Cyclometalated Phosphine-Based Pincer Complexes: Mechanistic Insight in Catalysis, Coordination, and Bond Activation

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Contents

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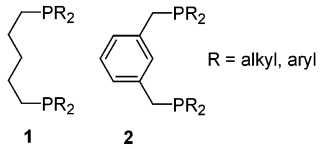
I. Introduction

Bernard Shaw's pioneering research[1−15] on cyclometalated phosphine-based pincer complexes has inspired many others.[16−208] Although the first metal complexes with ligands **1** and **2** were reported about 30 years ago, it is still a hot and emerging topic covering all aspects of modern organometallic chemistry and touching other fields as well.



1 **2**

During the past decade, interest and activity in this area have rapidly increased. For instance, cyclometalated phosphine-based pincer complexes and structurally/electronically related systems are about to become a valuable asset in the formation of functional nanoscale assemblies, while various mechanistic, structural, catalytic, synthetic, theoretical, and coordination studies are ongoing.[26,60,83,90] Major recent findings have been the generation of efficient dehydrogenation[24−28,31,33,116−120,122,187,191,202,205] and Heck type catalysts,[19−21,29,30,55,91,128,141−144] activation of strong C−O[66,68] and C−C bonds,[18,22,41,44,46−48,52−54,56,58−62,67,70,71,73] and trapping of various intermediates and unusual molecules.[83] Pincer-based metal complexes possess an unique balance of stability vs reactivity which can be controlled by systematic ligand modifications and/or variation of the metal center, allowing enhancement of metal complex reactivity, stability, reaction selectivity, and simultaneously provide a flurry of new fundamental insight. The use of the PCP ligands **1** and **2** opens a large number of interesting research possibilities given the complex reaction chemistry which is not yet fully understood. For instance, how are the physicochemical properties of PCP-based metal complexes influenced by (i) the nature of the metal center (i.e., periodic table position, oxidation state), (ii) substituents on P and on the aryl and alkyl ligand backbones, (iii) ancillary ligands, and (iv) coordination geometry? Systematic structural/environmental variations can be studied with **1** and **2** in

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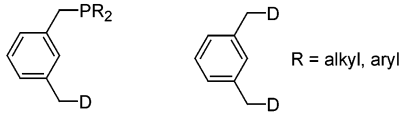
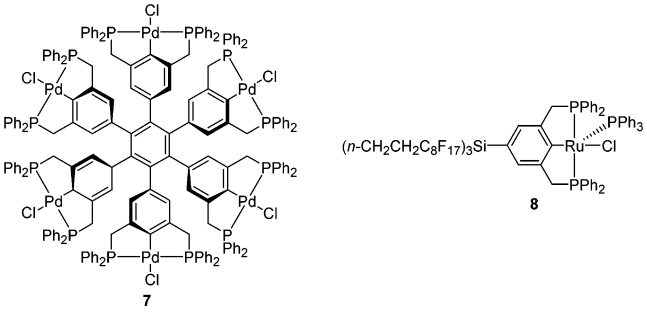
detail by focusing on and acquiring quantitatively analyses describing reactivity and metal complex stability by varying only one component while other variables are held constant. For the interested reader: catalytic dehydrogenation with **2**-based iridium complexes and metal-stabilized formation of quinonoids has been reviewed in *Chemical Communications* as a feature article[26] and in *Accounts of Chemical Research*,[83] respectively. Two general reviews on metal-promoted C−C bond cleavage[60] and nitrogen and phosphine-based pincer systems[90] have been published in *Angewandte Chemie*. This review covers the latest developments in transition metal chemistry with PCP ligands **1** and **2** and derivatives and consists of three detailed sections primarily focusing on the mechanistic aspects of (i) catalysis, (ii) ligand coordination and activation of various organic substrates, and (iii) bond activation. Structurally related PCN (**3**),[41−45] PCO (**4**),[61] SCS (**5**),[19,20,129,208] and NCN(**6**)ligands,[85−90,92,93,95−97,99−101,103−109,111,112,114,134,157,170,171] which have evolved from **1** and **2**, are highlighted wherever appropriate.

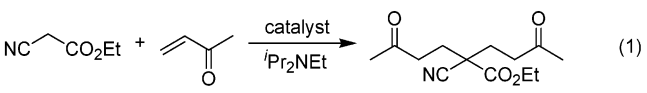


3: D = NR_2
4: D = OR
5: D = SR
6: D = NR_2

II. Catalytic Applications

Various homogeneous catalytic processes with cyclometalated phosphine-based pincer complexes have been reported, including asymmetric adol condensation of methyl isocyanoacetate and aldehydes,[130,131] ketone reduction by hydrogen transfer,[89,95] dehydrogenation of alkanes,[24−28,31,33,118−120,122,187,191,202,205] Suzuki biaryl coupling,[133] polymerization of phenylacetylene,[132] and Heck olefin arylation.[19−21,29,30,55,91,128,141−144] Conceptually new, nanosize multimetallic pincer compounds (**7**) have been applied by van Koten et al. as Lewis-acid catalysts in the double Michael reaction between methyl vinyl ketone and ethyl α-cyanoacetate (eq 1),[96−98] and modified ruthenium pincer complexes (**8**) having fluoro-alkyl arene substituents show good solubility in fluorinated solvents allowing the formation of biphasic catalytic systems.[90,137,138] Moreover, fundamentally important catalytic C−X (X = C, N) single bond activation processes were demonstrated using PCP- and PCN-based substrates.[43,54,60]





(1)

The scope of catalytic processes reported with one ligand system and structurally/electronically

Table 1[a]

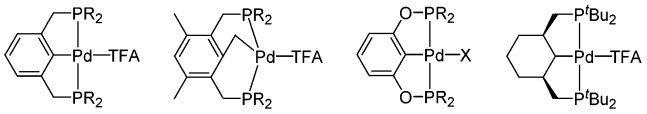
	ArX	catalyst	time (h)	TON	yield
1	PhI	**9**	60	142 900	100
2	PhI	**11**	20	142 900	100
3	PhI	**12**	40	142 900	100
4	PhBr	**11**	63	132 900	93
5	4-CHO−C_6H_4Br	**11**	63	113 300	79

[a] Temp = 140 °C, haloarene/methylacrylate = 5/6 (mmol/mmol), catalysts: 3.5×10^{-5} mmol. Yield determined by GC and is based on both haloarene and product formed (PhC(H)=C(H)COOMe).

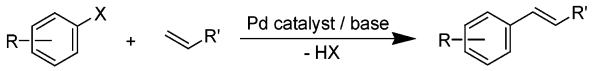
related metal complexes is remarkable and is not fully explored yet. For instance, enantiomerically pure complexes functionalized at the benzylic positions[89,93,130,131,135,136] and novel P-stereogenic[115] PCP-based catalysts afforded only moderate ee's. An efficient chiral PCP-based catalyst will open a window of opportunities in all of the aforementioned catalytic processes. Moreover, large numbers of reported selective, stoichiometric transformations with PCP complexes may be amenable to catalysis (section III).[31,57,75,81,124,126,139,173,174] The robust, rigid aromatic backbone of the tridentate PCP ligand **2** tolerates structural modifications and limit the number of open (= reactive) sites on the metal center ensuring reaction selectivity and catalyst stability. Reactions with relatively high kinetic barriers may proceed smoothly at elevated temperatures without noticeable catalyst degradation. Fine-tuning of steric and electronic properties resulted in enhanced catalytic reactivity by orders of magnitudes with turnover numbers (TONs), yields, and catalyst lifetimes rapidly approaching industrial figures-of-merit.[21,24−31,33,55,91,122,133,140,141] Furthermore, the rigid PCP backbone can impose planarity on the metal center, which may have significant consequences on reactivity and stability.[209,210] New mechanistic insight in catalysis supported by computational studies has been obtained and catalysis utilizing less reactive substrates (i.e., aryl bromides and chlorides in the C−C bond forming reactions, alkane C−H bond activation) has been accomplished.[19−21,24−31,33,43,54,55,91,118−120,122,128,141−144]

A. Heck Olefin Arylation

The cyclometalated d^8 palladium pincer complexes **9**−**15** are extremely efficient catalysts for the synthetically important Heck reaction (eq 2).[21,29,30,55,91,141−144] Excellent catalysts based on Pd(II) complexes of metalated monophosphines were reported previously.[211−213] The first pincer-type complexes reported to catalyze the Heck reaction were **9**, **11**, and **12** leading to turnovers numbers >100 000 and high yields for unactivated aryl bromides without observable catalyst degradation (Table 1).[55]

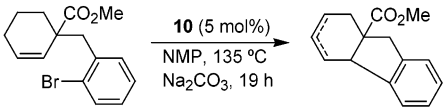


9. R = ^{i}Pr **11**. R = ^{i}Pr **13**. R = 4-MeOC$_6$H$_4$O, X = I **15**
10. R = c-C$_5$H$_9$ **12**. R = ^{t}Bu **14**. R = ^{i}Pr, X = Cl



(2)

Intramolecular Heck reactions with **10** afforded carbocyclic ring systems (eq 3),[21] and 980.000 TONs (98% yield) were obtained with the extremely active catalyst **13** using *p*-iodoanisole and *n*-butyl acrylate.[141] The highest TONs with this catalyst were obtained with iodobenzene as substrate (8 900 000 TONs, 400 000 TONs per h, 89% yield). Thermally induced radical polymerization of the starting materials was prevented by addition of hydroquinone to the reaction mixtures.



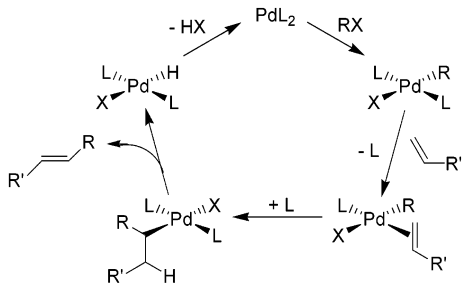
(3)

Notably, complex **13** was prepared by a one-pot reaction starting from 2-iodoresorcinol and can be purified by conventional silica gel column chromatography. The industrially important aryl chlorides were successfully functionalized with good yields and ~200 TONs by the modified pincer system **14**.[30] Similar catalytic activities with unactivated aryl chlorides were observed previously with other systems as well.[95,103,214−218] For instance, bisphosphine Pd(0) systems are equally efficient with unactivated aryl chlorides.[217,218] The PCP catalyst design **9**−**15** prevents known decomposition routes such as P−C or P−O bond cleavage usually accompanied by palladium black formation, and even allows aerobic reaction conditions at elevated temperatures. Bergbreiter has supported PCP and SCS−Pd complexes on polymers, allowing easy catalyst recovery and reuse.[19,20] The observed reactivity trend **11** > **9** and **11** > **12** reveals a delicate balance between metal complex reactivity, electron density, and steric hindrance. The metal center of **11** is more electron-rich than in **9** and less sterically crowded than in **12**. Milstein's catalysts (**9**, **11**, **12**)[55] and related complexes (**10**, **13**−**15**)[21,29,30,91,128,141,143,144,213] are also highly intriguing for mechanistic reasons. The vast majority of textbook palladium-catalyzed Heck reactions proceed by five consecutive steps: (i) aryl halide oxidative addition to a coordinately unsaturated, 14 electron Pd(0) species, (ii) phosphine ligand dissociation followed by olefin coordination, (iii) olefin migratory insertion in the Pd(II)−aryl σ-bond, (iv) Pd(II)−H generation by β-H elimination and product dissociation, and (v) regeneration of the catalytically active Pd(0) complex by deprotonation of Pd(II)−H or by HX reductive elimination followed by trapping by base (Scheme 1).[142,219,220]

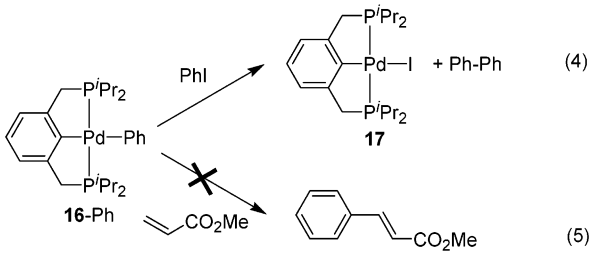
An intriguing issue is the mechanism of these reactions. Is the traditional Pd(0)/Pd(II) mechanism operative in these systems? For the metalated monophosphine complexes, this is proposed to be the case, the metalated complex being reduced to the active Pd(0) complex.[221] In contrast, a non-Pd(0) mechanism may be operative in the case of pincer PCP complexes, possibly a Pd(II)/Pd(IV) mechanism.

Competition experiments in the Heck olefination reaction with the PCP catalyst **9** and various *para*-

Scheme 1



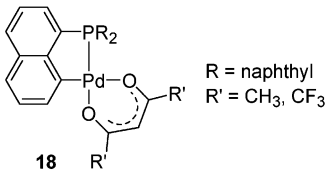
substituted aryl iodides and methyl acrylate suggested the olefin insertion step to be rate-determining.[55] Similar observations were reported by Shibasaki et al. with complex **13**, *n*-butyl acrylate, and aryl iodides,[141] and kinetic studies on Pd-systems with monodentate phosphorus ligands also identify alkene coordination or insertion as the slow step.[212,222] Pathways involving Pd(0) are unlikely with the PCP−Pd complexes. Formation of an anionic PCP−Pd(0) complex followed by a nucleophilic attack of the metal center on an aryl halide to afford a PCP−Pd(II)−Ph complex can be discarded.[55] A mechanism involving intermediacy of a PCP−Pd−H complex as a route to Pd(0) by reductive elimination is also highly unlikely. This is based on the fact that Pd(R)[2,6-($CH_2P^iPr_2$)$_2C_6H_3$] (**16**, R = Ph, H) complexes were prepared and shown not to be involved in the overall process, rendering a classical Pd(0)/Pd(II) mechanism in the PCP-based systems a remote possibility.[55] Complex **16**−Ph reacted with *para*-substitutes aryl halides affording the Pd−I complex (**17**) and mixed biaryls (eq 4), whereas reactions of **16**−Ph with olefins did not lead to formation of organic coupling products and **16**−H (eq 5).[51,55] Complex **16**−H reacted with *p*-iodoanisole to afford **17** and anisole. Biaryl or arene formation was not observed during catalysis.



Beletskaya and Cheprakov proposed a mechanism for Heck catalysis by PCP−Pd complexes involving Pd(0) formation, ring opening, and phosphine dissociation.[143] They suggested that the PCP−Pd(II) complex is regenerated by air oxidation of an unobserved, catalytically active Pd(0) species (without affecting the PCP ligand). No experimental data were provided. However, the catalytic reactions are equally efficient when carried under an inert atmosphere or under air, and the PCP catalyst can be recovered under inert atmosphere as well as in air, ruling out possible O_2-mediated oxidation of Pd(0) to Pd(II) as a major route. Moreover, complex **15** is a highly efficient, air-stable precatalyst with a relative large P−Pd−P angle (∼166°) arguing also against a phosphine dissociation mechanism driven by release of strain.[128]

The controversial issue of Pd(IV) intermediacy in phosphine-based palladium-catalyzed Heck reactions attracted much interest and is still under debate.[21,30,55,141,211,212,220,223−227] Recent reports by Jensen, Shaw, and others suggested Pd(II)/Pd(IV)-based mechanisms.[30,141,223,224] For instance, tri(1-naphthyl)phosphine cyclopalladates (**18**) are highly stable and excellent Heck-type catalysts proposed to involve Pd(IV).[224] A recent report of an isolated Pd(IV)-monophosphine intermediate has been retracted.[225] A recent density functional theory (DFT) study by Martin et al. on a model system consisting of 1,2-diphosphinoethane-based palladium complexes iodobenzene and ethylene demonstrated that a Pd(II)/Pd(IV) cycle may be indeed an alternative to the well-known Pd(0)/Pd(II) mechanism (Scheme 1).[226]

In general, kinetic and mechanistic studies in other metal-mediated transformations implied formation of Pd(IV)−phosphine complexes.[228−232] For instance, reaction of optically active α-deuteriobenzyl bromides with $Me_2Pd(PR_3)_2$ resulting in formation of α-deuterioethylbenzene with inversion at the α-carbon proceed evidently by Pd(IV)−phosphine intermediacy.[228]



Catalysts **13** and **14** show an enhanced reactivity relative to analogous phosphinato-based systems in Heck coupling reactions (**9**−**12**).[30] Similar trends have been observed with other palladium systems as well.[222] The phosphinito complex **13** showed good catalytic activity with unactivated aryl chlorides, whereas the related Pd−Cl analogue of **9** under identical reaction conditions did not. Moreover, commercially important trisubstituted alkenes were formed by reaction of aryl bromides and styrene in the presence of **14** under aerobic conditions.[29] This example of catalyst fine-tuning demonstrates the importance and potential of PCP-ligand modifications. A fundamentally new Pd(II)/Pd(IV) cycle was proposed by Jensen et al. involving four key steps: (i) oxidative addition of a vinyl C−H bond (**A**), followed by (ii) rate-determining HX reductive elimination (**B**), (iii) aryl chloride oxidative addition (**C**), and (iv) subsequent reductive C−C bond elimination to afford the desired organic products and **14** (Scheme 2).[30]

Migratory insertion—a key step in the Pd(0)/Pd(II) and the proposed Pd(II)/Pd(IV)-based Heck reaction mechanisms—is not necessary here. The relatively lower catalytic activity of **9**-Cl in this reaction supports the involvement of a rate-determining Pd(IV) to Pd(II) step—the reduced electron density by the more electron withdrawing $^iPr_2P$−OR groups on the metal center with the phosphinito system **14** is expected to facilitate Pd(IV)/Pd(II) reductive elimination processes. No direct experimental data were provided to support this postulated mechanism

Scheme 2

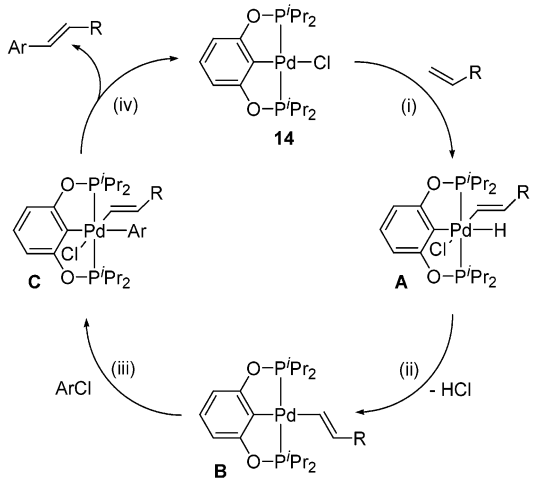
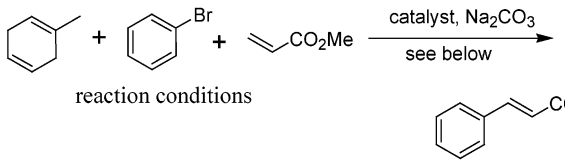


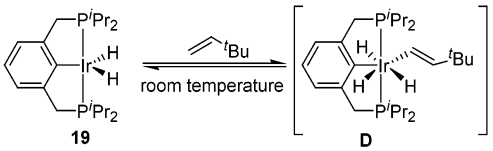
Table 2



reaction conditions	half-life (h) ($t_{1/2}$)[a]
10 (0.5 mol %), Na_2CO_3, NMP, 135 °C, no diene	4.5
10 (0.5 mol %), Na_2CO_3, NMP, 135 °C, diene (2 equiv)	150
$Pd(OAc)_2$ (2 mol %), Ph_3P (6 mol %), Na_2CO_3, NMP, 135 °C, no diene	4.5[b]
$Pd(OAc)_2$ (2 mol %), Ph_3P (6 mol %), Na_2CO_3, NMP, 135 °C, diene (2 equiv)	3.5

[a] Reaction did not proceed to completion presumably due to catalyst decomposition as evidenced by the formation of palladium black.

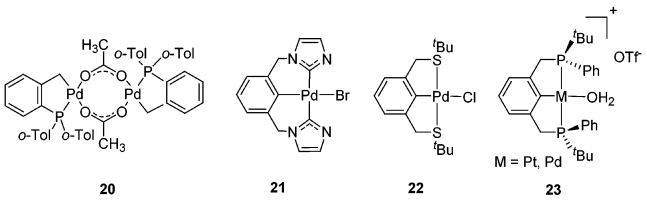
(Scheme 2).[30] Step **14** → **A** is partly based on deuterium labeling studies with *tert*-butylethylene and the Ir(III) pincer complex **19** showing a room-temperature H/D exhange process, suggested to proceed by reversible Ir(V) (**D**) mediated vinylic C−H bond activation (eq 6).[27]



(6)

Bergbreiter and Sulikowski observed that 1-methyl-1,4-cyclohexadiene and other 1,4-dienes inhibit the catalytic activity of **10**,[21] probably by coordination (Table 2), whereas typical Pd(0)/Pd(II) Heck catalysts (i.e., $Pd(OAc)_2/Ph_3P$) are not affected by 1,4-diene-based substrates lending support to a non-Pd(0)/Pd(II) mechanism with PCP catalysts. While 1,4-diene ligands can coordinate to Pd(II)[233,234] in both systems, coordination to (PCP)Pd(II) probably results in saturation and hence deactivation.

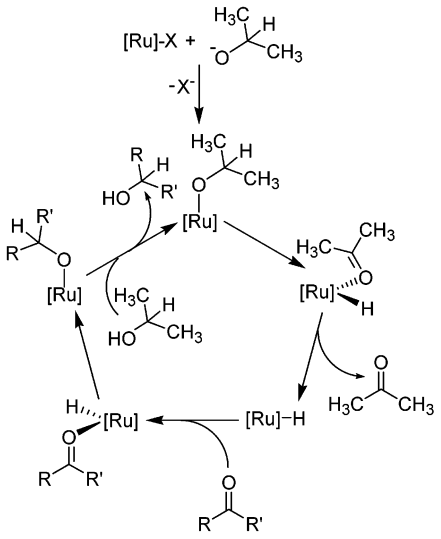
Thus, in some systems, a classical Pd(0)−Pd(II)−Pd(0) catalytic cycle may be not readily accessible, and other routes might be operative instead. The challenge is clear: more detailed mechanistic studies are certainly needed to provide compelling evidence to clarify or to disregard some of the here presented fascinating Pd(II)/Pd(IV) reaction pathways. In this respect, the metalated catalyst **20** was suggested to operate by a Pd(II)/Pd(IV) mechanism;[211,212] however, recent kinetic studies by Herrmann revealed intermediacy of Pd(0).[221] Regardless of the exact mechanism involved with the present (PCP)Pd systems **9**−**15**,[21,29,30,55,91,128,141−144,213] the recent flurry of activity in this field catalyzed by arguable interpretations of mechanistic data led to highly efficient olefin arylation processes with a wide range of olefins and unactivated aryl halides and contributed to the development of new, structurally related catalysts, including carbene-pincer (**21**)[235−237] and (polymer supported) sulfur-based complexes (**22**).[19,20,129] Enantioselective Heck reactions and related palladium-catalyzed C−C bond forming reactions (i.e., Stille reactions)[139] perhaps by utilizing new chiral PCP-based catalysts (**23**)[115] and perfluoro-aryl or -alkyl halides[238] are awaiting further exploration.



