *2*, 4075–4078.

[61] R. Dorta, R. A. Kelly III, S. P. Nolan, *Adv. Synth. Catal.* **2004**, *346*, 917–920.

[62] P. J. Fagan, M. D. Ward, J. V. Caspar, J. C. Calabrese, P. J. Krusic, *J. Am. Chem. Soc.* **1988**, *110*, 2981–2983.

[63] B. K. Campion, R. H. Heyn, T. D. Tilley, *J. Chem. Soc., Chem. Commun.* **1988**, 278–280.

[64] L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl, W. A. Herrmann, *Tetrahedron Lett.* **1999**, *40*, 4787–4790.

[65] D. S. McGuiness, M. J. Green, K. J. Cavell, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1998**, *565*, 165–178.

[66] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374.

[67] D. S. McGuiness, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **1999**, *18*, 1596–1605.

[68] K. Selvakumar, A. Zapf, A. Spannerberg, M. Beller, *Chem. Eur. J.* **2002**, *8*, 3901–3906.

[69] K. Selvakumar, A. Zapf, M. Beller, *Org. Lett.* **2002**, *4*, 3031–3033.

[70] R. Jackstell, M. G. Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch, M. Beller, *Angew. Chem. Int. Ed.* **2002**, *41*, 986–989.

[71] R. Jackstell, A. Frisch, M. Beller, D. Rottger, M. Malaun, B. Bildtein, *J. Mol. Catal. (A)* **2002**, *185*, 105–112.

[72] C. Zhang, J. Huang, M. L. Trudell, S. P. Nolan, *J. Org. Chem.* **1999**, *64*, 3804–3805.

[73] H. Lee, S. P. Nolan, *Org. Lett.* **2000**, *2*, 2053–2055.

[74] C. W. K. Gstöttmayr, V. P. W. Böhm, E. Herdtweck, M. Grosche, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1363–1365.

[75] W. A. Herrmann, C.-P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93–96.

[76] S. R. Stauffer, S. W. Lee, J. P. Stambuli, S. I. Hauck, J. F. Hartwig, *Org. Lett.* **2000**, *2*, 1423–1426.

[77] S. P. Stambuli, M. Buhl, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 9346–9347.

[78] S. Caddick, F. G. N. Cloke, P. B. Hitchcock, J. Leonard, A. K. de K. Lewis, D. McKerrecher, L. R. Titcomb, *Organometallics* **2002**, *21*, 4318–4319.