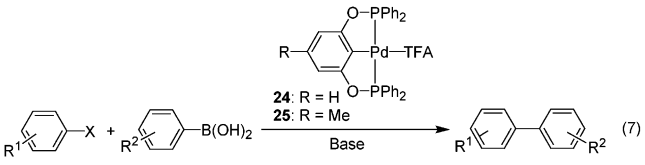
B. Suzuki Biaryl Coupling Reactions

Coupling of aryl halides with arylboronic acids is mechanistically similar to the abovementioned Heck chemistry and therefore proceeds with many Heck catalysts.[129,213,227,239,240] The phenyl analogues (**24**, **25**) of **14** (with phenyl groups replacing isopropyl substituents on P) were readily prepared by reaction of chlorodiphenylphosphine with aromatic 1,3-diols in the presence of triethylamine and successfully applied as high activity catalysts in the Suzuki reaction by Welch and co-workers (eq 7).[29,30,133] High TONs with moderate to very good yields were observed for various aryl bromides (i.e., 92 000 TON, 92% with **24** and 4-bromoacetophenone). Catalytic $C_{aryl}-C_{aryl}$ bond formation with sterically hindered, electronically deactivated substrates such as 2-bromo-*p*-xylene and 2-bromo-*m*-xylene was demonstrated as well. Moderate activity was reported with activated aryl chlorides such as 4-chloronitrobenzene, whereas little or no activity was observed with unactivated chlorides. The analogous complex **14** showed good catalytic activity in the Heck olefin arylation with unactivated aryl chlorides,[30] which can be attributed to electronic factors. The higher electron density on the metal center may promote an unobserved Ar−Cl oxidative addition process despite the higher steric bulk of isopropyl vs phenyl substituents on P. Complexes **24** and **25** are robust catalysts: no noticeable decomposition was observed in wet solutions at elevated temperatures under air. Catalysts **24** and **25** show essentially the same activity with 4-bromoacetophenone and 4-bromoanisole, suggesting that

Scheme 3



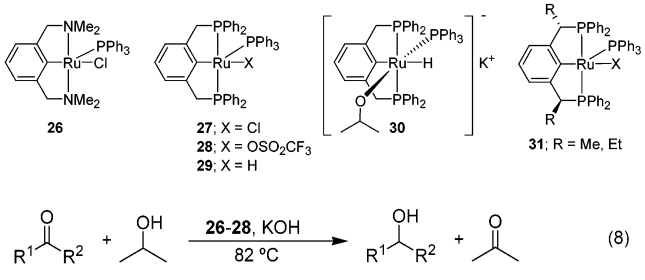
aryl bromide oxidative addition is not the slow, rate-limiting step in the overall process. Similar observations were made in the Heck reaction with **9**,**13** and aryl iodides.[55,141] The reaction efficiency depends on the nature of the base: Suzuki reactions with **24** and **25** proceed well in the presence of K_2CO_3, whereas only a few hundreds of turnovers and low yield were observed with KF.



(7)

C. Ruthenium-Catalyzed Hydrogen Transfer

Van Koten's NCN- and PCP-Ru(II) pincer complexes (**26**−**28**) efficiently catalyze the reduction of ketones to the corresponding alcohols with ^{i}PrOH as the hydrogen source and KOH as promotor (eq 8).[95] Inorganic bases are often used to increase the 2-propoxide ion concentration.[219] Coordination of the latter to the metal center followed by β-hydrogen elimination yield acetone and the reactive metal-hydride species, capable of efficiently reducing carbonyl substrates to secondary alcohols (Scheme 3).[241]

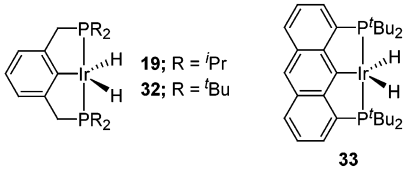


(8)

The PCP-based catalysts **27**, **28** showed higher turnover frequencies than the related NCN complex **26**. Excellent turnover numbers and good yields were observed under reflux conditions with alkyl−aryl, diaryl, and dialkyl ketones (i.e., 27 000 h^{-1} for cyclohexanone; 98% yield with **27**) exceeding those reported with established monodentate phosphine complexes such as $[RuCl_2(PPh_3)_3]$ and $[RuCl(H)(PPh_3)_3]$.[241] Reduction of cyclohexanone occurred even at room temperature. In situ ^{31}P NMR studies under catalytic conditions did not reveal free PPh_3 or PCP ligand dissociation. Formation of an anionic ruthenium(II)−alkoxyhydrido complex (**30**) was observed by NMR in the absence of ketone substrates, suggesting that Ru−H species akin to known (PCP)Ru(II)−H (**29**) complexes may catalyze the hydrogen transfer process.[37,165] Most probably **30** represents a resting state of reactive, neutral d^6 ruthenium hydrido complexes, which are generally believed to be the actual catalysts in reduction processes (Scheme 3).[241] Hydrogenation of prochiral ketones to chiral secondary alcohols is highly desirable, but a difficult process.[93] Asymmetric hydrogen transfer from alcohols to prochiral carbonyl compounds to afford enantiomeric pure alcohols using recently reported chiral PCP and NCN ruthenium(II) complexes may be an interesting alternative.[89,91] The chiral ruthenium complex **31** exhibits very high catalytic activity similar to the achiral analogues (**26**−**28**) in the hydrogen transfer process between ^{i}PrOH and acetophenone.[93,95] However, at present, the asymmetric induction is rather poor (14% ee).[89]

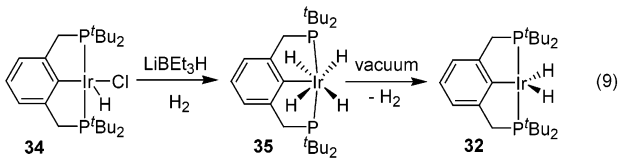
D. Iridium-Catalyzed Alkane Dehydrogenation

The thermally robust iridium pincer complexes **19**, **32**, **33** are efficient alkane dehydrogenation catalysts affording alkenes and dihydrogen, including dehydrogenation of cycloalkanes to cycloalkenes and arenes, tetrahydrofuran to furan, and ethylbenzene to styrene.[24−28,31,33,119,122,187]



The endothermic dehydrogenation of alkanes is symmetry forbidden and usually takes place under UV irradiation or in the presence of a hydrogen acceptor.[219,242] Although several homogeneous catalysts capable of alkane dehydrogenation have been reported,[120,219,242−247] the performance of the PCP-based systems is superior in terms of TONs, stability, and scope (for an excellent feature article, see ref 26). The combination of high catalyst stability, efficiency, and process reversibility are desirable also for advanced fuel cell technologies utilizing hydrocarbons as hydrogen storage. Selective dehydrogenation of linear alkanes to afford α-olefins was achieved with **32** and the analogous isopropyl complex **19** (with isopropyl groups replacing *tert*-butyl substituents on P).[28] Steric factors play an important role in PCP-based catalyst activity. Complex **19** yields turnover rates an order of magnitude larger than the sterically crowded *tert*-butyl complex **32** for the dehydrogenation of cyclodecane. Bulky substituents also largely influence catalyst activity with Heck catalysts **9**, **11**, and **12**.[55] Interestingly, no sacrificial hydrogenation sink (i.e., *tert*-butylethylene)[247] is necessary to drive

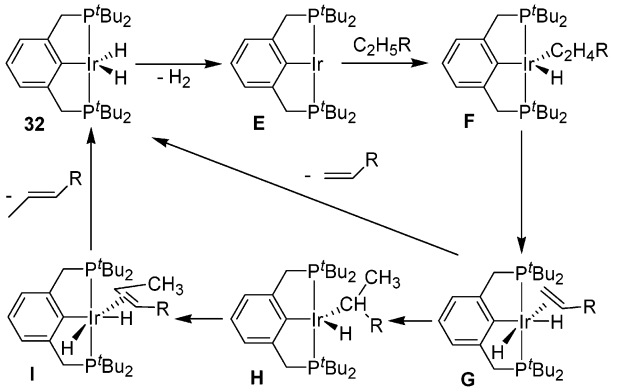
the overall process,[33] although the process is more efficient in the presence of *tert*-butylethylene. Dihydrogen can be removed from the equilibrium by purging the reactor with an inert gas other than dinitrogen. However, the relatively large endothermicity of the acceptorless dihydrogenation process requires higher temperatures. Complex **32** is a much more effective catalyst than the isoelectronic rhodium complexes,[120] in line with the general trend that third row transition metal complexes undergo more readily C−H oxidative addition than *iso*-structural second row complexes. Catalyst preparation is straightforward, i.e., catalyst **32** is obtained in good yield by treatment of the hydrochloride precursor **34** with $LiBEt_3H$ under H_2, followed by thermolysis of the resulting tetrahydrido iridium(V) complex (**35**) in vacuo (eq 9). Recrystallization of the dehydrogenation catalysts is essential to remove possible borate impurities which may inhibit catalysis.



(9)

The Ir(III) catalyst remains active after the reaction is complete and upon addition of more alkane substrate catalysis is resumed, leading to the same dehydrogenation products at essentially the same rate. The mercury test did not affect the reactivity, suggesting that metallic iridium is not involved. Catalysis is inhibited by high alkene concentration (hydrogen acceptor and/or product) and by traces of "inert" nitrogen gas affording catalytically inactive, crystallographically characterized μ-N_2 complex (section IIIJ, Scheme 7, **67**).[27] Dinitrogen coordination to unsaturated low-valent PCP complexes is common.[35,37,45,68,74,81] End-on dinitrogen coordination to (PCP)Rh(I) systems is known to inhibit intramolecular β-H elimination (section IIIM; Scheme 9, **60**, **95**).[77] Homogeneous dehydrogenation was observed at very high temperatures (200−250 °C) with the structurally related, rigid "antraphos" PCP complexes **33**, allowing the pursuit of new solution-based catalytic processes with high kinetic barriers.[122] Related Ni(II) and Pd(II) complexes were reported as well.[122,145,146] The rigidity of the polycyclic aromatic ligand apparently enhances the metal complex thermostability. On the other hand, catalysts **19** and **32** show much higher reactivity than **33** at lower temperatures but decompose above 200 °C. Comparison of calculated relative accessible molecular surfaces (ams)[248] of catalysts **19**, **32**, and **33** showed a distinctly lower ams value for **33**, which is in good agreement with experimental observations.[146] Mechanistically, both dissociative and associative pathways for acceptorless dehydrogenation processes can be considered.[16,17,26,117,219,249] In combined experimental and computational studies, Goldman and co-workers have shown that a dissociative route involving reductive elimination of H_2 from **32** has a slightly higher calculated energy barrier ($\Delta E^{\ddagger}$) and a significantly lower free-energy barrier than the barriers for an associative Ir(V)-based mechanism (Scheme 4).[117−119]

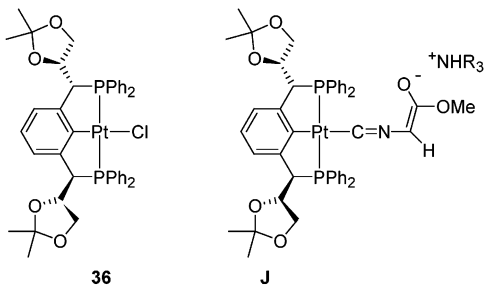
Scheme 4

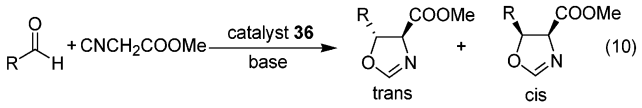


These findings strongly indicate that the associative mechanism is not kinetically viable under the reaction conditions. Ir(V) species have been reported (i.e., **D**, eq 6; **35** eq 9).[25,27] Hall proposed that the large endothermicity of the overall dehydrogenation process involving an associative mechanism is overcome stepwise in energetically balanced stages.[17] The dissociative route is likely to involve the following four key-steps: (i) rate determining[118] reductive elimination of H_2 (**32** → **E**), (ii) alkane C−H bond activation by a Ir(I)/Ir(III) oxidative addition process (**E** → **F**), (iii) β-H elimination to yield an olefin π-complex (**F** → **G**), and (iv) product dissociation. (**G** → **32**; Scheme 4).[26] If product release is slow (**G** → **32**), substrate double bond migration may occur (**H**, **I**).

E. Enantioselective Platinum-Catalyzed Adol Condensation of Methyl Isocyanoacetate and Aldehydes

The first enantiomerically pure PCP ligands, complexes, and asymmetric catalysis were reported by Venanzi et al.,[131,136] and have been further developed by others.[89,93,115,130,135] Chiral PCP ligands functionalized on the benzylic positions with acetals can be generated by enantioselective Sharpless epoxidation. Optically active platinum complexes such as **36** can catalyze the asymmetric aldol addition of methyl-α-isocynaoactetate to aldehydes, giving moderate ee's of 65% for the trans and 32% for cis oxazolines with excellent yields (eq 10).[131] For the aldol condensation, a cocatalytic amount of base is needed to generate the (unobserved) isocyano enolate metal complex **J**.

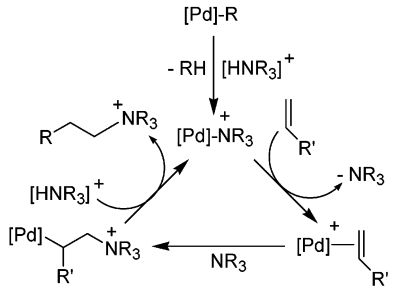




(10)

Competition experiments between *para*-substituted benzaldehydes indicated that electrophilic attack of

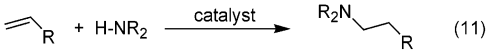
Scheme 5



the aldehyde on a coordinated isocyano enolate is the slow step. Hammett analysis showed a linear free energy relationship with a positive slope ($\rho = 1.6$), indicative of a reduced electron density at the carbonyl carbon in the transition state of the C−C bond forming step,[250] suggesting that coordination of the aldehyde to the platinum center is not involved. A significantly improved synthetic route to related optically pure PCP ligands and their Pt(II) and Pd(II) complexes was reported by Zhang et al. which may lead to a new family of chiral PCP-based catalysts.[130,135] Higher efficiency and enantioselectivity in the adol reaction (eq 10) was observed with a palladium catalyst analogous to **36**. The enantioselectivity was also enhanced by solvent polarity: THF > CH_2Cl_2 > toluene. In contrast to Venanzi's Lewis acid catalyst **36**, other factors including concentration, addition rate, and base had little effect on the reaction outcome with the Pd(II) analogue. Moreover, the stereochemical product distribution with **36** differ from palladium-based systems, underscoring again the importance of metal−ligand modifications.

F. Palladium-Catalyzed Hydroamination

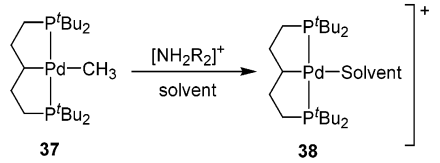
Hydroamination of olefins with alkali metals requires high temperatures and pressures (eq 11).[251,252] Catalytic amination of olefins under mild reaction conditions has been reported with lanthanide and early transition metals.[253−256] Very few examples of catalytically active late transition metal complexes are known.[257−260]



(11)

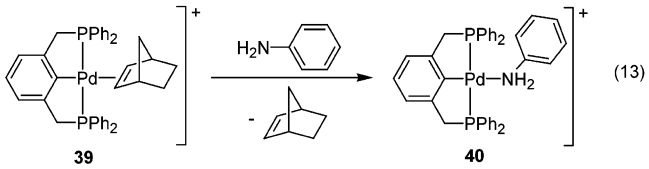
Mechanistically, oxidative addition of amine N−H bonds to low-valent late transition metals may produce hydrido amido complexes. Olefin insertion into the metal-amide bond may afford a hydrido-alkyl species, which may be followed by facile C−H reductive elimination of the product amine, regenerating the coordinatively unsaturated catalyst. Such a mechanism was demonstrated with Ir(I) as catalyst.[257] Another mechanism may involve nucleophilic attack of the amine on the coordinated alkene as shown by theoretical calculations. Trogler reported catalytic amination of activated olefins with palladium(II) complexes **37** and **38** (eq 12), which proceed via the latter mechanism (Scheme 5).[148,150]

Catalytic amounts of the catalyst precursor Pd−Me complex **37** and $[NH_3Ph][BPh_4]$, combined with aniline and acrylonitrile at room temperature, are almost quantitatively converted to 3-anilinopropionitrile. Hunderds of turnovers with no loss of activity were observed. Catalyst **38** is robust and therefore active longer than the known $PdR_2(R_2'PCH_2CH_2PR_2')$-based catalysts, where R = CH_3 or CH_2SiMe_3 and R′ = Me, Ph. The reactions with **37** and **38** appear also to be more selective. Protonolysis of **37** with ammonium salts yields the solvent coordinated complex **38** and not the corresponding amine complexes (eq 12).



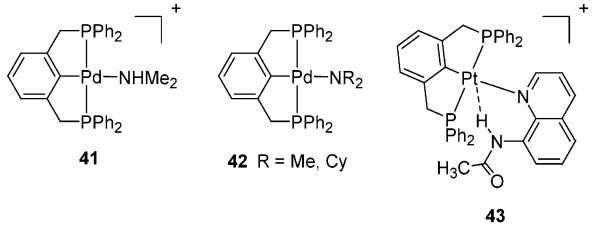
37 38 (12)

However, Kraatz and Milstein showed that addition of aniline to a THF solution of **39** (having phenyl substituents on P) resulted in the exclusive formation of the crystallographic characterized amine complex **40** (eq 13).[50]



39 40 (13)

The difference in coordination behavior between Trogler's catalyst **38** and complex **39** is likely to be of steric origin. Amine complexes akin to model complex **40** are postulated intermediates in hydroamination processes with **37** (Scheme 5). Likewise, the cationic dimethylamine complex $[Pd(NHMe_2)\{2,6\text{-}(CH_2PPh_2)_2C_6H_3\}]^+$ (**41**) and analogous neutral $[Pd(NR_2)\{2,6\text{-}(CH_2PPh_2)_2C_6H_3\}]$ (R = Me, Cy) (**42**) systems have been reported recently.[152,153] Pregosin reported several cationic bivalent platinum complexes **43** containing N−H···Pt interactions.[156] Amination of olefins involving metal-mediated N−H bond cleavage may involve similar metal-substrate interactions.

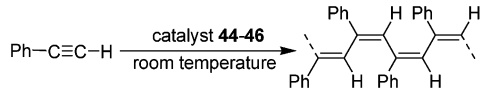


41 42 R = Me, Cy 43

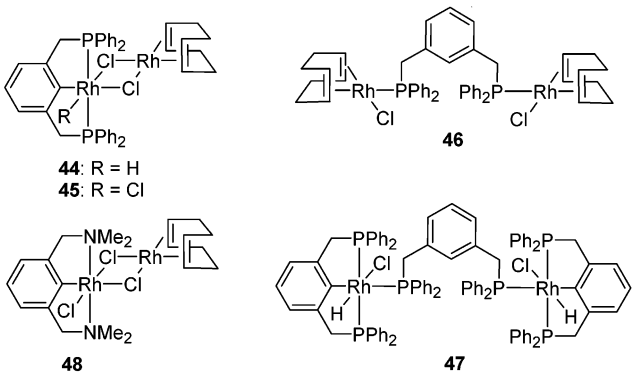
G. Phenylacetylene Polymerization by Dinuclear Rh(III)−Rh(I) Complexes

Reaction of phenylacetylene with the dinuclear Rh(III)−Rh(I) complexes (**44**−**46**) at room-temperature resulted in the formation of stereo regular *cis*-transoidal poly(phenylacetylene) with a molecular weight of about 50 000 (∼490 TONs; eq 14).[132] X-ray analysis unambiguously confirmed the structure of **45**, which is similar to the previously reported dinuclear $RhCl(NCN)(\mu\text{-}Cl)_2Rh(COD)$ complex (**48**;

COD = 1,5-cyclooctadiene).[157] The polymerization process is probably catalyzed by the (COD)Rh(I) moiety of **44**−**46**, since the (PCP)Rh(III) moeties are coordinatively saturated. As expected, the PCP-bridged dinuclear Rh(III) complex **47** is not catalytically active. Numerous d^8 Rh(diene) complexes are known to polymerize terminal aromatic acetylenes in a similar fashion.[261−264] In-situ NMR studies did not reveal any intermediates with **45** and **46**, whereas formation of several uncharacterized rhodium complexes (lacking a Rh−H moiety) was observed with **44**.

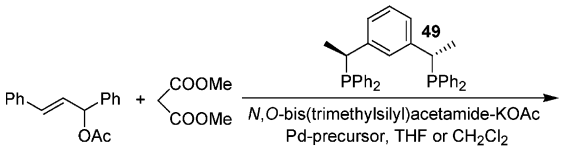


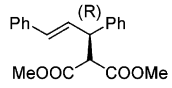
(14)



H. Asymmetric Allylic Alkylation by Palladium

The palladium-catalyzed reaction of dimethylmalonate with 1,3-diphenyl-2-propenyl acetate in the presence of **49** afforded the alkylation products with high yields and promising enantioselectivities (ee range: 50−79%; eq 15). The reaction proceeds smoothly at room temperature; however, running the reactions at lower temperatures resulted in significant ee enhancements by about 23% (0 °C) and 27% (−20 °C), respectively. $Pd(OAc)_2$ and $[Pd(C_3H_5)Cl]_2$ were used as catalyst precursors and much higher yields (>99%) were observed with the latter. The enantiomerically pure PCP ligand **49** was readily prepared from commercially available starting materials.[135] Although various PCP complexes (M = Ru, Ir, Rh, Pd, Ni, Pt) were prepared starting from racemic **49**,[131] no comprehensive study on the catalytic properties in the allylic alkylation or closely related reactions using enantiomerically pure **49**-based complexes has been reported yet.

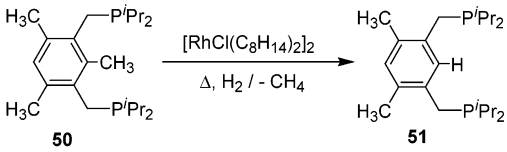




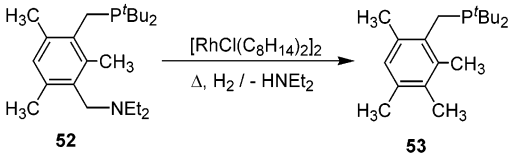
(15)

I. Catalytic C–C and C–N Bond Activation by Rhodium

Catalytic metal-mediated C−C and C−N single bond activation are rare processes; catalytic C−C bond activation is often limited to relatively weak bonds α to a carbonyl group and/or strained systems,[60,265−273] and even fewer examples have been reported with C−N single bonds.[274−276] Catalytic hydrogenolysis of strong C−C and C−N single bonds by rhodium was demonstrated with PCP (**50** → **51**; eq 16) and PCN (**52** → **53**; eq 17) substrates, respectively.[43,54] Catalytic transfer of a CH_2 group from **50** to a silane and de-ethylation of a PCP substrate was observed as well.[54]



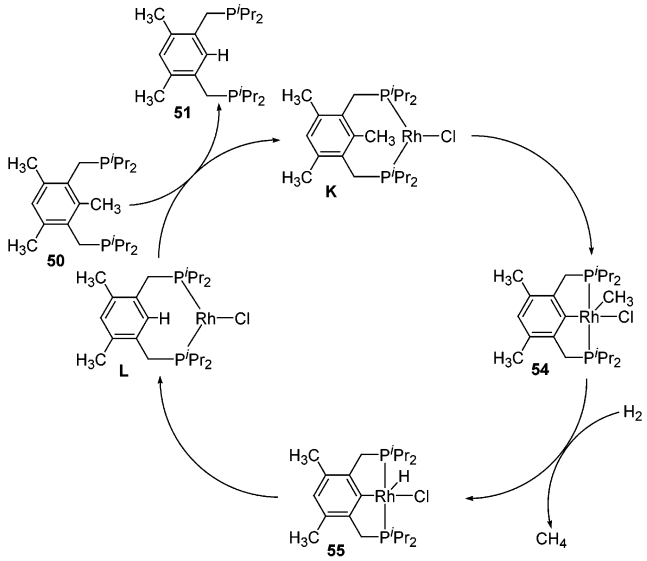
(16)



(17)

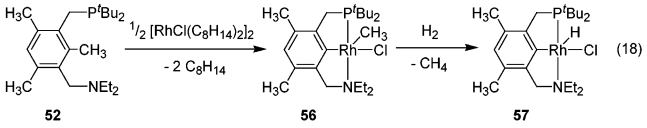
The bond activation reactions are remarkably selective and highly substrate dependent. Only one alkyl group is affected with the PCP substrate **50**,[54] whereas with the PCN system **52** selective sp^3 C−N bond cleavage occurs.[43] Although the catalytic processes were not fully optimized, 109 turnovers were observed with **50**. The postulated catalytic cycle for the C−C bond activation process is outlined in Scheme 6 and is based on stoichiometric reactions.

Scheme 6



Reaction of **50** with 0.5 equiv of $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) resulted in selective oxidative addition of only one of the three strong Ar−CH_3 bonds available (**54**), presumably by precoordination of both phosphines "arms" to one metal center (**K**). Subsequent treatment of the reaction mixture with dihydrogen (25 psi) at elevated temperatures afforded the Rh(III)−H complex **55** and one equivalent of

methane. The latter process is suggested to proceed via an unobserved Rh(V) intermediate or σ-bond metathesis. Mild heating in the presence of excess PEt_3 gives the dealkylated substrate **51** and $RhCl(PEt_3)_3$ by phosphine exchange (**L**).[54] Interestingly, different reactivity is observed with the similar PCN system (**52**).[43] Reaction of **52** with a catalytic amount of $[RhCl(C_8H_{14})_2]_2$ resulted in C−N bond activation affording **53** and diethylamine in good yield (eq 17), which is in sharp contrast with the stoichiometric reactions (eq 18). Treatment of **52** with 0.5 equiv of $[RhCl(C_8H_{14})_2]_2$ quantitavively yielded the crystallographic characterized (PCN)Rh(CH_3)Cl complex **56**.[41] No C−C or C−H bond activation was observed in parallel to the catalytic C−N bond cleavage. Reaction of **56** with dihydrogen yields the hydrido chloride complex **57** and one equivalent of methane. Formation of a stoichiometric amount of methane (based on Rh) is observed during catalysis indicating that **57** is formed initially. Indeed, **57** can be used instead of $[RhCl(C_8H_{14})_2]_2$. The catalytic cycle probably involves a complex exchange sequence of competing phosphine/amine coordination in line with recent reported transcyclometalation reactions with late transition metals in which pincer NCN complexes are precursors for the formation of PCP complexes by amino/phosphine ligand exchange.[87,92,93,98,113] In general, phosphines coordinate more strongly to low-valent transition metals than amines.[277] Consumption of all the PCN substrate **52** does not lead to decomposition of the catalytically active species. Catalysis is resumed by addition of more substrate; however, the yield decreased with higher ligand/catalyst ratios indicative of inhibition of the overall process by the substrate and/or product.



(18)

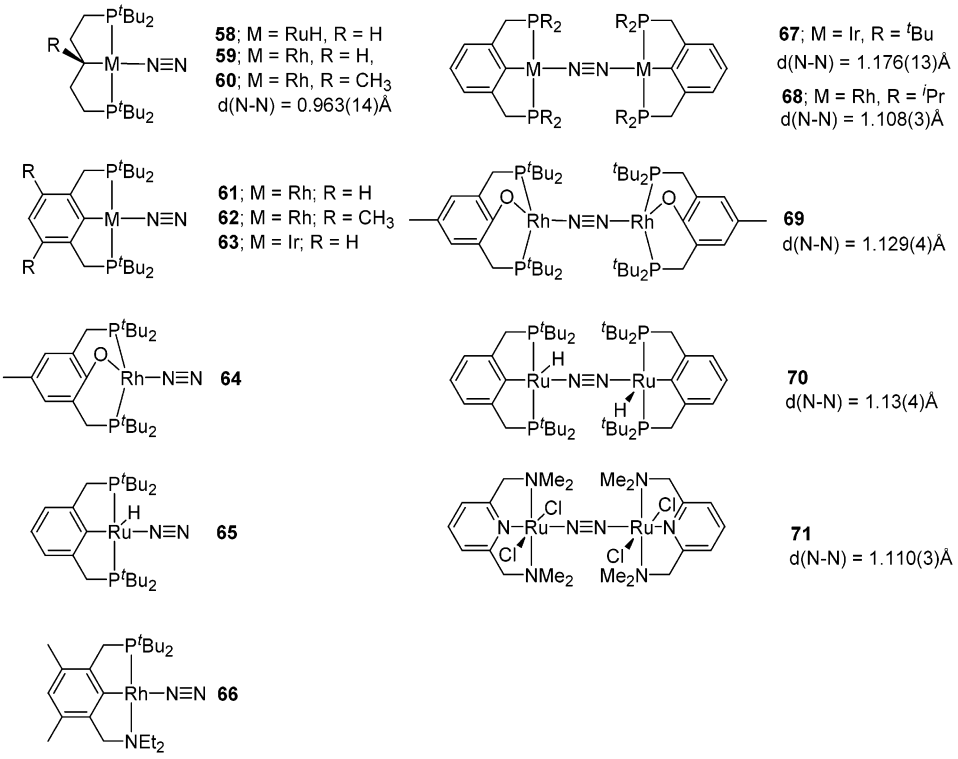
III. Coordination and Activation of Small Molecules

Reversible substrate coordination is a prerequisite for almost any catalytic metal complex transformation to occur. Therefore, in-depth fundamental studies of the coordination behavior of potential reagents and substrates are crucial for further development of metal-mediated transformations. For a given substrate, what are the necessary requirements to balance coordination with substrate reactivity? Strong, irreversible coordination may shut down a catalytic process, while relatively weak metal−substrate binding may not lead to substrate activation and functionalization. In the latter case, nonproductive substitution reactions may dominate. A substantial amount of solid data are available regarding alkene and dihydrogen coordination to unsaturated metal complexes,[219,242,278−282] while less is known about the coordination chemistry of water and carbon dioxide and relatively chemically "inert" compounds such as molecular nitrogen. Dinitrogen is generally considered and widely applied as a relatively cheap source of an inert gas, believed to not affect reaction outcome, product distribution, or rate. Formation of transient N_2 adducts during metal-mediated transformations is often not considered, but it may play a significant role in organometallic chemistry by coordinating to catalytically active complexes, slowing down or even inhibiting reactions. Recent findings with unsaturated, low-valent PCP and similar pincer complexes unambiguously demonstrate that dinitrogen is certainly not an innocent spectator, but actively participates in the following reactions: (i) traces of N_2 inhibit iridium-catalyzed dehydrogenation of alkanes,[24,26,27] (ii) N_2 competitively coordinates to Rh(I) complexes by replacing η^2-bound carbon dioxide, ethylene, and η^2-bound dihydrogen,[74] (iii) N_2 trapping of an unsaturated intermediate inhibits intramolecular β-H elimination,[77] and (iv) N_2 coordination may result in formation of various bimetallic dinitrogen bridged PCP and related pincer complexes.[26,27,31,34,35,37,45,68,74,77,81,85,174] Rhodium low-valent dinitrogen complexes undergo readily alkyl-I oxidative addition,[67,70−72] and are excellent precursors for formation of metal-carbenes.[45,81,174] Coordination and/or activation of H_2,[32,36,38,74,160,200] alkynes,[39,154,155] alkenes,[50,74] solvents,[50,74,173] H_2O,[31,115,147−149] and CO_2 have been reported with various PCP systems.[74,123,126,151]

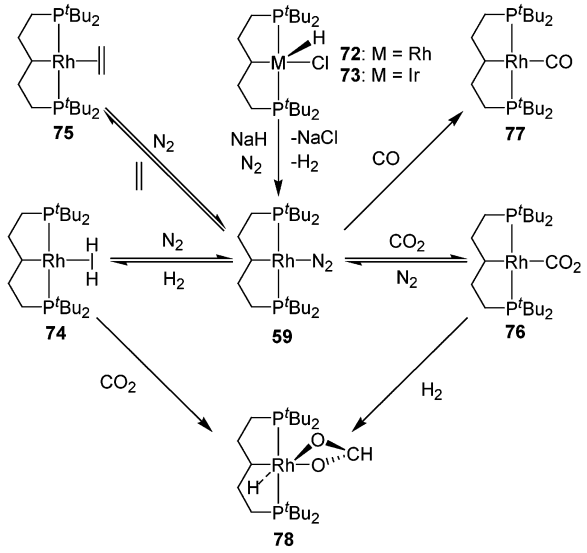
A. Rhodium, Iridium, Osmium, and Ruthenium Dinitrogen Complexes

Formation of low-valent Rh(I), Ir(I), Os(II), and Ru(II) dinitrogen pincer complexes have been reported in the past five years by Milstein,[22,45,67,68,74,77,81,174] van Koten,[85] Jensen,[26,27] and Gusev.[34,35,37] Examples and crystallographically determined N−N bond distances are listed in Scheme 7. The N_2 ligand is coordinated "end-on" to one (**58**−**66**) or two low-valent metal centers (**67**−**71**). There are several issues here to be addressed. Which factors govern the dimerization process of some of the mononuclear complexes? No dimerization of **58**−**60** having an "aliphatic" PCP ligand has been reported. Is it possible to activate and functionalize the η^1-N_2 or μ-N_2 ligands? Monomeric dinitrogen complexes might be in equilibrium with unobserved 14-electron complexes (i.e., section III, Scheme 10, **O**; Figure 6, **N**).[68] Subsequent recombination of these species may afford the observed dinitrogen bridged complexes. In Gusev's ruthenium systems (**70**), associative pathways cannot be ruled out.[37] All reported PCP-based dinitrogen complexes have basic, sterically demanding *tert*-butyl or *iso*-propyl substituents on the phosphorus donor atoms. Steric factors undoubtedly play here a major role in stabilizing the kinetically labile Rh-η^1-N_2 moiety by preventing or at least hindering associative ligand exchange and prohibiting coordination of relatively large substrates, including solvents.[74] However, it seems that electronic factors are equally important as evidenced by van Koten's bimetallic NNN-based dinitrogen complex **71**,[85] in which the far less bulky and strongly electron donating NMe_2 groups are present. Crystallographic studies in combination with IR data (for the monomeric complexes) show that η^1-N_2−M and M−μ−N_2−M coordination only slightly affects the N−N bond order. Bond lengths vary from

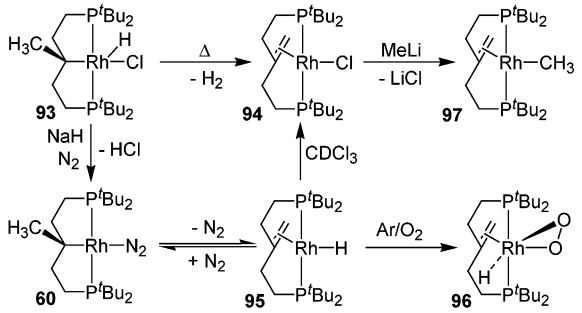
Scheme 7



Scheme 8

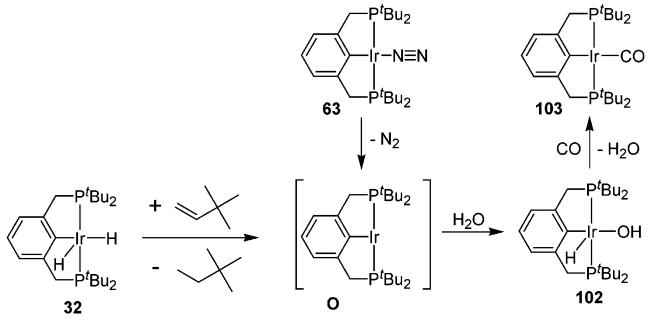


Scheme 9



0.963(14) Å (**60**) to 1.13(4) Å (**70**), suggesting a relatively small π-delocalization in the M−N_2 moeties in comparison with other dinitrogen complexes and

Scheme 10



is in range with that of molecular nitrogen (1.0977 Å) and N_2^+ (1.116 Å; bond order $2^1/_2$).[283−285] Since an elongated bond length of coordinated N_2 is not a necessary prerequisite for N_2 activation,[286] N_2 functionalization in the recent series of new, well-defined PCP-based dinitrogen complexes (**58**−**71**) is worth studying.

B. Competitive Coordination of N_2, CH_2=CH_2, H_2, and CO_2 to Rhodium(I)

The Rh(III) complex **72** and the analogous Ir(H)(Cl)[HC($CH_2CH_2P^tBu_2$)$_2$] (**73**) are readily obtained by reaction of **1** (R = ^{t}Bu) with $MCl_3 \times H_2O$ (M = Rh, Ir) as metal complex precursors (Scheme 8).[1,3] Reaction of **72** with an excess of NaH results in the quantitative formation of the Rh(I) η^1-dinitrogen complex **59** and H_2.[74] Apparently, the reaction proceeds by the formation of an (unobserved) Rh(III)−dihydride complex, which undergoes H_2 reductive coupling to afford the η^2-dihydrogen Rh(I) complex **74**. The coordinated H_2 is replaced by N_2 used as an "inert" gas. The IR spectrum of **59** showed a band at ν = 2108 cm^{-1},[74] characteristic of "end-on" coordi-

Table 3[a]

incoming ligand (L)	K_{eq} (298 K)	ΔG°_{298k}, kcal/mol
74 H_2	8.08 (± 0.48)	−1.24 (± 0.04)
75 $CH_2{=}CH_2$	7×10^{-2} ($\pm 1 \times 10^{-3}$)	+1.57 (± 0.01)
76 CO_2	7×10^{-3} (1×10^{-3})	+2.97 (± 0.06)

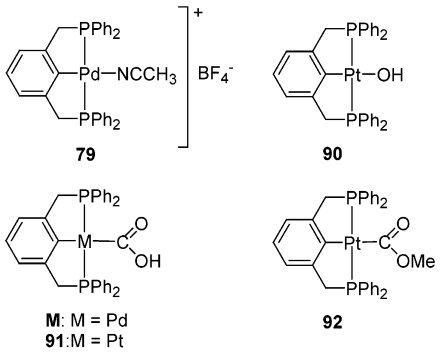
[a] $Rh{-}N_2$ (**59**) + L ⇌ Rh−L + N_2 with $K_{eq} = [Rh{-}L][N_2]/[Rh{-}N_2][L]$. Temp = 25 °C in cyclohexane.

nated N_2 to low-valent Rh(I).[81,287,288] Treatment of **59** with various gaseous molecules (H_2, ethylene, CO_2, and CO) and resulted in replacement of the kinetically labile dinitrogen ligand and formation of the corresponding η^2-H_2 (**74**), η^2-$CH_2{=}CH_2$ (**75**), η^2-CO_2 (**76**), and η^1-CO (**77**) complexes.[74] Although all compounds (**59**, **74**−**77**) are coordinatively unsaturated, the sterically demanding *tert*-butyl substituents on the phosphine donor atoms may hinder an associative mechanism for ligand exchange. Exposing **74**−**76** to a dinitrogen atmosphere resulted in rapid ligand exchange affording quantitative formation of the Rh(I)−η^1-N_2 complex **59**.

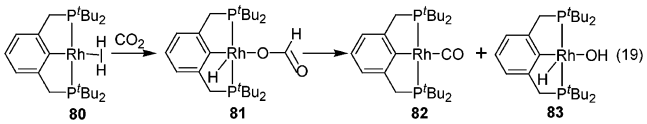
$^{31}P\{^1H\}$ NMR equilibria studies of the reaction: $Rh{-}N_2$ (**59**) + L ⇌ Rh−L (**74**−**76**) + N_2 with L = H_2, C_2H_4, CO_2, respectively, showed that the relative stability toward ligand (L) dissociation is as follows: η^2-H_2 (**74**) > η^1-N_2 (**59**) > η^2-C_2H_4 (**75**) > η^2-CO_2 (**76**; Table 3). The basic trialkyl P groups certainly promote complexation of weak donor ligands and stabilize the resulting adducts; however, steric factors play here a dominant role given that ethylene is a much better σ-donor and π-acceptor than dinitrogen. Similar observations were made with $RhCl[P(C_6H_{11})_3]_2$-(η^2-N_2), which does not undergo ligand exchange with C_2H_4 or H_2.[288] Slow H/D exchange between deuterated aromatic solvents and the aliphatic backbone of **59** was observed. Although no kinetic studies were performed, it is likely that reversible N_2/solvent exchange occurred followed by C−D bond activation. All abovementioned observations are in line with the fact that even traces of N_2 inhibit catalytic alkane dehydrogenation with iridium and rhodium PCP complexes (section II, i.e., **32**).[26,27]

C. CO_2 Activation–Iridium and Rhodium Formate Complexes

Reduction of CO_2 is a topic of rapidly increasing interest,[151,289] since efficient functionalization of this cheap greenhouse gas to valuable liquid fuels (i.e., methanol) may contribute to a balanced CO_2 emission. Stoichiometric reduction of CO_2 with PCP complexes has been observed.[123,126,151] Palladium complexes have been used in studies toward the electrochemical reduction of CO_2, including $[Pd(NCCH_3)(2,6\text{-}(CH_2PPh_2)_2C_6H_3)]^+BF_4^-$ (**79**).[151] Complex **79** exhibits significant catalytic currents in the presence of acid and CO_2. Formation of an unobserved hydroxycarbonyl intermediate $Pd(CO_2H)[(2,6\text{-}(CH_2PPh_2)_2C_6H_3)]$ (**M**) was suggested, which decomposes in the presence of acid to give H_2 as catalytic product. Although these results seem encouraging, more detailed studies are definitely needed to further characterize the processes involved.

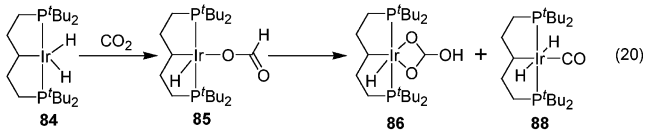


Formation of a Rh(III) hydrido formate complex **78** was observed by treatment of **74** with CO_2 and by reaction of **76** with H_2 (Scheme 8).[74] The rarely observed formate complexes are possible intermediates in rhodium-catalyzed CO_2 hydrogenation to formic acid.[290] Kaska et al. reported that complex **80** (analogous to **74**)[74] reacts also with CO_2 to afford an unstable formate species **81** which undergoes a secondary transformation forming carbonyl (**82**) and hydrido hydroxy (**83**) complexes (eq 19).[123] This interesting reaction (**80** + CO_2 → **82** + **83**) can be viewed as a metal-mediated reverse water-gas shift process: $CO_2 + H_2 \rightleftharpoons CO + H_2O$.



(19)

Reaction of the Ir(III)−dihydride complex **84** with CO_2 resulted in the formation of the unstable **85**, followed by formation of hydrogencarbonate complex **86** and carbonyl dihydride (**88**) complexes (eq 20).[126] The mechanism of this reaction sequence is not crystal clear, but may involve formate dissociation from **85** followed by an unsymmetrical disproportionation process. Complex **88** was independently prepared by reacting CO with $Ir(H)_4[HC(C_2H_4P(^tBu)_2)_2]$ (**89**).[6,126] In all three systems (Scheme 8, eqs 19 and 20), formate formation (**78**, **81**, **85**) has been observed,[74,123,126] but the final reaction outcome seems highly metal dependent.



(20)

Notably, crystallographic analysis showed the hydrogencarbonate **86** as a hydrogen bonded dimeric structure (Figure 4).[126] Bennett and co-workers reported a similar dimeric structure with Pt(II) exhibiting hydrogen-bonded carboxylate groups in the solid state.[159] Reaction of $Pt(OH)[2,6\text{-}(CH_2PPh_2)_2C_6H_3]$ (**90**) with CO resulted in the formation of the hydroxycarbonyl complex $Pt(CO_2H)(2,6\text{-}(CH_2PPh_2)_2C_6H_3)$ (**91**) by insertion of CO into the Pt−O σ bond. The latter is the Pt(II) analogue of the postulated **M**.[151] Complex **91** is monomeric in solution and reacts with methanol to afford $Pt(CO_2Me)(2,6\text{-}CH_2PPh_2C_6H_3)$ (**92**).

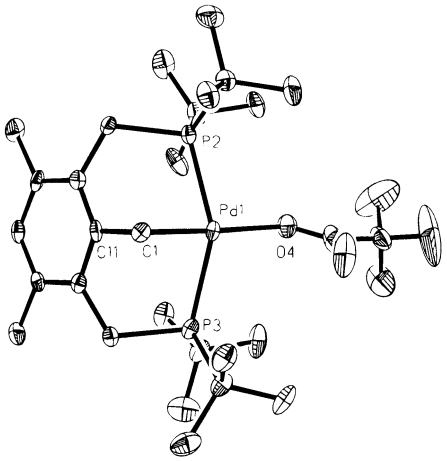


Figure 1. ORTEP drawing of the molecular structure of the Heck catalyst **12**. From ref 55. Copyright 1997 American Chemical Society.

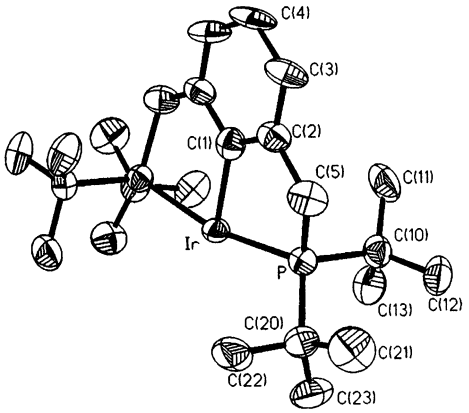


Figure 2. ORTEP drawing of the molecular structure of the dehydrogenation catalyst **32**. From ref 25. Copyright 1997 American Chemical Society.

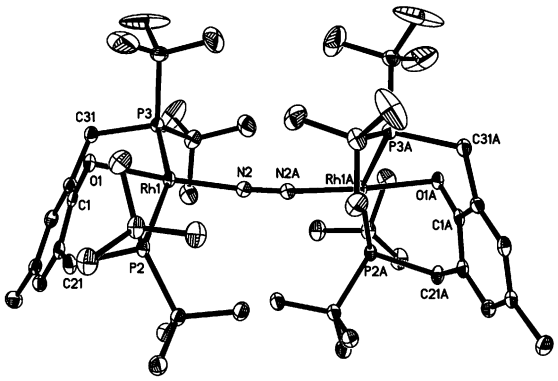


Figure 3. ORTEP drawing of the molecular structure of **69** showing the N_2 ligand coordinated to two Rh(I) metal atoms with $d(N{\equiv}N) = 1.129$ Å. From ref 68. Copyright 1998 American Chemical Society.

D. Dinitrogen Controlled trans β-H Elimination

Thermolysis of the Rh(III) hydrido chloride complex **93** resulted in the formation of **94**, presumably by a β-H elimination process and H_2 formation (Scheme 9).[1,2] Treatment of **93** with NaH resulted in formation of the Rh(I) η^1-dinitrogen complex **60** and the hydrido olefin complex **95**.[77] Both complexes (**60**, **95**) cocrystallized within one crystal lattice. Complex **60** was converted into **95** by sweeping the solution with

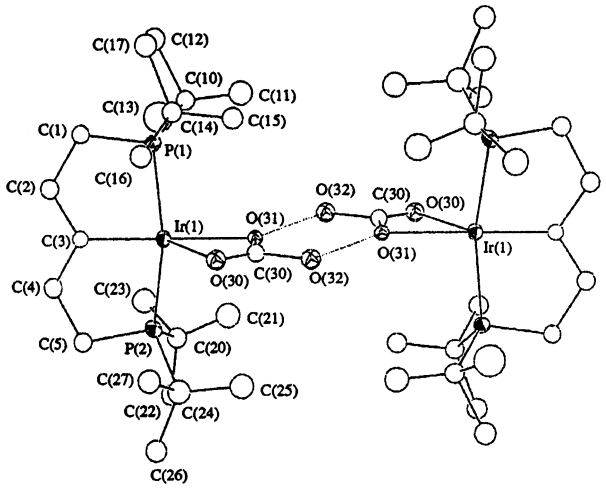


Figure 4. ORTEP drawing of the hydrogen-bonded molecular structure of **86**. From ref 126. Copyright 1999 American Chemical Society.