[79] J. Huang, G. Grasa, S. P. Nolan, *Org. Lett.* **1999**, *1*, 1307–1309.
[80] J. F. Hartwig, *Angew. Chem. Int. Ed.* **1998**, *37*, 2046- 2067.
[81] J. Louie, P. F. Hartwig, *Organometallics* **1996**, *15*, 2794–2805.
[82] C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314–321.
[83] A. K. de K. Lewis, Caddick, F. G. N. Cloke, N. C. Billingham, P. B. Hitchcock, J. Leonard, *J. Am. Chem. Soc.* **2003**, *125*, 10066–10073.
[84] P. A. Arnold, F. G. N. Cloke, T. Geldbach, P. B. Hitchcock, *Organometallics* **1999**, *18*, 3228–3233.
[85] V. P. W. Böhm, C. W. K. Gstöttmayr, T. Weskamp, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *595*, 186–190.
[86] S. Caddick, F. G. N. Cloke, C. K. B. Clentssmith, P. B. Hitchcock, D. McKerrecher, L. R. Titcomb, M. R. V. Williams, *J. Organomet. Chem.* **2001**, *617–618*, 635–639.
[87] L. R. Titcomb, S. Caddick, F. G. N. Cloke, D. J. Wilson, D. McKerrecher, *Chem. Commun.* **2001**, 1388–1389.
[88] C. W. K. Gstöttmayr, V. P. W. Böhm, E. Herdtweck, M. Grosche, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1363–1365.
[89] G. M. DiRenzo, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 6225–6234.
[90] A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Peterson, L. Cavallo, S. P. Nolan, *Organometallics* **2003**, *22*, 4322–4326.
[91] R. Dorta, E. D. Stevens, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2003**, *125*, 10490–10491.
[92] W. A. Herrmann, M. Elison, J. Fischer, C. Kocher, G. R. Artus, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374.
[93] S. Caddick, F. G. N. Cloke, P. B. Hitchcock, A. K. de K. Lewis, *Angew. Chem. Int. Ed* **2004**, *43*, 5824–5827.
[94] S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2003**, *22*, 4184–4186.
[95] A. J. Arduengo III, S. F. Gamper, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1994**, *116*, 4391–4394.
[96] W. Petz, F.Weller, J. Uddin, G. Frenking, *Organometallics* **1999**, *18*, 619–626.
[97] G. Wilke, *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 105–108.
[98] B. Bogdanovic, M. Kroener, G. Wilke, *Justus Liebigs Ann. Chem.* **1966**, *699*, 1–23.
[99] L. W. Gosser, C. A. Tolman, *Inorg. Chem.* **1970**, *9*, 2350–2353.
[100] K. Jonas, P. Heimbach, G. Wilke, *Angew. Chem. Int. Ed. Engl. A* **1968**, *7*, 949–950.
[101] B. Gabor, K. Krueger, B. Marczinke, R. Mynott, G. Wilke, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1666–1668.
[102] D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2002**, *124*, 9976–9977.
[103] M. Brookhart, M. L. H. Green, L. Wong, *Prog. Inorg. Chem.* **1988**, *36*, 1–124.
[104] R. H. Crabtree, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789–805.
[105] The experimental design of the FTIR cell has previously been described: B. R.Bender, G. J. Kubas, L. H. Jones, B. I. Swanson, J. Eckert, K. B. Capps, C. D. Hoff, *J. Am. Chem. Soc.* **1997**, *119*, 9179–9190.
[106] M. J. Doyle, M. F. Lappert, *J. Chem. Soc.*, *Chem. Commun.* **1974**, 679–680.
[107] W. A. Herrmann, L. J. Goosen, M. J. Spiegler, *J. Organomet. Chem.* **1997**, *547*, 357–366.
[108] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2493.
[109] I. Özdemir, B. Yigit, B. Çetinkaya, D. Ülkü, M. N. Tahir, C. Arici, *J. Organomet. Chem.* **2001**, *633*, 27–32.
[110] D. Enders, H. Gielen, *J. Organomet. Chem.* **2002**, *617/618*, 70–80.
[111] D. E. Morris, H. B. Tinker, U. S. Patent 3948962. **1976**.
[112] W. Z. Chen, M. A. Esteruelas, M. Martin, M. Oliván, L. A. Oro, *J. Organomet. Chem.* **1997**, *534*, 95–103.
[113] L. Perrin, E. Clot, O. Eisenstein, J. Loch, R. H. Crabtree, *Inorg. Chem.* **2001**, *40*, 5806–5811.
[114] J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **2000**, *19*, 1194–1197.
[115] S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *Chem. Commun.* **2001**, 2274–2275.
[116] S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473–10481.
[117] A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**. *23*, 2461–2468.
[118] H. Lebel, M. K. Janes, A. B. Charette, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 50460–5047.
[119] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[120] G. Sini, O. Eisenstein, R. H. Crabtree, *Inorg. Chem.* **2002**, *41*, 602–604.
[121] A. Kovaceic, S. Gründemann, J. R. Mieczikowski, E. Clot, O. Eisenstein, R. H. Crabtree, *Chem. Commun.* **2002**, 2580–2581.
[122] P. B. Hitchcock, M. F. Lappert, P. L. Pye, *J. Chem. Soc., Chem. Commun.* **1976**, 644–646.
[123] P. B. Hitchcock, M. F. Lappert, P. L. Pye, *J. Chem. Soc., Chem. Commun.* **1977**, 196–198.
[124] P. B. Hitchcock, M. F. Lappert, P. L. Pye, S. Thomas, *J. Chem. Soc., Dalton Trans.* **1979**, 1929–1942.
[125] P. B. Hitchcock, M. F. Lappert, O, Terreros, *J. Organomet. Chem.* **1982**, *239*, C26–C30.
[126] A. A. Danopoulos, S. Winston, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **2002**, 3090–3091.
[127] T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Whiheim, M. Scholl, T.-L. Choi, S. Deng, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 2546–2558.
[128] M. J. Chilvers, R. F. R. Jazzar, M. F. Mahon, M. K. Whittlesey, *Adv. Synth. Catal.* **2003**, *345*, 1111–1114.
[129] D. Guinta, M. Hölischer, C. W. Lehmann, R. Mynott, C. Wirtz, W. Leitner, *Adv. Synth. Catal.* **2003**,*345*, 1139–1145.
[130] K. Adbur-Rashid, T. Fedorkiw, A. J. Lough, R. H. Morris, *Organometallics* **2004**, *23*, 86–94.
[131] R. F. R. Jazzar, S. A. Macgregor, M. F. Mahon, S. Richards, M. K. Whittlesey, *J. Am. Chem. Soc.* **2002**, *124*, 4944–4945.
[132] M. Prinz, M. Grosche, E. Herdtweck, W. A. Herrmann, *Organometallics* **2000**, *19*, 1692–1694.
[133] L. A. Watson, O. V. Ozerov, M. Pink, K. G. Caulton, *J. Am. Chem. Soc.* **2003**, *125*, 8426–8427.
[134] X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, *Organometallics* **2004**, *23*, 755–764.
[135] S. Burling, M. F. Mahon, B. M. Paine, M. K. Whittlesey, J. M. J. Williams, *Organometallics* **2004**, *25*, 4537–4539.

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