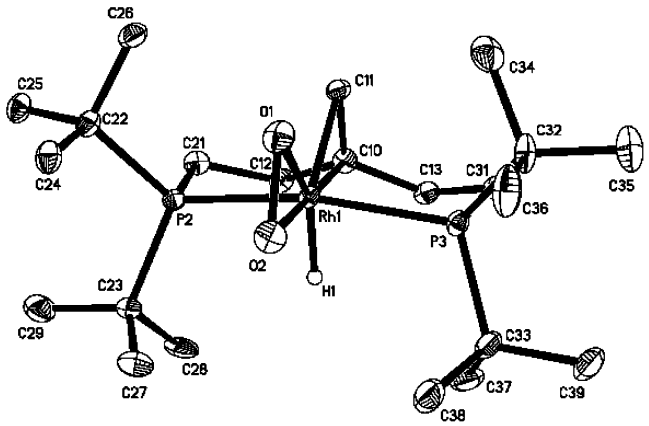


Figure 5. ORTEP drawing of the molecular structure of the dioxoalkene hydride complex **96**. From ref 75. Copyright 1996 Royal Society of Chemical.

argon, whereas exposing **95** to N_2 reversed the process. Formation of dimeric Rh$-\mu-$N$_2-$Rh complexes was not observed here (Scheme 7). Treatment of **95** with argon containing a trace amount of O_2 resulted in the selective formation of a crystallographically characterized, rare dioxo-alkene hydride complex **96** (Figure 5).[75] Complex **96** is stable at elevated temperatures (~60 °C), but in $CDCl_3$ quantitative H/Cl exchange and deoxygenation was observed, affording **94**. Catalytic alkene oxidation processes are believed to involve intermediates akin to **96**,[291] but only few isolated complexes containing alkene, dioxygen, and hydride ligands (mutually cis oriented) are known.[292,293]

The quantitative free energy profile for the overall, reversible transformation, **95** + $N_2 \rightleftharpoons$ **60**, was determined by kinetic and equilibrium NMR studies (Figure 6). This represents a rare case in which the free energy profile of a migratory insertion process has been completely mapped out. Variable temperature $^{31}P\{^1H\}$ NMR studies showed that **60** and **95** interconvert with an 1:1 equilibrium ratio at room temperature, while at elevated temperatures only **95** is observed. Equilibrium parameters at different temperatures are listed in Table 4. The $\Delta G \sim -3$ kcal/mol for the equilibrium between **60** and **95**

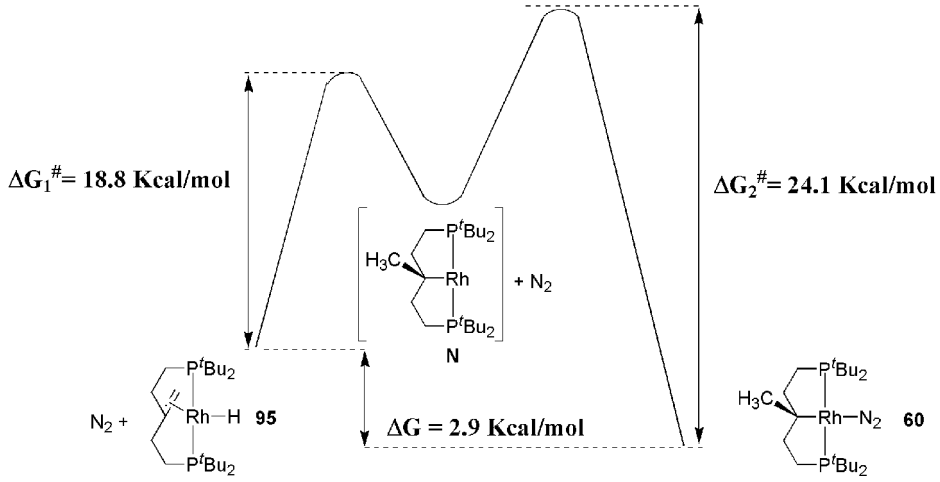


Figure 6. Free energy profile (**95** + N_2 ⇌ **60**): olefin insertion into Rh−H and N_2 trapping. Adapted with permission from ref 77. Copyright 1997 VCH Verlagsgesellschaft.

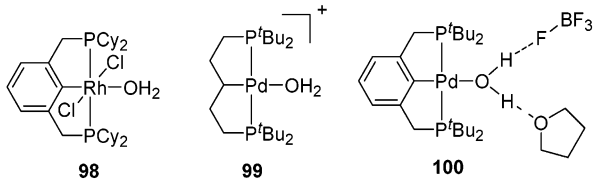
Table 4. Temperature Dependence of the Equilibrium: 95 + N_2 ⇌ 60

T (K)	K_{eq}	ΔG (kcal/mol)
294	163.7	−2.98
303	110.1	−2.83
313	77.9	−2.71
323	50.6	−2.51

indicates that N_2 coordination is preferred. Indeed, pressurizing a mixture of **60** and **95** with N_2 (80 psi) resulted in quantitative formation of **60**, representing a rare example of a N_2 controlled chemical transformation. The large negative entropy of activation, $\Delta S^{\#} = -39.3$ eu, for the migratory insertion process is consistent with a concerted, highly organized transition state. NOE spin saturation transfer difference experiments show that N_2 coordination to a transient 14-electron species (Figure 6, **N**) has a higher activation barrier than the competing trans β-hydrogen elimination, making N_2 dissociation from **60** the slow step for the transformation of **60** to **95** with $\Delta G^{\#}_{298} = 24.1$ (± 0.1) kcal mol^{-1}. Thus, this clearly demonstrates that N_2 can act as a trap in a migratory insertion process. Combined structural (NMR, X-ray) and kinetic studies suggest that essentially the trans geometry remained during the reversible β-H elimination step,[77] although β-H elimination and hydride migration to an olefin generally proceed via cis intermediates and/or involve trans−cis isomerization.[72] Structural disorder of the trans configuration of **95** in the ground state and the high $\Delta S^{\#}$ for the migratory insertion step are in support of this hypothesis. The methyl olefin complex **97**, obtained by reacting **94** with MeLi, does not undergo migratory insertion, in line with the normally Me < H migration rate and supporting the hypothesis that *cis*-intermediates are not readily available in these geometrically constrained systems.[77,82,294]

E. Coordination and Oxidative Addition of H_2O

Oxidative addition of H_2O by late transition-metal complexes has been proposed to occur in various catalytic processes,[140,295] and is a key step in the design of water-based metal-mediated transformations. Isolation and full characterization of late-transition-metal complexes having H−M−OH functionalities is relatively rare.[31,296−304] The X-ray structure of *trans*-Rh(Cl)$_2$(OH$_2$)[2,6-(CH$_2$PCy$_2$)$_2$C$_6$H$_3$] (**98**) (Cy = cyclohexyl) revealed that metal-coordinated H_2O is simultaneously hydrogen-bonded to propan-2-ol.[147] H_2O coordination is even favored in the presence of excess propan-2-ol. This M-OH$_2$ stability may be attributed to the sterically demanding cyclohexyl groups on the P donor atoms.[147,164,190] Likewise, the coordination chemistry of N_2 (**59**), H_2 (**74**), CH_2=CH_2 (**75**), CO_2 (**76**) to Rh(I) PCP systems is controlled by bulky *tert*-butyl substituents on P (Scheme 8). Trogler (**99**),[148] Bullock (**100**),[149] and van Koten (**23**)[115] reported the formation of (PCP)Pd−H$_2$O complexes. Interestingly, recrystallization of **100** from a THF solution resulted in a complex having H_2O coordinated to the palladium center and simultaneously hydrogen-bonded to a BF_4 counteranion and a THF molecule (Figure 7).[149] Crystallization of **100** from toluene resulted only in formation of a BF_4 counteranion adduct.



A comparison by Muir between various structurally characterized aqua complexes indicated that Rh−O bond distances are influenced by the electronic properties of trans ligands.[147] Unexpectedly, metal oxidation state, sterics, and charge play only a minor role. For instance, the Rh−O bond distances of **98** and the NCN analogue are 2.274(3) and 2.269(2) Å, respectively. Some of van Koten's unsaturated NCN-based complexes form adducts with water.[86,88,90,99−101,106,114] For instance, water exchange on a Pt(II) center has been studied with [Pt(OH$_2$)-(2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$)]$^+$(OSO$_2$CF$_3$)$^-$ (**101**) by ^{17}O NMR.[99] Moreover, H_2O induced C−C bond activation was observed with NCN platinum complexes (IVC, eq 40 **124** → **101**).[86,88,90,100,101,106,114] Jensen reported that **63** undergoes dinitrogen dissociation

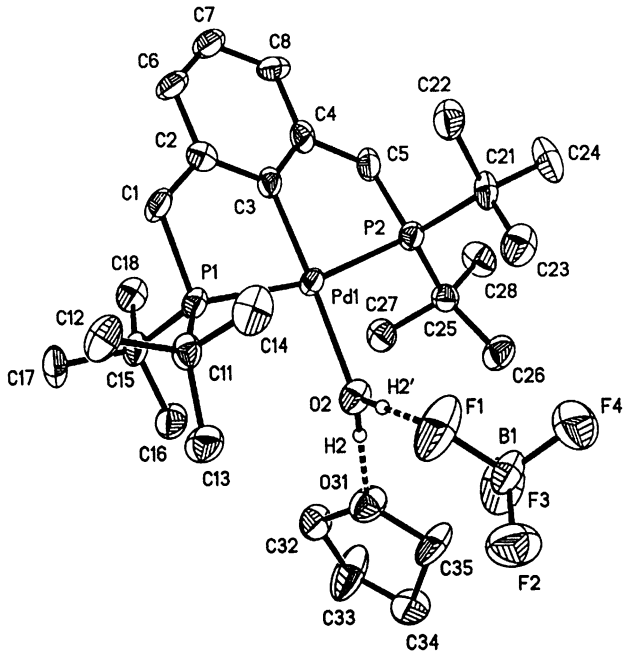


Figure 7. ORTEP drawing of the molecular structure of **100** having both a BF_4 counteranion and a THF solvent molecule hydrogen bonded to the coordinated H_2O ligand. From ref 149. Copyright 2002 Elsevier.

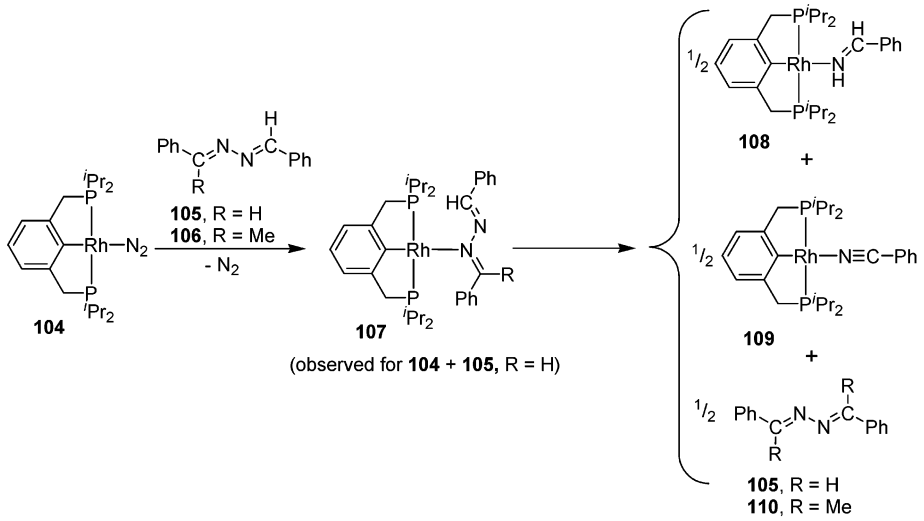
affording the postulated intermediate **O** followed by H−OH oxidative addition to afford the fully characterized hydrido hydroxy complex **102** (Scheme 10).[31] The reverse process, H−OH reductive elimination, was observed by addition of CO to **102** affording the Ir(I) carbonyl complex Ir(CO)[2,6-($CH_2P^tBu_2$)$_2C_6H_3$] (**103**).[32] Treatment of the dihydrogen complex **32** with *tert*-butylethylene followed by addition of H_2O to the product solution resulted also in the selective formation of **102**. The latter is a suitable catalyst precursor for catalytic transfer dehydrogenation of cyclooctane to cyclooctene at elevated temperatures (1200 TON/h). The analogous Rh(III) complex **83** is obtained by reaction of Rh(H)(Cl)[2,6-($CH_2P^tBu_2$)$_2C_6H_3$] (**203**; section IVA, eq 38) with NaOH or by reaction of **80** with CO_2 (eq 19).[123] Alkane dehydrogenation with **32** or **102** proceeds even in the presence of water,[31] whereas N_2 competely inhibits the reaction by formation of **63** and **67** (Scheme 7).[24,26,27] Although no alcohols, ketones, or ethers were observed yet, these H−OH oxidative reactions provide hope that future metal complex modifications may lead to catalytic hydroxylation of alkanes by water.

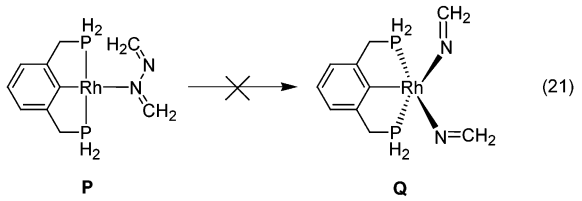
F. Reactions of Azines (R_2C=N–N=CR_2) with Rh(I) Dinitrogen Complexes

Various transition metal complexes of cobalt, iron, titanium, zirconium, and uranium are known to activate azine N−N bonds in a symmetrical fashion.[305−309] The two resulting imide units, −N=CR_2, remain bound to a metal center. No catalysis has been observed. Recently, reactions of azines with PCP-based Rh(I) dinitrogen complexes has been reported.[173] The low-valent metal center promotes a cascade of unique transformations, including asymmetric N−N bond cleavage accompanied by symmetric N−N coupling, C−H activation, and even catalysis. For instance, reaction of complex **104** with a stoichiometric amount of benzalazine (**105**) at −30°C results in the formation of three complexes (**107**−**109**; Scheme 11).

Apparently, complex **107** is an intermediate in the formation of complexes **108** and **109** as **107** converts to **108** and **109** in a 1:1 ratio within 1 h at room temperature. The imine coordination of **108** is not fully understood and may involve an equilibrium between η^1-N and η^2-C,N coordination. Interestingly, performing the reaction of **104** with a 10-fold excess of benzalazine results in the catalytic formation of benzonitrile. No reactivity between **104** and the ketazine CH_3(Ph)C=N−N=C(Ph)CH_3 was observed, whereas complexes **108** and **109** were formed in a 1:1 ratio upon reaction of **104** with the *asymmetrical azine*, PhC(H)=N−N=C(Ph)CH_3 (**106**). Quantitative formation of the *symmetrical ketazine* CH_3(Ph)C=N−N=C(Ph)CH_3 (**110**) was also observed by NMR and GC-MS. DFT calculations suggest that the N−N cleavage step does not proceed through direct rhodium insertion into the N−N single bond (**P**, **Q**; eq 21). Most likely a complex bimolecular reaction mechanism involving C−H activation takes place.

Scheme 11

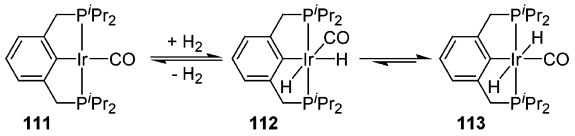




(21)

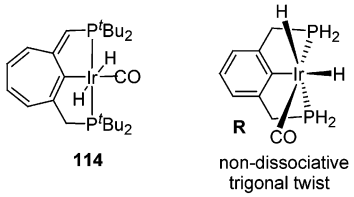
G. Formation and "Hydridic" Reactivity of *trans*-Dihydride Complexes

Addition of H_2 to **111** resulted in the reversible formation of the *cis*-dihydride complex **112** (eq 22). Complex **112** converts upon warming (under mild H_2 pressure to reverse H_2 reductive elimination) to the *trans*-dihydride **113**, indicating that the latter isomer is thermodynamically favored.[57]



(22)

The high stability of the trans isomer **113** is counterintuitive. Whereas numerous *cis*-dihydride complexes are known,[126] *trans*-dihydride isomers are relatively rare and often not stable for electronic reasons.[10,69,127,310−313] The iridium *trans*-dihydrides **88** and **114** are other examples of this seemingly electronically unfavorable ligand arrangement (eq 20).[126,127,161] Reaction of $HIr(PPh_3)_3CO$ with the PCP ligand 1,3-$(CH_2P^iPr_2)_2C_6H_4$ (**115**) resulted directly in the quantitative formation of the *trans*-dihydride complex (**113**). Apparently, formation of the thermodynamic trans product **113** is kinetically preferred here. Density functional theory (B3LYP) has been used by Hall et al. to reveal the mechanism of this intriguing cis−trans isomerization process.[16] Five possible metal complex isomerization pathways were considered involving: (i) CO dissociation/reassociation, (ii) CO migratory insertion into the Ir(III)−H bond, (iii) PCP ligand C_{aryl}−H reductive elimination/oxidative addition, (iv) phosphine dissociation, and (v) nondissociative trigonal twist. Rather surprisingly, the theoretically preferred mechanism involves two consecutive trigonal twists (v) in which the complex passes through a distorted octahedral intermediate. The calculated intermediate **R** and transition states (TS) **S** and **T** are generated from **U** (having H subsituents on P instead of $^tBu_2$) by the simultaneous twisting of P1, H2, and H1. Subsequent twisting of C2, H2, P2 affords the trans isomer (**V**; Figure 8). This low-energy pathway having energy barriers of 24.0 and 16.0 kcal/mol, respectively, seems preferred despite the rigid aromatic backbone of the tridentante PCP ligand.



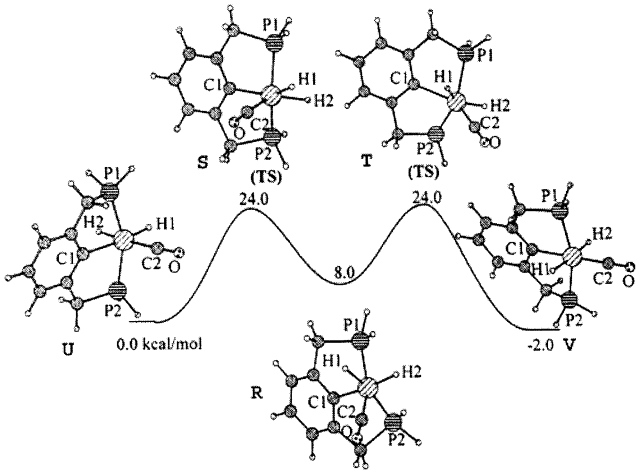
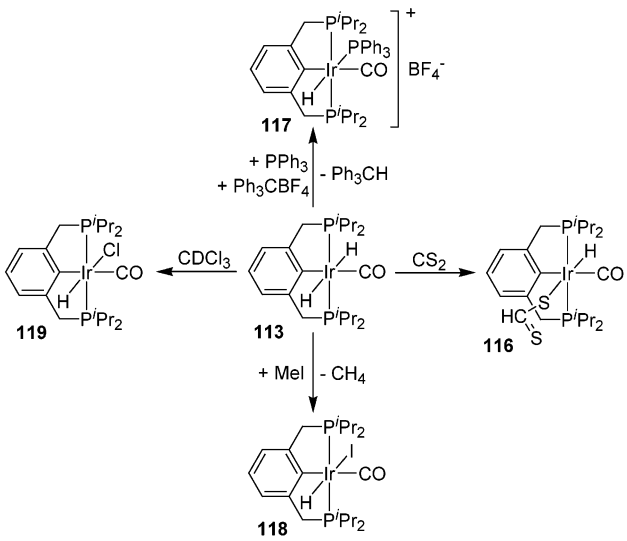


Figure 8. Potential energy profile for the isomerization of **U** → **V** via **R**. From ref 16. Copyright 1999 American Chemical Society.

Scheme 12

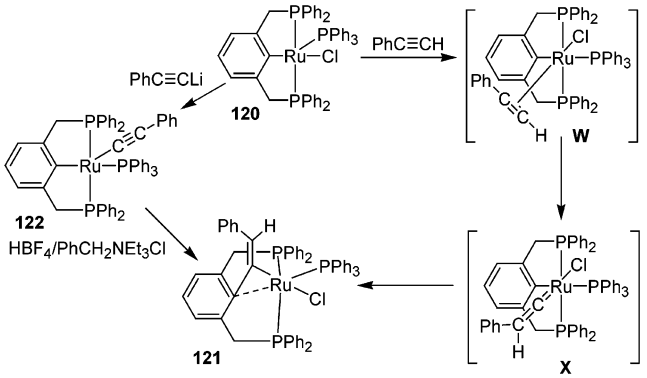


The reactivity and hydridic character of **113** were explored using various electrophilic reagents, including CS_2 (**116**), Ph_3CBF_4 (**117**; trityl cation), *p*-toluenesulfonic acid, MeI (**118**), $CDCl_3$, benzoyl and anisoyl chloride (**119**).[57] Hydride transfer took place, resulting in monohydrides (**116**−**119**) which are chemically inert toward excess of the electrophilic reagents, unambiguously demonstrating that the "hydridric reactivity" is unique for electronic reasons. A direct attack of the electrophile on one of the Ir−H groups is highly likely, taken into account that (i) complex **113** is coordinatively saturated, and (ii) no decarbonylation was observed with benzoyl and anisoyl chlorides (Scheme 12).

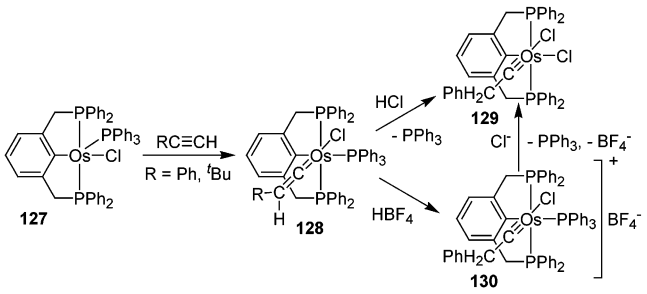
H. Reactions of Terminal Acetylenes with Ruthenium and Osmium Complexes

Selective C−C coupling reactions by insertion of substrates into the relatively strong aryl−M σ-bonds of cyclometalated pincer ligands is relatively rare.[22,39,48,154,155] Jia and Gusev independently reported series of alkylidene and vinylidene complexes obtained by reacting (PCP)Ru and Os complexes with

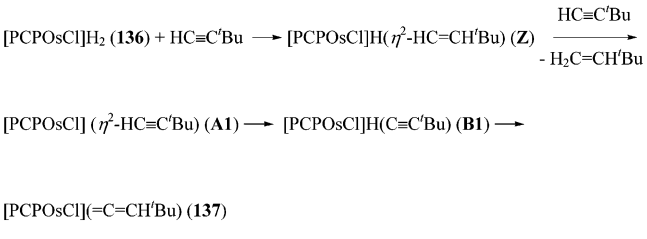
Scheme 13



Scheme 14



Scheme 15



terminal acetylenes (Schemes 13−15, eqs 23 and 24).[39,154,155,175] In the past five years, several ruthenium and osmium PCP complexes were reported with ligand **2**.[36−38,56,73,92,94,95,102,137,154,163,165,175] Related NCN-based ruthenium complexes are also known.[40,90,92,108,111,162] Reaction of **120** with PhC≡CH resulted (via **W** and **X**) in the quantitative formation of **121** (Scheme 13), whose structure was unambiguously elucidated by NMR and X-ray diffraction (Figure 9).[154,155] Other terminal acetylenes can be used as well, including $Ph_2C(OH)C{\equiv}CH$. The presence of δ protons allowed the formation of conjugated stabilized dienyl structures by a secondary dehydration process with $PhC(Me)(OH)C{\equiv}CH$ and $HC{\equiv}C$-*cyclo*-$C_6H_{10}(OH)$;[314,315] δ protons are not available with $PhC{\equiv}CH$ and $Ph_2C(OH)C{\equiv}CH$.

Mechanistically, the reaction **120** + $HC{\equiv}CR \rightarrow$ **121** may proceed by coordination of the terminal acetylenes to the unsaturated **120** followed by formation of a vinylidene complex (Scheme 13: **W** → **X**).[154,155] Migratory insertion of the aryl group of the PCP system at the α carbon of the vinylidene ligand affords the isolated **121**. No intermediates were observed. Reaction of **120** with $LiC{\equiv}CPh$ afforded **122**. Attempts to trap vinylidene intermediates such as **X** by protonation of **122** failed. However, various PNP-ligand based vinylideneruthenium complexes

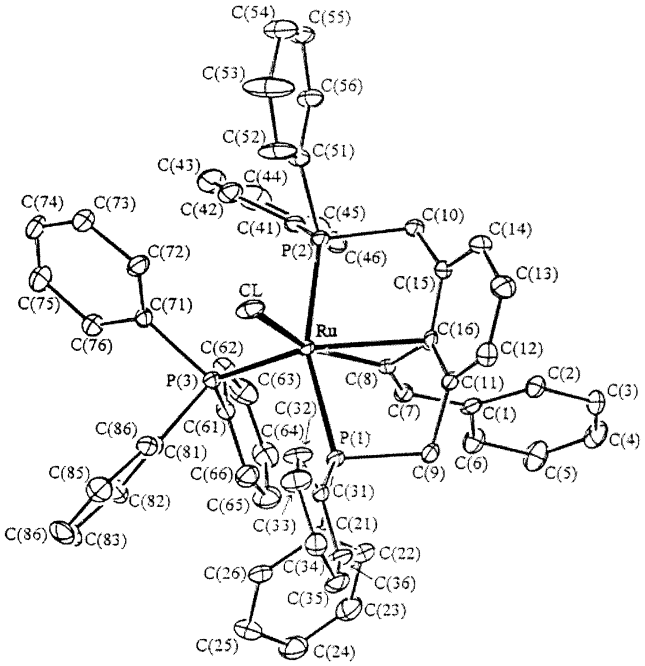
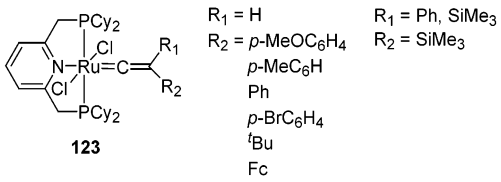
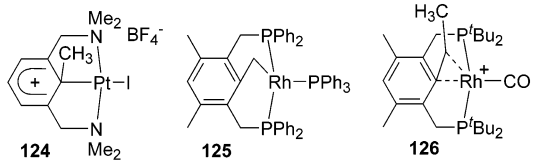


Figure 9. ORTEP drawing of the molecular structure of **121** showing a relative short Ru···C_{aryl} distance of 2.007 Å. From ref 154. Copyright 1999 American Chemical Society.

123, lacking the reactive $C_{aryl}-M$ σ bond, were recently isolated.[166]



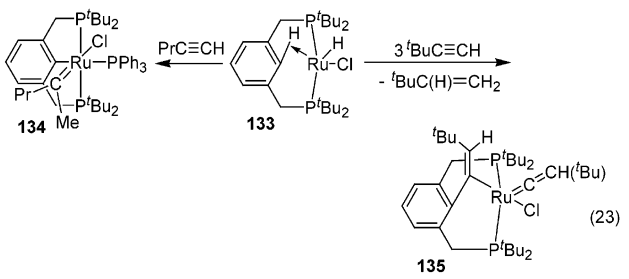
X-ray analysis of **121** shows a relatively short Ru···C_{aryl} distance of only 2.007 Å (Figure 9),[154] and solution NMR studies reveal that the C_{ispo} of the aryl ring remains close to the metal center. The reason for the formation of this unusual ligand arrangment is not straightforward. The PCP ligand might be "forced" to be in close proximity to the ruthenium center. Alternatively, a "real" bonding interaction may exist involving electron donation of the vinylidene ligand to the unsaturated metal center. Relatively short $M-C_{aryl}$ and $M-C_{alkyl}$ distances were observed for other PCP and NCN complexes as well (**124**−**126**).[47,80,82,107,114] C−C···M agostic interactions may play here a stabilizing role. Such interactions are well-established for aliphatic C−H bonds (section IVA). Examples of well-defined metal complexes having an agostic C−C single bond are extremely rare.[80,83,272,316]



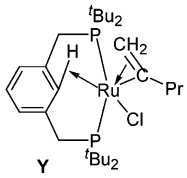
Remarkably, reaction of the osmium complex **127** with RC≡CH (R = Ph, ^{t}Bu) resulted in the quantita-

tive formation of the vinylidene complex **128** (Scheme 14).[175] The reason for this striking metal-based selectivity is not obvious. In contrast to the ruthenium chemistry (Scheme 13),[154,155] no migratory insertion of the aryl group of the PCP ligand at the α carbon of the vinylidene ligand occurred with osmium. Jia pointed out that the formation of vinylidene complexes such as **128** from terminal acetylenes may proceed by various pathways, including intramolecular (i) coordination of acetylene followed by an 1,2-hydrogen shift, and (ii) formation of a hydrido-alkynyl intermediate by a 1,3-hydrogen shift of the hydride to the *β*-carbon of the alkynyl ligand.[210,317,318] No intermediates such as *π*-acetylene and hydrido-alkynyl species were here observed. Deuterium-labeling experiments excluded the involvement of intermolecular hydrogen shift processes. For instance, treatment of **127** with PhC≡CD and ^{t}BuC≡CH produced OsCl(=C=CDPh)(PPh_3)[2,6-(CH_2PPh_2)$_2C_6H_3$] (**128′**) and OsCl(=C=CH^{t}Bu)(PPh_3)[2,6-(CH_2PPh_2)$_2C_6H_3$] (**128″**). No deuterium inclusion was observed in the osmium complexes when reactions were performed in the presence of D_2O. Therefore, it is highly likely that **128** is formed via acetylene coordination and an intramolecular 1,2-hydrogen shift,[175] which is in line with calculations showing that 1,2-hydrogen shifts are generally more favorable than 1,3-hydrogen shifts.[210,317] Treatment of **128** (R = Ph) with HCl afforded the carbyne complex **129**. Mechanistically, initial protonation of the vinylidene ligand might be followed by PPh_3/Cl^- ligand exchange. In support of this proposition, complex **128** was reacted with HBF_4 to afford the cationic **130**. Subsequent treatment of **130** with $PhCH_2NEt_3Cl$ resulted also in formation of **129**. Notably, Shaw and Moulton reported the reaction of M(Cl)[2,6-($CH_2P^tBu_2$)$_2C_6H_3$] (**131**; M = Pd, Ni) with LiC≡CPh affording M(C≡CPh)[2,6-($CH_2P^tBu_2$)$_2$-C_6H_3] (**132**).[9] Polymerization of HC≡CPh has been observed with PCP-based rhodium complexes (section IIG, **44**−**46**, eq 14).[132]

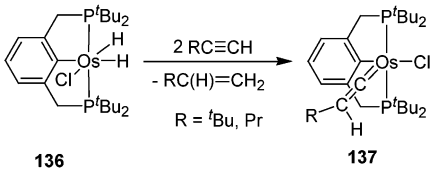
Recently, Gusev et al. reported on reaction of ruthenium and osmium hydrides with 1-pentyne and *tert*-butylacetylene (eqs 23 and 24, Scheme 15).[39] Note that these systems (**133**−**137**) have bulky *tert*-butyl substituents on the phosphines, whereas the aforementioned complexes (**120**−**122**; **127**−**130**) have phenyl substituents on the P donor atoms. Reaction of **133** with 1-pentyne resulted in the formation of the alkylidene complex **134** via **Y**, whereas reaction of **133** with three equivalents of *tert*-butylacetylene resulted in the formation of the vinyl-vinylidene complex **135** (eq 23).



(23)



Reaction of the osmium complex **136** with 1-pentyne or *tert*-butylacetylene afforded the vinylidene complexes **137** (R = ^{t}Bu, Pr; eq 24). All addition products **134**, **135**, and **137** were fully characterized by a full battery of NMR techniques and X-ray analysis.



(24)

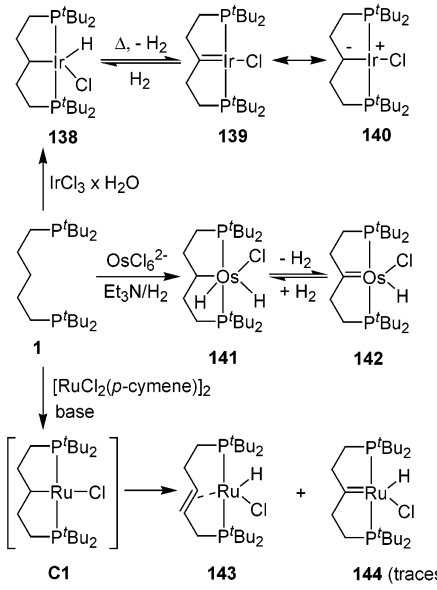
Mechanistic details were elucidated by low-temperature NMR and deuterium labeling studies. For instance, the authors proposed that the addition of *tert*-butylacetylene to the osmium dihydride complex **136** proceeds by insertion of the alkyne into a Os−H bond (**Z**), which is followed by formation of η^2-HC≡^{t}Bu (**A1**) and hydrido alkynyl complexes (**B1**). The latter (**B1**) rearranges to the isolated vinylidene complex **137** (R = ^{t}Bu, Pr; eq 24) by a 1,3-hydrogen shift (Scheme 15).

I. Formation of Pincer Metal Alkylidenes

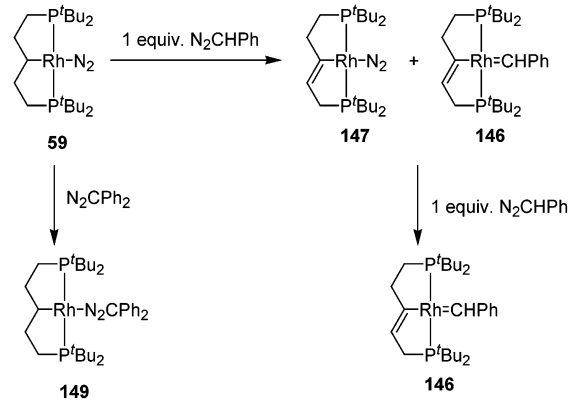
Two types of PCP-based alkylidene complexes are known: (i) the carbene moiety is covalently bound to the PCP ligand,[1−3,5,7,40] or (ii) the M = CR_2 moiety is not stabilized by additional (phosphine) ligand coordination.[45,81] The latter case is not only interesting fundamentally but might have synthetic utility. Formation of a type (i) "carbene" PCP-based complex was observed by thermolysis of **138** resulting in formation of **139** and loss of H_2 (Scheme 16). Similar carbene structures have been postulated as intermediates in the formation of iridium *trans*-dihydrides (**114**).[127] Complex **138** was regenerated by addition of H_2 to **139**.[3,5,7] X-ray analysis revealed a structure resembling both a Ir(III) carbene (**139**) and a Ir(I) ylide (**140**), whereas solution NMR studies favor the latter structure. Thermolysis of the osmium complex **141** resulted in the formation of the carbene complex **142** and H_2 (Scheme 16).[40] The X-ray derived Os=C bond distance is about 0.086 Å shorter than the Ir=C bond in **139**.[3,5,7] Reaction of the PCP ligand **1** (R = ^{t}Bu) with [$RuCl_2$(*p*-cymene)]$_2$ afforded the olefin complex **143**. Only traces (1.5%) of the carbene complex **144** were indicated by NMR. Mechanistically, it is likely that the postulated intermediate **C1** undergoes α- and *β*-hydrogen elimination in parallel pathways affording **143** and **144**, respectively.

Dinitrogen Rh(I) complexes are suitable precursors for the formation of type (ii) metal alkylidene complexes.[45,81] For instance, complex **62** reacts with phenyldiazomethane, to afford the benzylidene complex **145** (eq 25), whereas the analogous Rh(I) pre-

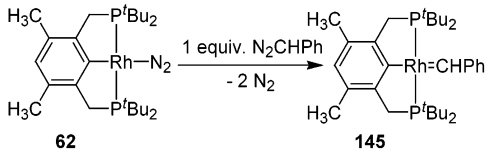
Scheme 16



Scheme 17



cursor **59** reacts with 2 equiv of phenyldiazomethane to yield the vinyl carbene complex **146** (Scheme 17).[81] Reaction of **59** with a stoichiometric amount of phenyldiazomethane afforded two products: the vinyl dinitrogen complex **147** and the carbene complex **146**. Complex **147** was converted into **146** quantitatively by addition of excess of phenyldiazomethane to the reaction mixture (Scheme 17).

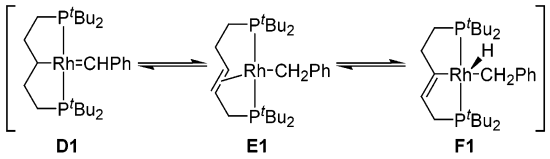


(25)

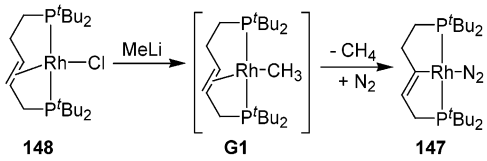
The transformation **59** + $N_2CHPh \rightarrow$ **146** + N_2 may proceed as follows. The postulated carbene complex **D1** (Scheme 18) may undergo hydride migration to give the benzyl complex **E1**. The latter probably undergoes metal insertion into the C_{ipso}−H bond affording **F1**. C−H reductive elimination from **F1** followed by N_2 coordination affords the isolated **147**.

In line with this postulated mechanism, reaction of the olefinic complex **148** with MeLi resulted exclusively in **147** and CH_4 via intermediacy of **G1** (eq 26). The reactivity of the diazomethane substrate

Scheme 18



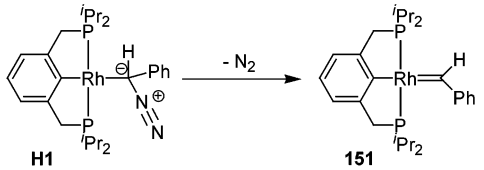
plays an important role in metal carbene formation. Addition of the less reactive diphenyldiazomethane to **59** resulted in the quantitative formation of the diphenyldiazomethane complex **149**. No carbene formation was observed (Scheme 17).



(26)

Reaction of the Rh(I)−dinitrogen complex (**104**) with phenyl diazomethane at −70 °C results in the formation of the end-on η^1-N diazo complex **150**. Increasing the temperature of the product solution leads to carbene formation (**151**). However, this process is not selective. Performing the reaction of **104** with phenyl diazomethane at room temperature results in quantitative formation of **151** (Scheme 19).

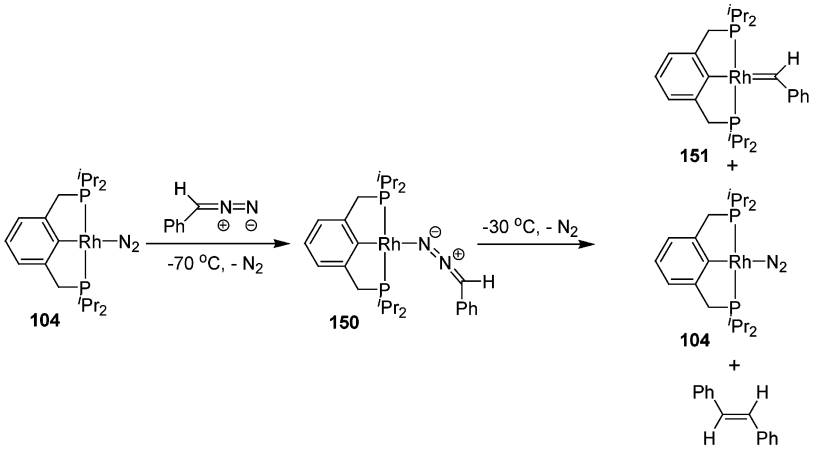
This remarkable temperature effect on the reaction outcome is in agreement with previous reports stating that diazocomplexes such as **150** may not readily lose N_2, which hampers the carbene (**151**) formation. Coordination of phenyl diazomethane is reversible upon warming the product solution, and irreversible loss of N_2 leads to the metallacarbene (**151**). As shown by DFT calculations, the key intermediate in the metallacarbene formation is an η^1-C diazo complex (**H1**; eq 27), which is formed most likely by a direct attack of the diazo molecule on the metal center. It is known that diazoalkane complexes such as **150** are often stabilized through η^1-N or η^2-NN coordination. Such systems do not form carbene complexes, but merely serve as a spectator or competitive ligands in the metallacarbene formation. Since formation of the η^1-C diazo intermediate is sterically demanding, steric factors play an important role in carbene formation from diazoalkanes.

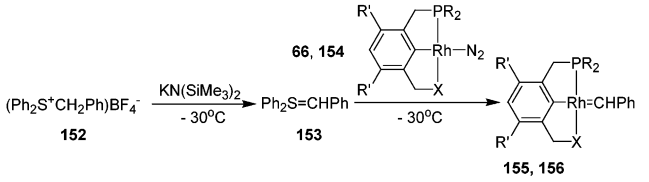


(27)

A straightforward procedure toward metal-carbene preparation was developed by using sulfur ylides as carbenoid precursors.[45] Benzyldiphenylsulfonium tetrafluoroborate (**152**), the precursor of ylide (**153**), can be conveniently prepared by a one-pot reaction synthesis (eq 28). Deprotonation of the sulfonium salt **152** yields the benzyl ylide **153**. Reaction of **153** with dinitrogen complexes **66** and **154** resulted in quantitative formation of the new rhodium benzylidene complexes **155** and **156**.

Scheme 19

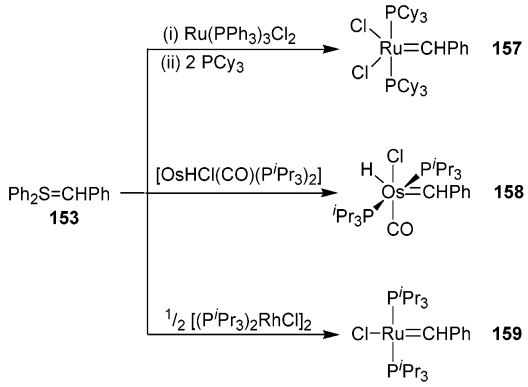




154, 155: R = ^{i}Pr, R' = H, X = P^{i}Pr$_2$
66, 156: R = ^{t}Bu, R' = CH$_3$, X = NEt$_2$ (28)

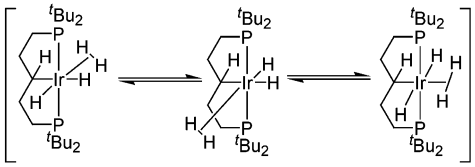
Importantly, this synthetic route is safer than the one using diazo precursors and is not limited to PCP (**155**) and PCN (**156**) complexes. Various carbene complexes were prepared, including Grubbs' catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$ (**157**), and new metal alkylidenes (**158**, **159**) which could not be obtained by other methods (Scheme 20).

Scheme 20



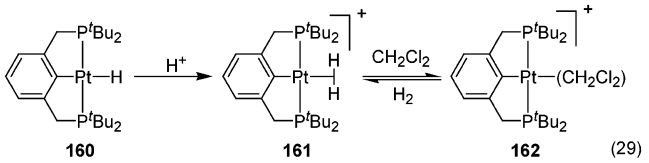
J. Dihydrogen Coordination

Complexes having η^2-H_2 ligand(s) may show interesting reactivity and can be viewed as models or trapped intermediates for the study of H_2 coordination, oxidative addition, and reductive elimination processes. η^2-H_2 type PCP complexes can be obtained by several methods, including (i) reaction of metal hydrido halide precursors with reagents such as NaH or $[BH_4]^-$ (higher yields are reported by performing the synthesis under H_2), (ii) addition of H_2 to unsaturated complexes or to complexes having a kinetically labile ligand (e.g., N_2), or by (iii) protonation of metal hydrides with strong acids.[32,36,38,74,160,162,163] As aforementioned in other sections of this review, coordination chemistry and reactivity of low-valent rhodium and iridium η^2-H_2 complexes with N_2 and CO_2 have been studied.[32,74,123,126] The first PCP-type η^2-H_2 complex (section IIIC; eq 19, **80**), the aryl analogue of **74** (Scheme 8), was reported by Kaska in 1983.[32] Complex **80** was obtained in high yield by reaction of Rh(H)(Cl)[2,6-$(CH_2P^tBu_2)_2C_6H_3$] (**203**; section IVB, eq 38)[9] with KH under H_2. Various iridium η^2-H_2 complexes were reported as well; for example, $Ir(H)_2$-$(\eta^2$-$H_2)(CH(C_2H_4P^tBu_2)_2)$ (**I1**) was proposed to explain the fluctional behavior of $Ir(H)_4[HC(C_2H_4P(^tBu)_2)_2]$ (**89**).[6,125]



I1

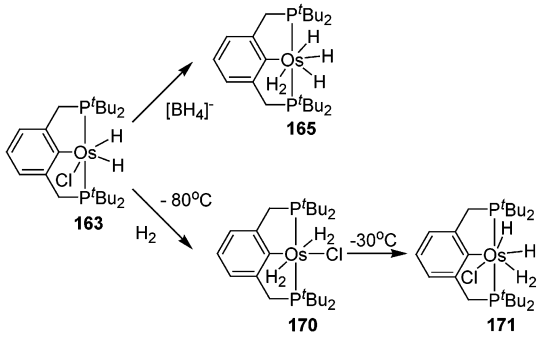
A recent example of η^2-H_2 complex formation by M−H protonation chemistry is the reaction of **160** with strong acids such as HOTf, HBF_4, or $[H(OEt_2)_2]^+$-$BAr'_4{}^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl)], resulting in the quantitative formation of the cationic dihydrogen complex **161** (eq 29).[160] The kinetically labile H_2 ligand is readily displaced by CH_2Cl_2 (used as solvent) at room temperature (**162**). H_2/CH_2Cl_2 ligand exchange was observed in other platinum complexes as well.[319] Solvent and anion coordination including CH_2Cl_2 was also observed with other unsaturated, cationic PCP complexes.[42,50,59,61,149] Pressurizing the product solution of **162** with H_2 resulted again in formation of **161**. The nature of the H_2 coordination was revealed by low-temperature T_1 NMR measurements and deuterium labeling (by reaction of **160** with DOTF). T_1 measurements, for instance, T_1 = 14 ms at −80 °C for **161**-OTf, are consistent with η^2-H_2 coordination. A relatively large $^1J_{HD}$ = 33.4 Hz was observed, indicative of a relatively short H−D bond. Notably, protonation of related PNP-based Os−H complexes with HBF_4 afforded Os-η^2-H_2 complexes (PNP = 2,6-$(Ph_2PCH_2)_2$-C_5H_3N).[158]



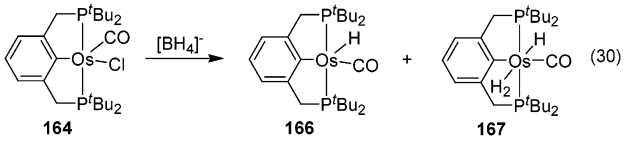
(29)

Osmium polyhydrides and dihydrogen complex precursors were also obtained via reaction of 2,6-$(CH_2P^tBu_2)_2C_6H_4$ (**2**) with $[OsCl_6]^{2-}$ in 2-propanol (**163**; Scheme 21) and methanol (**164**; eq 30).[38]

Scheme 21



Subsequent reaction of the distorted hexacoordinated dihydride **163** with $[BH_4]^-$ resulted in formation of the isolated polyhydride **165** (Scheme 21), whereas reaction of **164** with $[BH_4]^-$ afforded **166** and **167** (eq 30).[37] Noteworthy, reaction of BH_3 with Ru(CO)(H)-[2,6-$(CH_2P^tBu_2)_2C_6H_3$] (**168**) resulted in formation of Ru(H)(CO)[1-BH_3-2,6-$(CH_2P^tBu_2)_2C_6H_3$] (**169**) (eq 31).[37] Extensive NMR studies were performed to elucidate the nature of the Os−H_2 bonds and to define the ligand arrangements. For **165**, T_1 measurements and deuterium labeling experiments indicated a relatively short H−H bond length of 0.97 Å. H/D exchange was observed in benzene-d_6, perhaps by reversible loss of H_2. Dissociation of H_2 is known to occur prior to catalytic dehydrogenation of cycloalkanes by Ir(H_4)-[2,6-$(CH_2P^tBu_2)_2C_6H_3$] (**35**; section II, eq 9).[25,26] Dissolving **163** at low temperatures under H_2 afforded **170**, which isomerized to the thermally unstable **171** (Scheme 21). H_2 is liberated upon further warming, and starting material **163** is regenerated. For **170**, an H−H bond distance of 1.08 Å was estimated by NMR. Bis-dihydrogen complexes are relatively rare.[38,320−322]



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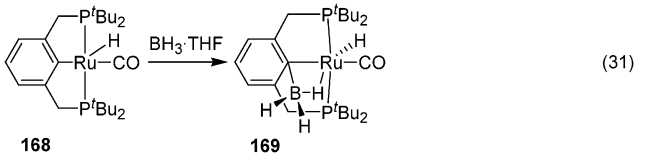
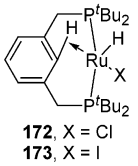
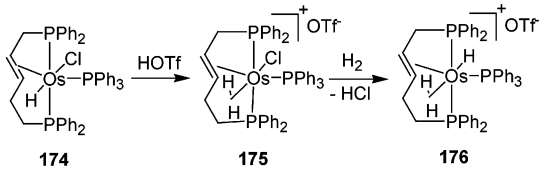


(31)

Interestingly, complexes **172** (X = Cl) and **173** (X = I), obtained by reaction of $[RuCl_2(p\text{-cymene})]_2$ and the PCP ligand **2** (R = ^{t}Bu) (and subsequent reaction with methyl iodide to obtain **173**), exhibit structural similarities with RuH(η^2-H_2)I(PCy_3)$_2$.[36,323,324] For instance, **173** exhibits elongated η^2-C−H and η^2-H−H bonds (compare: η^2-C−H = 1.32(5) Å (**172**) vs 1.08 Å in C_6H_6 and 1.03(7) Å (**173**) vs 0.74 Å in H_2). Moreover, short C−H···H−Ru (1.68(7) Å, **172**) and H−H···H−Ru (1.66(6) Å, **173**) bond distances were determined, indicating some degree of interligand dihydrogen bonding. The fact that the η^2-C−H moieties in **172** and **173** are directed toward the Ru−H moiety and not toward the empty coordination site indicates that this proposed interaction is strong enough to limit the number of possible isomers.



Protonation of the hydrido(olefin) complex **174** resulted in the formation of the dihydrogen(olefin) complex **175** (eq 32).[162] Subsequent reaction of the latter with H_2 afforded the (hydrido)dihydrogen complex **176** with elimination of HCl. Remarkably, no hydrogenation of the double bond was observed. DFT (B3LYP) calculations suggested that the hydrogenation of the double bond is thermodymanically favorable but not feasible for kinetic reasons.

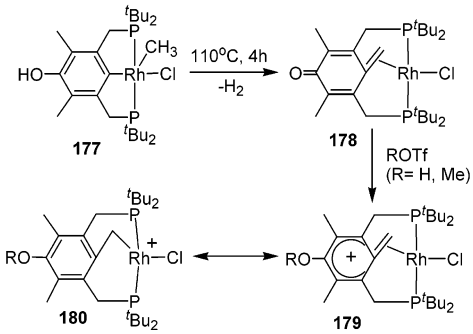


(32)

K. Formation and Reactivity of Quinonoid Compounds

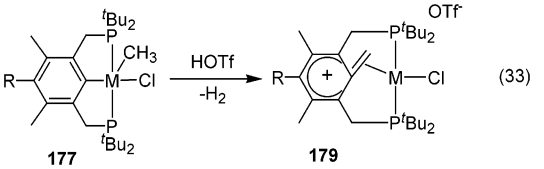
An unusual series of cationic rhodium and iridium complexes has been reported by Milstein in which dearomatization of the aromatic ring of the PCP ligand backbone took place.[23,71,76,78,80,82,83] Quinonoid and related complexes are of much current interest,[325−329] and this topic has been reviewed recently[83] and will only be briefly mentioned here. Thermolysis of the Rh(III) complex **177** yielded the Rh(I) quinone methide complex **178** and H_2 (Scheme 22).[76] Using

Scheme 22



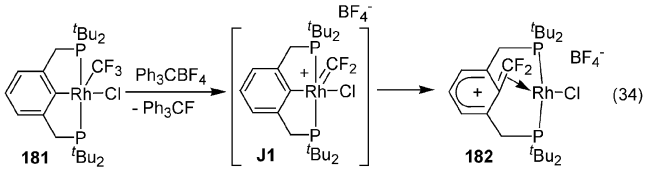
strong electrophiles such as Me_3SiOTf and HOTf resulted in the formation of methylene arenium metal complex **179**, the resonance form of a benzyl cation (**180**; see also section IVC, Scheme 29).

Treatment of **177** and derivatives with strong acids afforded also **179** by a cascade of organometallic transformations.[80] Kinetic studies suggest that protonation of the five-coordinated d^6 complex trans to the apical methyl group affords a transient Rh(V) species which undergoes 1,2-migration of the methyl group to the aromatic ring. β-H elimination and subsequent H_2 formation afforded the isolated **179** (eq 33).



(33)

Difluoromethylene arenium rhodium complexes (**182**) were obtained from **181** by an entirely different mechanistic route (eq 34).[70] Fluoride abstraction from the Rh(III)−CF_3 moeity of **181** with strong Lewis acids (i.e., BF_3, Ph_3CBF_4, HOTf) probably affords Rh=CF_2 species (**J1**) which is followed by migratory insertion of the aryl group to the (unobserved) difluorocarbene ligand (**182**).[71] It is known that Lewis acids can abstract fluorides from activated M-CF_3 groups due to π-back-bonding to afford M=CF_2 species.[330]

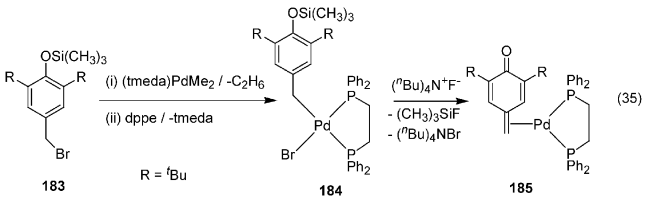


(34)

The quinonoid chemistry explored with PCP-ligand stabilized metal-quinone methide complexes, methylene arenium metal complexes, and metallaquinones[23,83] has been successfully extended to other metal complexes in which the biologically important quinone methide is generated and released in a controlled fashion without the support of additional heteroatom coordination.[328,329] Reaction of **183** with nitrogen-based Pd(II) precursors followed by nitrogen/phosphine ligand exchange afforded **184** (eq 35). Desilylation of the Pd(II) complex **184** with standard quarternary ammonium fluoride reagents resulted in the formation of the stable quinone methide Pd(0) complex **185**. Controlled release of the quinone methide was achieved by reaction of **185** with diphenylacetylene or dibenzylideneacteone. At the same time, $P_2Pd(0)$ olefin complexes are generated.

L. Coordination-Based Multinuclear Complexes

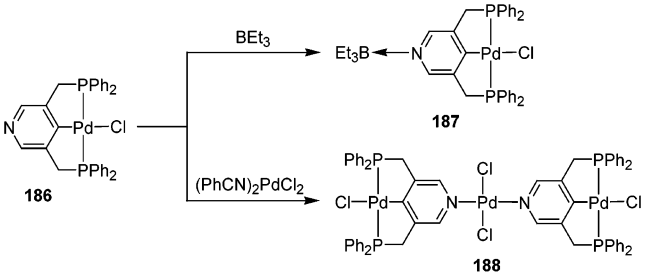
Introduction of substituents on the aromatic ring of the PCP ligands allows fine-tuning of the electron density on the metal center.[58,73,121] Likewise, introduction of heteroatoms such as nitrogen into the



(35)

aromatic system of a PCP ligand leads to a lower electron density on the carbon atoms.[84] For instance, after complexation of a 3,5-lutidine-based PCP ligand to transition metals such as Pd(II) (**186**) or Rh(I), the nitrogen of the pyridine ring is available for binding to a second metal moiety (Scheme 23).[84] Coordination

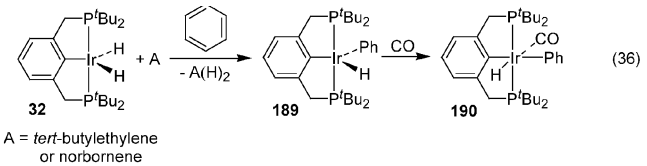
Scheme 23



of a Lewis acid (**187**) or a second metal moiety (**188**) to the nitrogen of the pyridine ring influences the electron density on the first metal center, which allows one to fine-tune its reactivity. Electronic fine-tuning might lead to the design of better catalysts. Moreover, coordination of a second metal moiety offers a new approach for the generation of oligo- and multinuclear complexes, which is of much current interest.[90,331]

IV. Demonstration, Mechanistic Aspects, and Scope of C–H, C–O, and C–C Single Bond Activation

Metal insertion into strong single bonds and subsequent functionalization of the resulting metal-substrate moieties are key transformations for the rational design of new metal-mediated stoichiometric reactions and homogeneous catalytic processes. Selective C−H bond activation and functionalization have been studied extensively.[219,332−345] In particular, PCP and related pincer complexes (often formed by cyclometalation reactions)[333] may react with hydrocarbons by (reversible) C−H bond fission.[24−28,32,33,48,49,74,116,117,122,140,167] Importantly, Goldman et al. observed the products of vinyl and aryl C−H oxidative addition to complex **32** in the presence of a sacrificial hydrogen scavenger (eq 36).[116,117] Complex **189** undergoes fast, dissociative hydrocarbon exchange and can be stabilized by reaction with CO affording the saturated six-coordinated complex **190**.



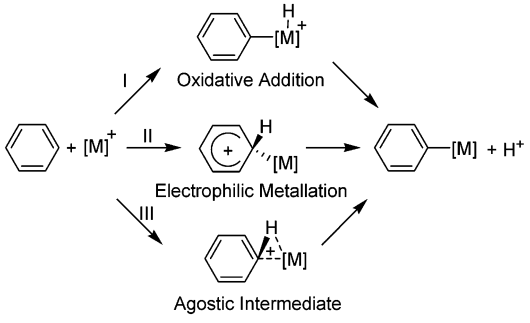
(36)

Unsaturated H−M-alkyl/aryl complexes are rarely observed[116,346,347] and undergo facile reductive elimination with concurrent C−H bond formation.[64,348,349] Catalytic dehydrogenation of alkanes by PCP−iridium complexes including **32** (section II, Scheme 4),[24−28,31,33,167] mechanistic studies on C−H bond activation and formation of novel PCP complexes exhibiting agostic aryl C−H bonds represent major advancements,[26,27,79,87,92,116] although substrate functionalization via C−H bond cleavage is still uncommon. In contrast to C−H bond activation, much less is known about the oxidative addition of unstrained C−R (R = C, O, Si, N, F) single bonds to low-valent metal complexes.[60,90,109,271,272,330,350−353] PCP[22,46−48,52−54,58−60,62,66−68,70,71,73] and related PCN,[18,41,43,44] PCO,[61] and NCN systems[86,88,90,100,101,105,106,109,112,114,170,171] have been used to demonstrate and to study metal insertion into various strong C−C,[18,22,41,44,46−48,52−54,58−62,67,70,71,73,86,88,100,101,107,114] C−Si,[105,106,109,112,170,171] C−O,[66,68] and even C−N single bonds.[43] Ar−CF_3 and Ar−OR (R = H, CH_3, CH_2CH_3) bonds have been activated as well.[66,68,70,71] C−C bond activation with several derivatives of PCP (**2**), PCN (**3**), and PCO (**4**) ligands has been studied extensively by Milstein,[22,41,42,44,46−48,52−54,58−61,67,70,71,73] and several computational studies have been reported.[18,61,62,168,169] Many variables have been explored including metal periodic table position (Rh,[41,44,47,48,52−54,58,59,67,70,71] Ir,[58,59] Ru,[73] Ni,[354] Pt,[65,73] Os[46]), neutral vs cationic systems,[58,59] solvent,[58,59] bond type,[53,67,70,71,73] electron density,[52,58] and bulk.[52,67] In the following three sections, formation of aryl agostic C−H and C−C complexes and selective activation of strong C−O and C−C single bonds will be discussed.

A. Aryl C–H and C–C Agostic Complexes

There are two generally accepted mechanistic pathways accounting for most metal-based aromatic C−H bond activation processes (Scheme 24).[333−337]

Scheme 24



Route I involves a concerted oxidative addition process (via an η^2 metal arene complex) with the formation of metal-hydride species (i.e., **189**, eq 36);[116] alternatively an electrophilic attack of the metal center on the aryl ipso-carbon may afford a metal arenium (Wheland) complex followed by proton loss (route II). An alternative route, which does not involve the arene π-system, can be considered as well (route III).[79] It is based on the isolation and reactivity of η^2-C−H agostic PCP arene complexes and on the observation that little, if any, charge is dissipated

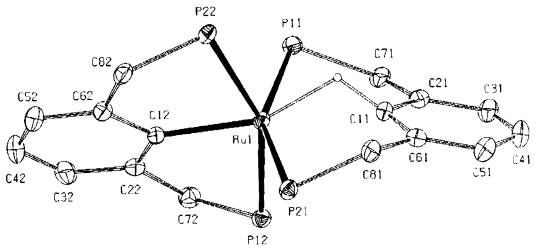
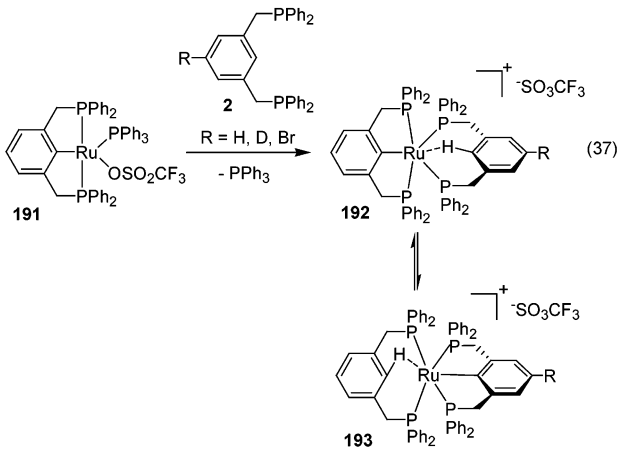


Figure 10. ORTEP drawing of the molecular structure of **192** showing the agostic C−H···Ru(II). From ref 87. Copyright 2000 American Chemical Society.

into the arene π system of PCP rhodium complexes[79] (see below). Van Koten,[92,94,110,172] Milstein,[79] and Gusev[36] reported the isolation and full characterization of agostic intermediates for aromatic C−H bond activation with ruthenium and rhodium (see also section IIIJ; **172** and **173**).[36]

Treatment of **191** (obtained from reaction of Me_3SiOTf[355] with the analogous Ru−Cl precursor)[102] with an additional PCP ligand **2** (R = Ph) resulted in ligand exchange and subsequent formation of the cationic complex **192**, having two PCP ligands coordinated/cyclometalated to one metal center (eq 37).[92,94,110,172] The X-ray crystal structure and detailed NMR studies of this interesting compound unambiguously showed the formation of an intriguing aryl η^2-C−H agostic Ru(II) complex with the agostic proton commuting between the η^2- and η^3-PCP ligands (**192**, **193**; Figure 10).[92,94] An electrophilic aromatic substitution mechanism involving arenium-type intermediates has been proposed to account for this reversible intramolecular proton shuffle. Proton transfer between PCP and NCN ligands was observed as well using deuterium labeling studies.[93] The η^2-C−H distance of **192** is elongated (∼1.15 Å) while there is a relatively short Rh···H distance (∼1.76 Å) (compare C_6H_5−H = 1.101 Å,[356] Ru−H = 1.52 Å). No loss of aromaticity was indicated and a significantly reduced C−H coupling constant ($^1J_{CH}$ = 112 Hz; $\Delta J_{CH(ligand-complex)}$ = 46 Hz) was observed, typical for agostic interactions.[357] Attempts to selectively deprotonate **192** using organic bases or to H/D exchange the agostic proton by reaction of **192** with methanol-d_4 were unsuccessful. Agostic alkyl complexes are known,[36,74,219,345] whereas examples of agostic aryl complexes are extremely rare. Nevertheless, it has been assumed that aromatic C−H bond activation might occur via η^2-C−H intermediacy.[358]



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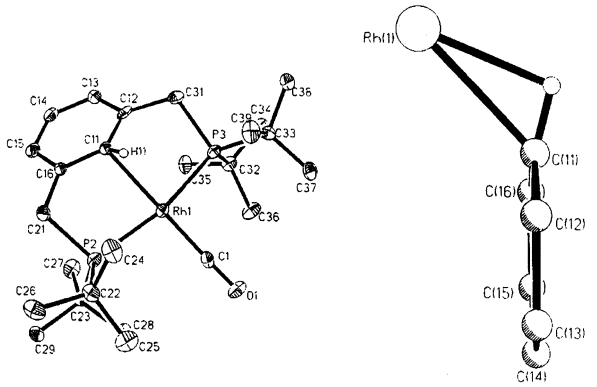
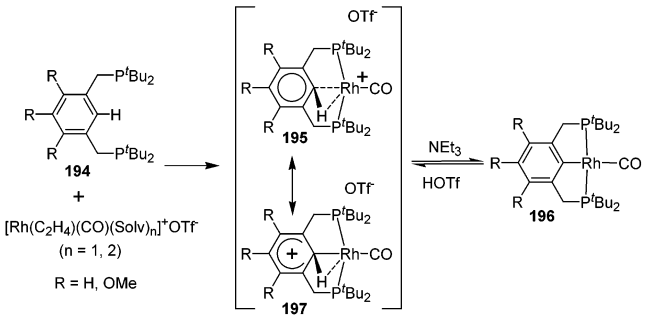


Figure 11. (a) ORTEP drawing of the molecular structure of **195** showing the agostic C−H···Rh(I). (b) Molecular view of **195**. From ref 79. Copyright 1998 American Chemical Society.

Reaction of ligand **194** with $[Rh(C_2H_4)(CO)(Solv)_n]^+$ (n = 1, 2) afforded the crystallographically characterized complex **195** having also a metal bound η^2-C−H group (Scheme 25 and Figure 11).[79] In sharp contrast

Scheme 25



to **192**,[92,94] the agostic proton of **195** undergoes H/D exchange with D_2O and reaction with collidine or Et_3N results in formation of the Rh(I) η^1-carbonyl complex **196**. Deprotonation of aliphatic η^2-C−H bound substrates are known; however, this has not been observed with aromatic hydrocarbons.[338−340,359] Treatment of **196** with HOTf resulted again in formation of **195**. The electron density on the aromatic ring does not play a major role as even three methoxy substituents do not influence the η^2-C−H acidity, suggesting that there is an insignificant contribution (if at all) of a metal arenium structure (**197**). This is also supported by the X-ray structure of **195**, which shows no significant distortion of the aromatic ring.

These experimental observations were confirmed by Martin et al. using B3LYP/LANL2DZ density functional calculations showing that most of the positive charge is located on the metal center and on the P groups (Figure 12).[79] Thus, η^2-C−H interaction between an aromatic hydrocarbon and a metal center (followed by deprotonation) without intermediacy of an arenium complex should be considered as an alternative route to electrophilic metalation of aromatic substrates (Scheme 24).[79] A similar mechanism was proposed by Bercaw for metalation by scandium complexes.[360]

Examples of complexes having some sort of agostic C−C···M bonds are extremely rare, and little structural information is available.[80,82,83,316,361] Weak reversible binding of saturated hydrocarbons to unsaturated metal centers might be of prime importance for many existing and new organometallic transformations. There are many issues to be resolved. Are agostic C−C bonds formed during C−C coupling reactions? Is the formation of an agostic C−C bond a necessary requirement for C−C bond activation? Detailed mechanistic studies on C−C bond oxidative addition to a *neutral* Rh(I) complex did not reveal the intermediacy of an agostic C−C bond (or any charge separation).[44] Clearly, more examples are needed to gain fundamental insight into the requirements for the formation of complexes having agostic C−C···M bonds. In any case, the charge distribution in cationic metal complexes might play a significant stabilizing role as exemplified in Scheme 26.[80,83] Treatment of

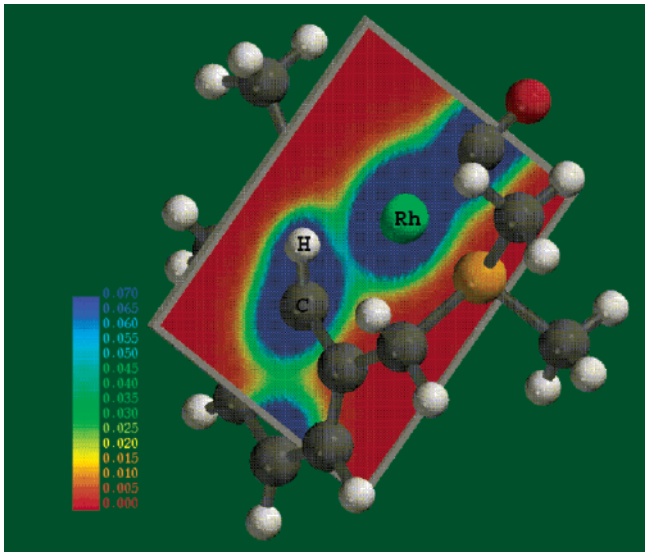
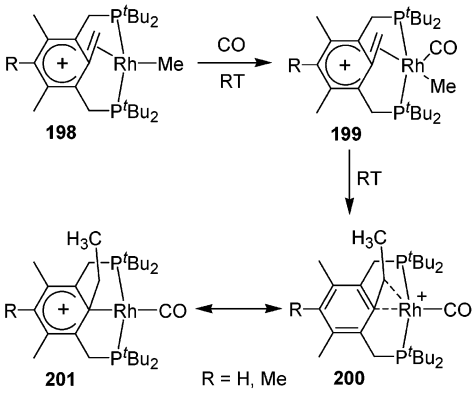


Figure 12. B3LYP/LANL2D2 electron density plot in the C_{ipso}−H−Rh plane of **195**. From ref 79. Copyright 1998 American Chemical Society.

Scheme 26



complex **198** with CO resulted in the selective formation of the η^1-CO adduct **199** which undergoes selective methyl migration to the coordinated olefin (**200**). X-ray and NMR analysis of the latter shows that the C−C agostic (**200**) structure prevails over that of the ethyl arenium (**201**) form.[80] For instance, the distance between the C−C bond and the rhodium metal center is shorter than the sum of the van der Waals radii of the atoms involved (2.817 Å), whereas the metal−

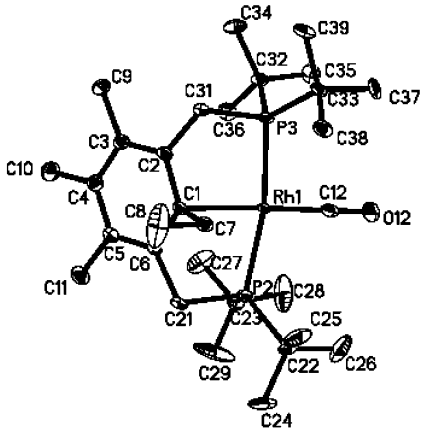
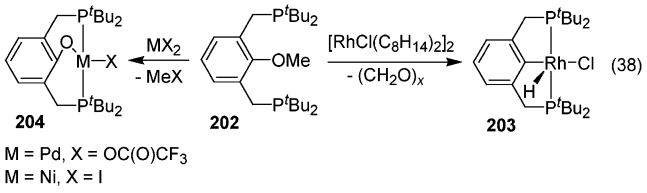


Figure 13. ORTEP drawing of the molecular structure of **200** showing the agostic C−C···Rh(I). From ref 80. Copyright 1999 American Chemical Society.

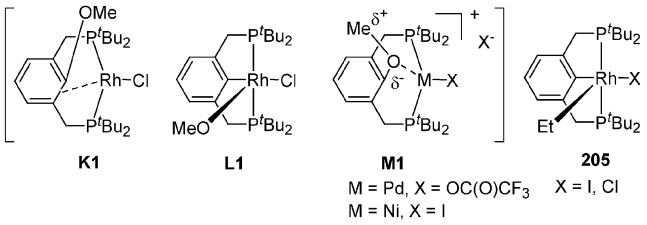
C_{ipso} bond distance of 2.354(3) Å is longer than regular rhodium−carbon σ bonds (Figure 13). The C−C bond is slightly elongated, and the aromaticity in the ring is not significantly disturbed.

B. Competitive sp^2–sp^3 and sp^3–sp^3 C–O Bond Activation

C−O bond cleavage by soluble transition-metal complexes is well-developed for strained systems (i.e., cyclic ethers), weak C−O bonds, and for reactions driven by substrate aromatization.[353,362−367] Only a few examples of platinum group metal-mediated alkyl-O bond cleavage with little mechanistic information provided have been reported.[4,8,368−373] The first examples of metal insertion into a strong aryl-OR (R = H, Me, Et) bond under mild reaction conditions in solution were observed with alkoxy and hydroxyl functionalized PCP-type substrates (i.e., **202**, eq 38).[66,68] For instance, reaction of $[RhCl(C_8H_{14})_2]_2$ with 2 equiv of **202** resulted in quantitative formation of **203**. No intermediacy of C−H bond activation or insertion into an adjacent weaker alkyl−O bond was observed. The iodide analogue of the expected product of Rh(I) insertion into the ArO−CH_3 bond, prepared separately, is stable under reaction conditions in which **202** readily undergoes aryl−O bond cleavage. Remarkably, dealkoxylation reactions (with PCP ligands having phenyl substituents instead of *tert*-Butyl groups on P) performed in the presence of primary silanes ($HSiR_3$; R = CH_2CH_3, OCH_2CH_3) resulted in transfer of the alkoxy group to the silane,[68] providing the first example of hydrosilation of an unstrained C−O single bond. This indicates that cleavage of the ArO−CH_3 bond is not involved either on the reaction coordinate or as a side equilibrium (compare bond dissociation energy (BDE) values of Ph-OCH_3 = 91 kcal/mol vs PhO−CH_3 = 80 kcal/mol).[356,374] We observed that the C−O bond activation process can be directed at either the aryl−O or alkyl−O bond of the PCP substrate depending on the applied metal complex precursor and the alkoxy group (−OCH_3, −OCH_2CH_3).[68] Reaction of the methyl aryl ether **202** with $Pd(CF_3CO_2)_2$ or NiI_2 resulted in exclusive activation of the sp^3−sp^3 ArO−CH_3 bond (**204**).



On the other hand, reaction of an analogous ethyl aryl ether PCP ligand with Pd(II) results in both sp^3−sp^3 and sp^2−sp^3 C−O bond cleavage in parallel pathways, demonstrating that both C−O bonds are accessible to the d^8 metal center. The overall C−O bond activation processes may be kinetically controlled with only a small difference between sp^2−sp^3 and sp^3−sp^3 C−O bond cleavage. Mechanistically, the nucleophilic Rh(I) promoted aryl−O bond fission may proceed via an η^2-arene complex **K1**, followed by formation of (unobserved) Rh(III)−OCH_3 intermediate **L1**, which undergoes β-hydrogen elimination to afford complex **203** and formaldehyde. Thermolysis of the analogous Rh(III)−CH_2CH_3 complex **205** gives ethylene and also **203** (eq 39).[72] The electrophilic Pd(II) and Ni(II) centers may react as Lewis acids and coordinate to the ether oxygen (**M1**), accelerating alkyl group removal by an internal interaction with a coordinated anion, as suggested by Shaw,[8,372] or by an external nucleophilic attack affording **204** and an alkyl halide. Regardless of the mechanism involved, the metal-based selectivity is clear: the Rh(I) metal center only activates the very strong aryl−O bond, whereas the Pd(II) or Ni(II) systems preferentially cleave the alkyl−O single bond. Notably, hydrodeoxygenation (HDO)[375] of **204** (M = Pd) was observed as well under mild H_2 pressure at elevated temperatures.[68]

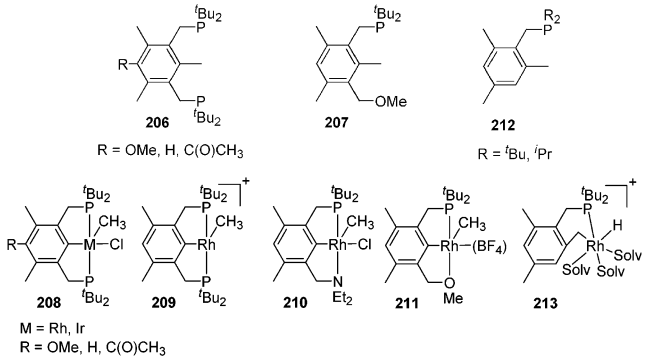


C. New Mechanistic Insight into Selective C–C Bond Activation

Reviews on C−C bond activation, including PCP ligand systems, have recently appeared.[60,106,271] Here we will summarize the most recent results regarding metal insertion into C−C single bonds. Reaction of the PCX ligand systems **52**, **206**, **207** with various Rh(I) precursors resulted in formation of Rh(III) aryl−alkyl complexes by oxidative addition of a strong Ar−CH_3 bond (**208**−**211**).[41,42,44,58,59,61] X-ray analysis of **208**,[58] **210**,[41] **211**[61] showed that the metal atom is at the center of a square pyramid with the methyl group trans to the empty coordination site. For **211**, the BF_4^- anion is coordinated to the d^6 metal center through a fluorine atom.[61] Reaction of monophosphine ligands (PC; **212**) with Pt(II), Pd(II), and Rh(I) resulted in selective $ArCH_2$−H bond activation (**213**).[64,69,376]

Table 5

entry	ligand	precursor	solvent	kinetic products	thermodynamic product
1	PCN (**52**)	neutral	benzene	C−C	C−C
2	PCN (**52**)	neutral	toluene	C−C	C−C
3	PCN (**52**)	neutral	3-fluorotoluene	C−C	C−C
4	PCP (**206**)	neutral	benzene	C−H;C−C	C−C
5	PCP (**206**)	neutral	THF	C−H;C−C	C−C
6	PCP (**206**)	cationic	THF	C−H;C−C	C−C
7	PCP (**206**)	cationic	MeCN	C−H	C−H
8	PCO (**207**)	cationic	THF	C−H	C−C
9	PCO (**207**)	cationic	acetone	C−H	C−C
10	PCO (**207**)	cationic	MeOH	C−H	C−C
11	PC (**213**)	cationic	MeOH	C−H	C−H

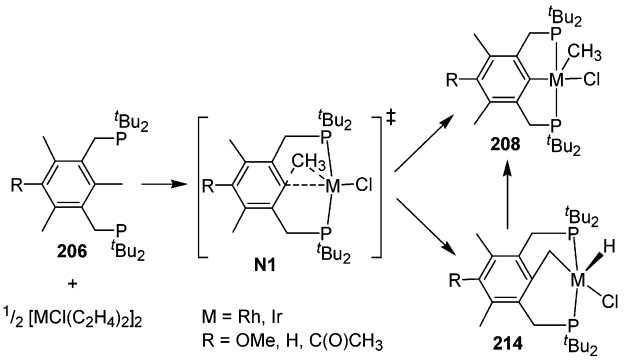


For neutral bischelating systems **208**−**211**,[58] C−C bond activation is thermodynamically favorable; however, the kinetic balance between C−H and C−C bond cleavage is significantly influenced by the nature of one of the donor atoms (P, O, N; Table 5: compare entries 1, 4 and 6, 8).[41,44,58,61] C−C bond activation becomes kinetically more favorable than insertion into the benzylic C−H bond with an increasing electron density on the metal center. A similar trend was observed by varying the phosphine substituents.[52,60] With the PPh_2 analogue of **206**, C−H activation is kinetically and thermodynamically preferred over C−C activation.

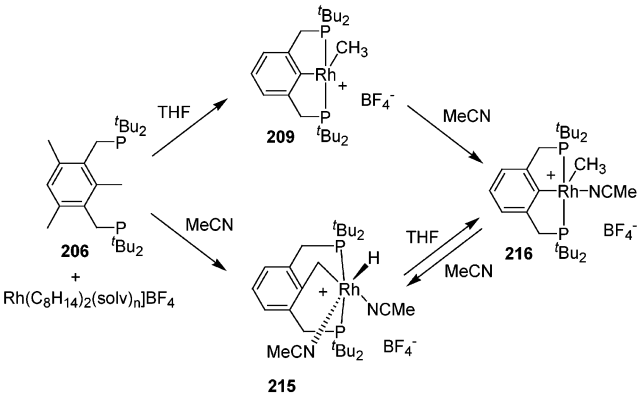
For **206**, the kinetic barrier for Ir(I) and Rh(I) insertion into the stronger C−C bond is lower than that for C−H bond activation by ∼0.3 and ∼0.5 kcal/mol, respectively. The reactions are selective—only the C−H and C−C bonds of the methyl group between the phosphine arms are being activated in parallel processes (**214** ← **N1** → **208**) indicating the formation of an intermediate having both phosphine "arms" coordinated to one metal center (Scheme 27). Thermolysis of **214** afforded the thermodynamically preferred product **208**.[58]

The product ratio with neutral complexes is temperature independent, and is not influenced by substituents on the aromatic system, indicative of nonpolar three-centered transition states for both C−H and C−C bond activation processes (**N1**). In line with these observations, solvent polarity has only a minor effect on the reaction outcome. However, a remarkable solvent effect on C−H vs C−C bond activation processes was observed by treatment of **206** with *cationic* Rh(I) precursors (Scheme 28).[59] In THF, metal insertion into the C−H and C−C bonds and conversion of the product of C−H bond activation into **209** was observed, whereas in acetonitrile activation of the C−H bond occurred (**215**). No other products

Scheme 27



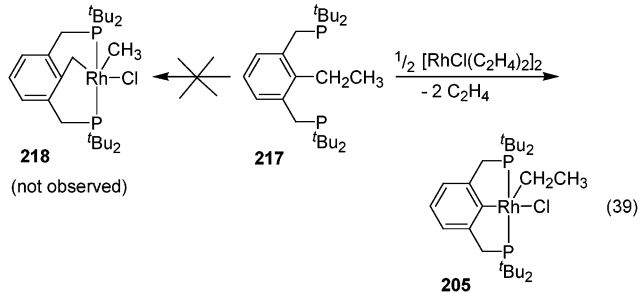
Scheme 28



were observed. The ratio between the cationic C−H and C−C activated complexes is identical as observed for the neutral systems in THF. Dissolving products **209** and **215** in acetonitrile and THF, respectively, resulted in the formation of the alkyl−aryl Rh(III) acetonitrile complex **216**. In neat acetonitrile, complex **216** slowly converted to product **215**, indicating that the C−H bond activation process with **206** and cationic Rh(I) precursors in acetonitrile is both kinetically and thermodyamically preferred. Thus, the solvent can provide a convenient tool in directing the bond activation process. The reason for this dramatic solvent effect is probably steric in nature. With the strongly coordinated nitrile, a four-coordinate intermediate is involved prior to insertion into the sterically less demanding C−H bond. On the other hand, THF is only loosely bound, and the species active in oxidative addition is likely to be a three-coordinate Rh complex with no coordinated solvent.

Direct Rh(I) insertion into an $Ar-CH_2CH_3$ bond with ligand **217** was observed as well, yielding a

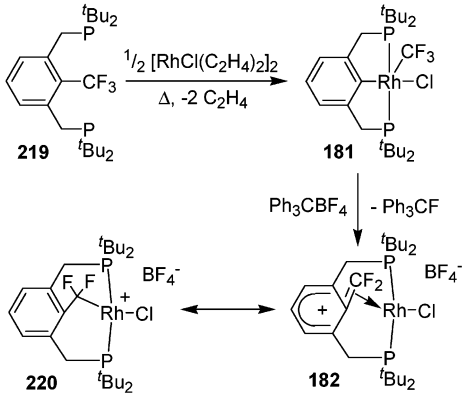
relatively stable 16 electron Rh(III)−ethyl complex **205**,[53,67] which undergoes β-H elimination at elevated temperatures (eq 39).[72] Although the Ar−CH_2CH_3 bond is ∼24.5 kcal/mol stronger than the adjacent $ArCH_2$−CH_3 bond, this is more than compensated by the stronger Ar−Rh than $ArCH_2$−Rh, and selective insertion into the Ar−C bond is kinetically and thermodynamically preferred. $ArCH_2$−CH_3 bond activation is not involved (**217** → **218**), either as a side equilibrium or as an intermediate process, even in the presence of H_2, which could have driven the overall process to a thermodynamically more favorable consecutive sp^3−sp^3, sp^2−sp^3 C−C bond activation process forming two equivalents of methane. Accessibility and orbital directionality of the sp^2−sp^3 vs sp^3−sp^3 C−C bonds are kinetic parameters favoring Ar−C bond oxidative addition.



(39)

Oxidative addition of the strong aryl−CF_3 bond to Rh(I) takes place upon treating **219** with $[RhCl(C_2H_4)_2]_2$ in dioxane or toluene at elevated temperatures, leading to quantitative formation of **181** (Scheme 29).[70,71] $ArCF_2$−F bond cleavage was not

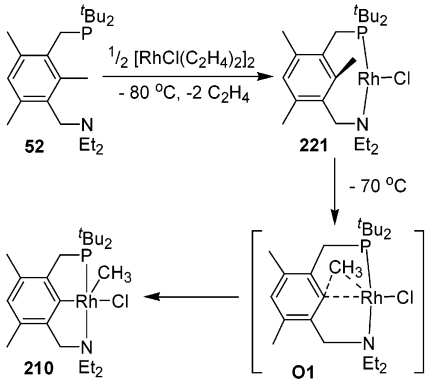
Scheme 29



observed, suggesting a lower kinetic barrier of the C−C vs C−F bond activation process. Interestingly, treatment of **181** with the strong electrophiles, BF_3 or Ph_3CBF_4, resulted in formation of difluoromethylene−arenium complex **182**—the resonance form of a difluorobenzyl cation (**220**; see also section IIIK, eq 34).[71]

The "hemilabile" phosphino-amine PCN ligand **52** exhibits a remarkable metal-dependent reactivity—reaction with Pt(II) precursors result in selective benzylic C−H bond cleavage followed by intramolecular deprotonation by the amine arm, whereas exclusive C−C bond activation occurs with Rh(I) (Scheme 30, **210**).[41,44] C−H bond activation was not

Scheme 30



observed with Rh(I) in this system perhaps as a result of a lower activation barrier of the C−C vs C−H oxidative addition as a result of better orientation of the metal toward the C−C bond. A relatively fast C−H reductive elimination process which is impossible to detect on the NMR time scale cannot be excluded. Remarkably, metal insertion into a strong sp^2−sp^3 C−C bond of **52** was directly observed at −70 °C by NMR (**221** → **210**), allowing the unprecedented determination of activation parameters of direct metal insertion into a C−C bond, $\Delta H^{\ddagger} = 15.0(0.4)$ kcal/mol, $\Delta S^{\ddagger} = -7.5(2.0)$ eu, and $\Delta G^{\ddagger}_{(298)} = 17.2(1.0)$ kcal/mol.[44] The high level of preorganization toward a three-center nonpolar transition state (**O1**) is reflected in the low activation barrier for this enthalpy-controlled process. The key 14-electron intermediate **221** was unambiguously characterized at −80 °C using ^{13}C and ^{15}N isotope labeling experiments and advanced multinuclear NMR techniques, ruling out the existence of agostic interactions, η^2 coordination of the aromatic ring or interaction with the aromatic π-system. Solvent coordination was excluded, and solvent polarity did not affect the reaction rate, which is in good agreement with a concerted, three-centered transition state oxidative addition process with no charge separation.

A combined experimental and computational study on C−H and C−C bond activation with cationic PCO-based Rh(I) systems reveals the role of chelation of the ligand system to the metal center on C−C bond activation and the importance of unsaturated species in both C−C and C−H bond activation processes.[61] For **207**, benzylic C−H bond activation is kinetically favored, whereas C−C bond activation is thermodynamically preferred, which is in contrast to the reactivity observed with ligands **52** and **206** (also with alkyl substituted phosphines) (Scheme 31; Table 5). Initially, two products of C−H bond activation are observed (**222**, **223**), which convert upon mild heating into complex **211**. Interestingly, C−C activation can be accomplished simply by solvent evaporation of **223** at room temperature, as a result of stabilization of the C−C activated product in the solid state by BF_4 coordination. Computations indicate that both C−C and C−H activation processes involve 14e, solvent (methanol) coordinated intermediates. The C−C bond oxidative addition with **207** and cationic Rh(I) complexes proceed by intermediacy of a three-centered

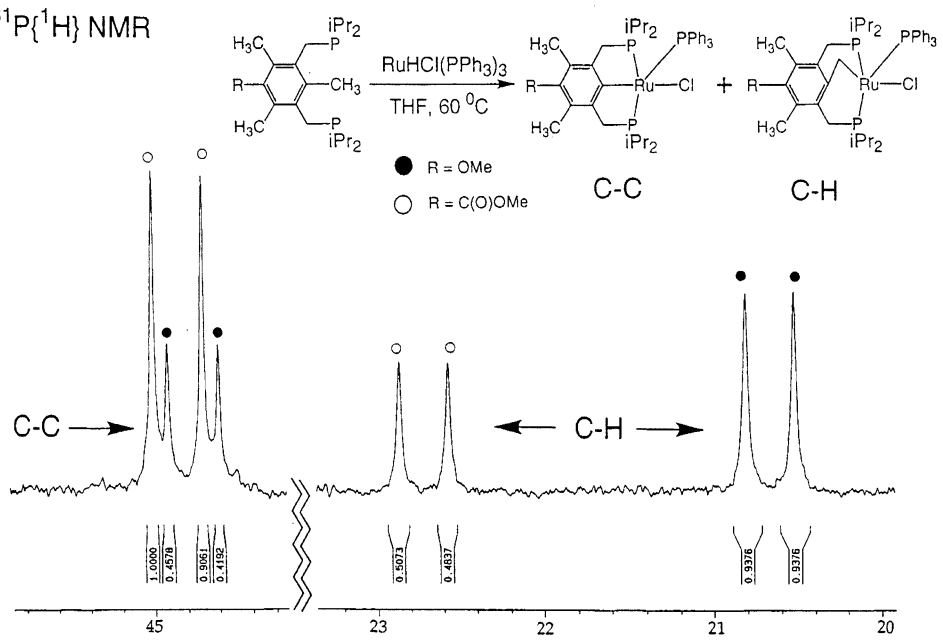
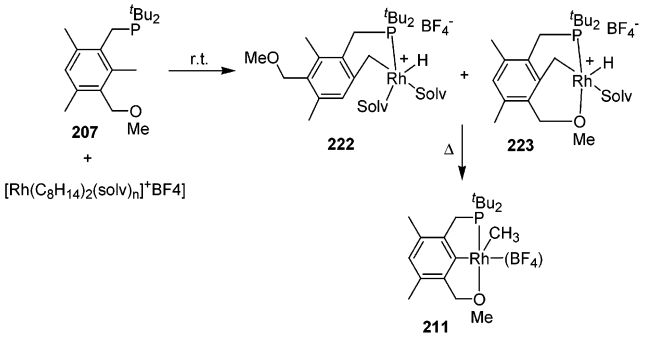
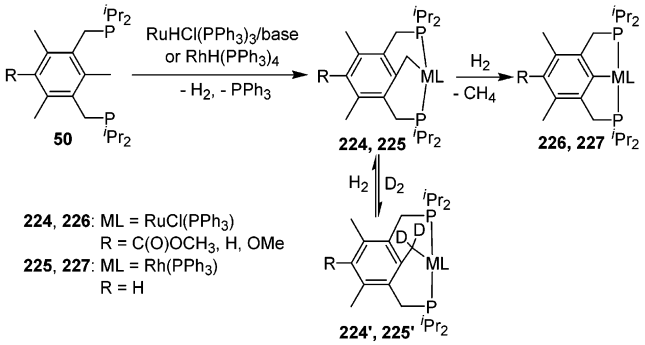


Figure 14. Competition $^{31}P\{^{1}H\}$ NMR experiment with ligand **50**−OMe and **50**−C(O)OMe and $RuHCl(PPh_3)_3$ showing an arene substituent effect on the conversion of the benzylic complexes **224** into the products of C−C bond activation (**226**; Only the P^iPr_2 groups are shown). From ref 73. Copyright 1999 American Chemical Society.

Scheme 31



Scheme 32

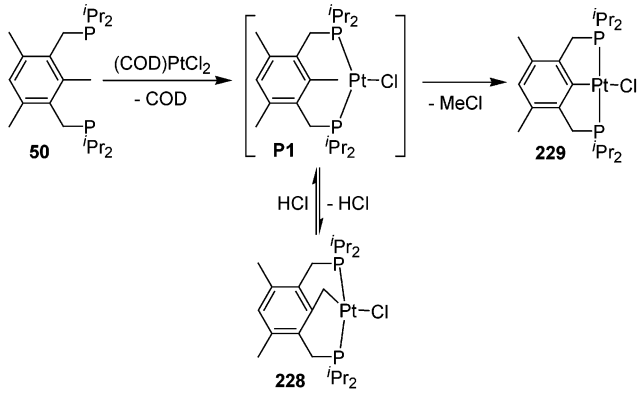


transition states as experimentally observed with ligands **206** and **52** and neutral Rh(I) precursors. C−C bond activation with an "open arm system" (**213**, **222**) is kinetically and thermodynamically not favorable, which is in good agreement with experimental results. One important question remains: is the formation of an eight-membered chelate a prerequisite for activation of strong C−C bonds or merely one of many factors determining the delicate balance between C−H and C−C bond activation kinetics and product stability? The relatively small difference between C−H and C−C product stability and kinetic barriers suggest that bischelating prior to C−C bond oxidative addition may not be necessary requirement. Further studies have to unambiguously clarify this point.

Under certain reaction conditions, C−H bond activation is the only kinetically observed process. An additional driving force is necessary to reverse the C−H bond activation and to thermodynamically drive the reaction toward C−C bond activation.[22,47,48,54,65,73] For instance, reaction of **50** with $RuCl_2(PPh_3)_3$/^{t}BuONa or $RhH(PPh_3)_4$ precursors resulted exclusively in formation of the benzylic complexes **224** and **225**, respectively (Scheme 32). Addition of H_2 to the product solution or performing the reaction in the presence of H_2 resulted in quantitative formation of **226** and **227** and an equimolar amount of methane. Reaction of **50** (R = H) with $MHCl(PPh_3)_3$ (M = Os, Ru) in a sealed vessel resulted also in C−C bond activation and methane formation.[56,73] Reducing the electron density on the arene had a positive effect on the overall rate of the Ru-based reaction **224** → **226** (R = C(O)Me > H > OMe; Figure 14).[73] Deuterium labeling experiments with **224** and **225** showed selective labeling of the benzylic groups prior to the metal insertion into the C−C bond. Thus, $ArCH_2$−H bond activation is merely a side-equilibrium, and not an intermediate process in the C−C bond activation step. The H/D exchange rate with **224** is dependent on the electron density of the arene and follows the same trend as observed for the conversion of the products of C−H bond activation into the products of C−C bond activation. The substituent effect on the actual metal insertion step into the C−C bond seems nil, pointing toward a concerted oxidative addition process as depicted in Schemes 27 (**N1**) and 30 (**O1**).

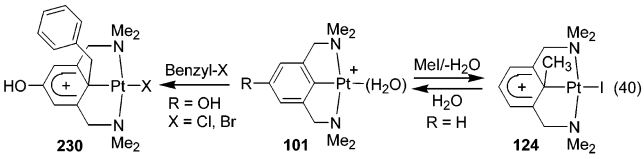
Reaction of **50** with $(COD)PtCl_2$ (COD = cycloocta-1,5-diene) resulted in formation of the thermally robust **228** and HCl (Scheme 33).[65,73] Addition of

Scheme 33

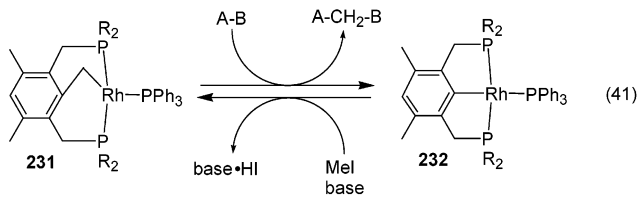


excess HCl to a solution of **228** afforded **229** and MeCl, which can be viewed as the transfer of a methylene group from an arene to a polar substrate (HCl). An inverse H/D kinetic isotope effect was observed, as expected for a competitive C−H and C−C bond activation process via **P1**. Metal insertion into the C−C bond becomes more favorable upon deuterium incorporation into the alkyl group. A Pt(II) complex analogous to the postulated **P1** (having phenyl substituents instead of *iso*-propyl substituents on phosphorus) has been isolated.[63]

Mechanistically, a concerted C−C oxidative addition process might be involved as oxidative addition of significantly weaker, strained C−C bonds to Pt(II) is well-known.[60,271,272] However, formation of an arenium complex akin to **124** by an electrophilic attack of the metal center on the ipso carbon of the arene cannot be excluded (eq 40). Van Koten et al. showed that the NCN-based Pt(II) complex **101** reacts with MeI and benzyl halides to afford the arenium complexes **124** and **230**.[86,88,90,100,101,106,107,114] Addition of H_2O to **124** resulted in C−C bond activation generating the starting complex **101**.



Methylene transfer from a hydrocarbon to another substrate is a conceptually unique process.[22,48,65,73] Treatment of the Rh(I) complex **231** (R = ^{i}Pr, Ph) with primary silanes, disilanes, and aromatic hydrocarbons resulted in selective transfer of the methylene group to the incoming substrate and formation of complex **232** (eq 41). Reaction of **232** with methyl iodide in the presence of a base regenerates the starting complex **231**. Catalysis has been demonstrated by using excess of **50** as a methylene source.[54]



A = H, B = H, $SiOEt_3$, SiPh, Ph; A = B = $(MeO)_3Si$
R = Ph, ^{i}Pr

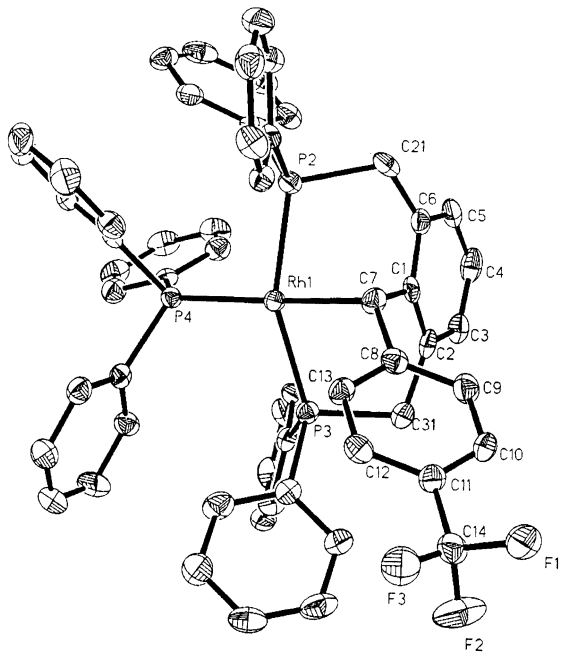


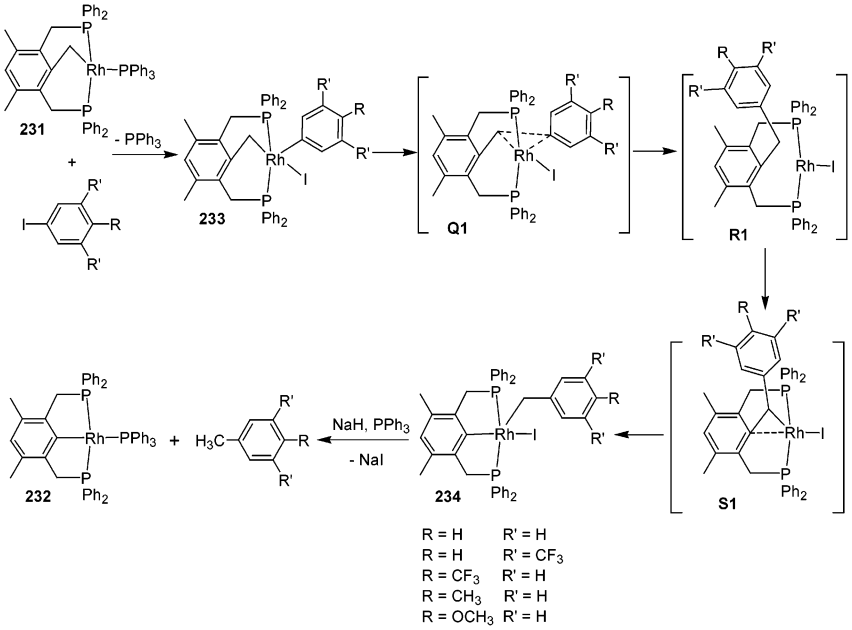
Figure 15. ORTEP drawing of the molecular structure of **236**. From ref 22. Copyright 2000 American Chemical Society.

The methylene transfer process and the alkyl migration into the strong σ aryl-Rh(I) bond combines a unique sequence of organometallic transformations including (i) H−Si, Si−Si, or C_{aryl}−H bond activation, (ii) benzyl C−H, C−Si, or C−C bond reductive elimination, (iii) metal insertion into the C_{aryl}−C bond, (iv) substrate elimination, and (v) regeneration of the aryl−alkyl moiety by ligand transcyclometalation or alkyl transfer.

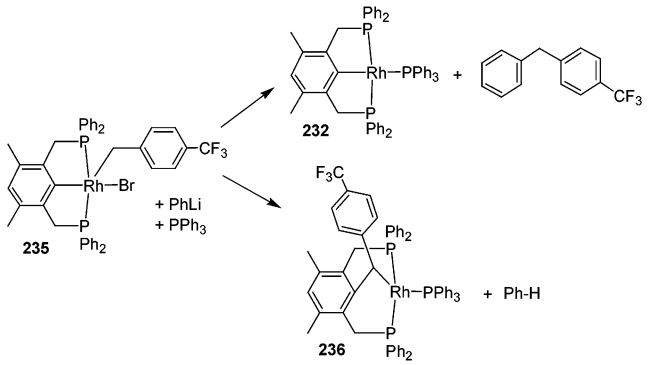
Complex **231** (R = Ph) was reacted with various aryl halides to gain mechanistic insight in the methylene transfer reaction (Scheme 34).[22] Initially, C_{aryl}−I oxidative addition occurs (**231** → **233**), followed by C−C reductive elimination (**Q1** → **R1**) and oxidative addition steps (**R1** → **S1**). The net result is an intramolecular arene to arene transfer of a methylene group (**233** → **234**). Treatment of **234** with NaH affords **232** and an organic product. Kinetic studies revealed that the C−C reductive elimination step is rate-determining with an organized nonpolar three-centered early transition state (**Q1**) as indicated by the activation parameters: $\Delta S^{\ddagger} = -23 \pm 4$ eu, $\Delta H^{\ddagger} = 17 \pm 3$ kcal/mol.

Methylene and benzyl transfer from incoming reagents into the σ aryl−metal bond of the bischelating ring has been studied as well as exemplified with the reaction of complex **235** with PhLi resulting in the formation of complexes **232** and **236** as a result of competitive carbon−carbon bond formation processes (Scheme 35; Figure 15).[22] Other carbon nucleophiles can be used as well. The migration of the benzyl group to the cyclometalated arene is kinetically controlled by electronic factors—relatively electron-rich benzyl groups favor transfer into the bischelating ring and C−H bond activation. This process is favored kinetically over sp^3−sp^3 C−C reductive elimination.

Scheme 34



Scheme 35



V. Concluding Remarks

The combination of synthetic, structural, coordination, mechanistic, and catalytic studies employing series of newly synthesized PCX (X = P, N, O) ligands and metal complexes has provided much fundamental insight into the factors dominating the reactivity of these intriguing complexes and has resulted in a far better understanding of how new reactive PCP-based complexes should be designed. Moreover, the isolation of "frozen" model intermediates provided much needed mechanistic data not possible to acquire with other ligand systems. Many more unique complexes might be isolated, but one of the issues facing the rich PCP-based model chemistry is the possibility to generalize the accrued knowledge. One example is the development of a general, safe method for metal carbene formation, which started from PCP-based carbene complexes to the recent formation of Grubbs catalysts.[45] The opposite trend is also observed. The combined knowledge in the field of catalytic alkane dehydrogenation led to the successful design of the alkane dehydrogenation PCP catalyst **32** and related complexes.[26] Applied chemistry with catalytic PCP-based system is in reach due to the favorable combination of complex stability, fidelity, selectivity and high reactivity. Design of a highly efficient enantioselective PCP catalyst capable of substrate activation under mild reaction conditions is still a highly desirable target. PCP and related ligands are also versatile building block for the formation of nanoscale, supermolecular structures promising much more exciting chemistry to come soon.

VI. Acknowledgments

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VII. References

(1) Crocker, C.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L.; Goodfellow, R. J. *J. Chem. Soc. Chem. Commun.* **1979**, 498.

(2) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373.
(3) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217.
(4) Empsall, H. D.; Hyde, E. M.; Jones, C. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 480.
(5) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589.
(6) Errington, R. J.; Shaw, B. L. *J. Organomet. Chem.* **1982**, *238*, 319.
(7) Errington, R. J.; McDonald, F. E.; Shaw, B. L. *J. Chem Soc., Dalton Trans.* **1982**, 1829.
(8) Jones, C. E.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 992.
(9) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
(10) Shaw, B. L.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 918.
(11) Shaw, B. L.; Moulton, C. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
(12) Briggs, J. R.; Constable, A. G.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1225.
(13) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Shaw, B. L. *J. Chem Soc., Dalton Trans.* **1982**, 387.
(14) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem Soc., Dalton Trans.* **1980**, 59.
(15) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem Soc., Dalton Trans.* **1979**, 1979.
(16) Li, S.; Hall, M. B. *Organometallics* **1999**, *18*, 5682.
(17) Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 3992.
(18) Sundermann, A.; Uzan, O.; Martin, J. M. L. *Organometallics* **2001**, *20*, 1783.
(19) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y.-S. *J. Am. Chem. Soc.* **1999**, *121*, 9531.
(20) Bergbreiter, D. E.; Osburn, P. L.; Wilson, A.; Sink, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 9058.
(21) Kiewel, K.; Liu, Y. S.; Bergbreiter, D. E.; Sulikowski, G. A. *Tetrahedron Lett.* **1999**, *40*, 8945.
(22) Cohen, R.; van der Boom, M. E.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 7723.
(23) Ashkenazi, N.; Vigalok, A.; Parthiban, S.; Ben-David, Y.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 8797.
(24) Gupta, M.; Hagen, C.; Kaska, W. C.; Flesher, R.; Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2083.
(25) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840.
(26) Jensen, C. M. *Chem. Commun.* **1999**, 2443.
(27) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1.
(28) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086.
(29) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redón, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*−*302*, 958.
(30) Morales-Morales, D.; Redón, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619.
(31) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144.
(32) Nemeh, S.; Jensen, C. M.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.
(33) Xu, W. W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273.
(34) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652.
(35) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 5091.
(36) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Y. *Organometallics* **2000**, *19*, 1734.
(37) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2000**, *19*, 3429.
(38) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2001**, *20*, 1001.
(39) Gusev, D. G.; Maxwell, T.; Dolgushin, F. M.; Lyssenko, M.; Lough, A. J. *Organometallics* **2002**, *21*, 1095.
(40) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 2601.
(41) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, *16*, 3981.
(42) Gandelman, M.; Konstantinovsky, L.; Rozenberg, H.; Milstein, D. Submitted.
(43) Gandelman, M.; Milstein, D. *Chem. Commun.* **2000**, 1603.
(44) Gandelman, M.; Vigalok, A.; Konstantinovsky, L.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 9848.
(45) Gandelman, M.; Rybtchinski, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 5372.
(46) Gauvin, R. M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2001**, *20*, 1719.
(47) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699.
(48) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42.
(49) Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21*, 812.
(50) Kraatz, H.-B.; Milstein, D. *J. Organomet. Chem.* **1995**, *488* (1−2), 223.
(51) Kraatz, H.-B.; van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Isr. J. Chem.* **2001**, *41*, 163.
(52) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774.
(53) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965.
(54) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687.
(55) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687.
(56) Regis, R. M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2001**, *20*, 1719.
(57) Rybtchinksi, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786.
(58) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406.
(59) Rybtchinski, B.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528.
(60) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 871.
(61) Rybtchinski, B.; Oevers, S.; Montag, M.; Vigalok, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 9064.
(62) Sundermann, A.; Uzan, O.; Milstein, D.; Martin, J. M. L. *J. Am. Chem. Soc.* **2000**, *122*, 7095.
(63) van der Boom, M. E.; Gozin, M.; Ben-David, Y.; Shimon, L. J. W.; Frolow, F.; Kraatz, H.-B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 7068.
(64) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 2562.
(65) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. *Chem. Commun.* **1996**, 2167.
(66) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Vigalok, A.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 625.
(67) van der Boom, M. E.; Shyh-Yeon, L.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415.
(68) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531.
(69) van der Boom, M. E.; Ott, J.; Milstein, D. *Organometallics* **1998**, *17*, 4263.
(70) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Chem. Commun.* **1998**, 917.
(71) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652.
(72) van der Boom, M. E.; Higgitt, C. L.; Milstein, D. *Organometallics* **1999**, *18*, 2413.
(73) van der Boom, M. E.; Kraatz, H.-B.; Hassner, L.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 3873.
(74) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839.
(75) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Chem. Commun.* **1996**, p 1673.
(76) Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 7873.
(77) Vigalok, A.; Kraatz, H.-B.; Konstantinovsky, L.; Milstein, D. *Chem. Eur. J.* **1997**, *3*, 253.
(78) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477.
(79) Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.
(80) Vigalok, A.; Rybtchinksi, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 895.
(81) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2061.
(82) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2341.
(83) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798.
(84) Weisman, A.; Gozin, M.; Kraatz, H.-B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 1792.
(85) Abbenhuis, R. A. T. M.; del Río I.; Bergshoef, M. M.; Boersman, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749.
(86) Albrecht, M.; Gossage, R. A.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1999**, *121*, 11898.
(87) Albrecht, M.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 11822.
(88) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233.
(89) Albrecht, M.; Kocks, B. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *624*, 271.
(90) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.
(91) Beletskaya, I. P.; Chuchurjukin, A. V.; Dijkstra, H. P.; van Klink, G. P. M.; van Koten, G. *Tetrahedron Lett.* **2000**, *41*, 1075.

(92) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317.
(93) Dani, P.; Albrecht, M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2000**, *19*, 4468.
(94) Dani, P.; Toorneman, M. A. M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2000**, *19*, 5287.
(95) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743.
(96) Dijkstra, H. P.; Steenwinkel, P.; Grove, D. M.; Lutz, M.; Spek, A. L.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2186.
(97) Dijkstra, H. P.; Meijer, M. D.; Patel, J.; Kreiter, R.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; Canty, A. J.; van Koten, G. *Organometallics* **2001**, *20*, 3159.
(98) Dijkstra, H. P.; Albrecht, M.; van Koten, G. *Chem. Commun.* **2002**, 126.
(99) Frey, U.; Grve, D. M.; van Koten, G. *Inorg. Chim. Acta* **1988**, *269*, 322.
(100) Grove, D. M.; van Koten, G.; Ubbles, H. J. C. *Organometallics* **1982**, *1*, 1366.
(101) Grove, D. M.; van Koten, G.; Louwen, J. N.; Nolles, J. G.; Spek, A. L.; Ubbles, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609.
(102) Karlen, T.; Dani, P.; Grove, D. M.; Steenwinkel, P.; van Koten, G. *Organometallics* **1996**, *15*, 5687.
(103) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New. J. Chem.* **1997**, *21*, 751.
(104) Schmülling, M.; Grove, D. M.; van Koten, G.; van Eldik, R.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 1384.
(105) Steenwinkel, P.; James, S. L.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 513.
(106) Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 759.
(107) Steenwinkel, P.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1998**, *17*, 5411.
(108) Steenwinkel, P.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 5647.
(109) Steenwinkel, P.; Gossage, R. A.; Maunula, T.; Grove, D. M.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 763.
(110) Steenwinkel, P.; Kolmschot, S.; Gossage, R. A.; Dani, P.; Veldman, N.; Spek, A. L.; van Koten, G. *Eur. J. Inorg. Chem.* **1998**, 477.
(111) Sutter, J.-P.; Grove, D. M.; Beley, M.; Collin, J.-P.; Veldman, N.; Spek, A. L.; Sauvage, J.-P.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1282.
(112) Valk, J.-M.; Boersma, J.; van Koten, G. *J. Organomet. Chem* **1994**, *483*, 213.
(113) van Klink, G. P. M.; Dani, P.; van Koten, G. *Chin. J. Chem.* **2002**, *20*, 207.
(114) van Koten, G.; Timmer, J. G.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250.
(115) Williams, B. S.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *Helv. Chim. Acta* **2001**, *84*, 3519.
(116) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017.
(117) Krogh-Jespersen, K.; Czerw, M.; Kanzelberger, M.; Goldman, A. S. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 56.
(118) Krogh-Jespersen, D.; Czerw, M.; Summa, N.; Renkema, K. B.; Achord, P. A.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 11404−11416.
(119) Krogh-Jespersen, K.; Czerw, M.; Goldman, A. S. *J. Mol. Catal. A.: Chem.* **2002**, *189*, 95.
(120) Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. *J. Organomet. Chem.* **1996**, *518*, 55.
(121) Grimm, J. C.; Nachtigal, C.; Mack, H. G.; Kaska, W. C.; Mayer, H. A. *Inorg. Chem. Commun.* **2000**, *3*, 511.
(122) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596.
(123) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13.
(124) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1998**, *7*, 13.
(125) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C.; Mayer, H. A. *Organometallics* **1994**, *13*, 3816.
(126) McLoughlin, M. A.; Keder, N. L.; Harrison, W. T. A.; Flesher, R. J.; Mayer, H. A.; Kaska, W. C. *Inorg. Chem.* **1999**, *38*, 3223.
(127) Nemeh, S.; Flesher, R. J.; Gierling, K.; Maichle-Mossmer, C.; Mayer, H. A.; Kaska, W. C. *Organometallics* **1998**, *17*, 2003.
(128) Sjövall, S.; Wendt, O. F.; Andersson, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1396.
(129) Gruber, A. S.; Zim, D.; Ebeling, G.; Monteiro, A. L.; Dupont, J. *Org. Lett.* **2000**, *2*, 1287.
(130) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374.
(131) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607.
(132) Yao, J.; Wong, W. T.; Jia, G. *J. Organomet. Chem.* **2000**, *598*, 228.
(133) Bedford, R. B.; Draper, S. M.; Scully, P. N.; Welch, S. L. *New. J. Chem.* **2000**, *24*, 745.
(134) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423.
(135) Longmire, J. M.; Zhang, X. *Tetrahedron Lett.* **1997**, *38*, 1725.
(136) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43.
(137) Dani, P.; Richter, B.; van Klink, G. P. M.; van Koten, G. *Eur. J. Inorg. Chem.* **2001**, 125.
(138) Richter, B.; Deelman, B.-J.; van Koten, G. *J. Mol. Catal. A.: Chem.* **1999**, *145*, 317.
(139) Cotter, W. D.; Barbour, L.; McNamara, K. L.; Hechter, R.; Lachicotte, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 11016.
(140) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723.
(141) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379.
(142) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Benchtop Edition; Academic Press: London, 1990.
(143) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.
(144) Crisp, G. T. *Chem. Soc. Rev.* **1998**, *27*, 427.
(145) Haenel, M. W.; Jakubik, D.; Krüger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 333.
(146) Haenel, M. W.; Oevers, S.; Bruckmann, J.; Kuhnigk, J.; Krüger, C. *Synlett* **1998**, 301.
(147) Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 207.
(148) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 738.
(149) Kimmich, B. F. M.; Marshall, W. J.; Fagan, P. J.; Hauptman, E.; Bullock, R. M. *Inorg. Chim. Acta* **2002**, *330*, 52.
(150) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 744.
(151) Steffey, B. D.; Miedaner, A.; Maciejewski-Farmer, M. L.; Bernatlis, P. R.; Herring, A. M.; Allured, V. S.; Carperos, V.; DuBois, D. L. *Organometallics* **1994**, *13*, 4844.
(152) Ryu, S. Y.; Kim, H.; Kim, H. S.; Park, S. *J. Organomet. Chem.* **1999**, *592*, 194.
(153) Ryu, S. Y.; Yang, W.; Kim, H. S.; Park, S. *Bull. Korean Chem. Soc.* **1997**, *18*, 1183.
(154) Jia, G.; Lee, H. M.; Xia, H. P.; Williams, I. D. *Organometallics* **1996**, *15*, 5453.
(155) Lee, H. M.; Yao, J.; Jia, G. *Organometallics* **1997**, *16*, 3927.
(156) Albinati, A.; Lianza, F.; Pregosin, P. S.; Müller, B. *Inorg. Chem.* **1994**, *33*, 2522.
(157) van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Vrieze, K.; Slob, C.; Krabbendam, H.; Spek, A. L. *Inorg. Chem.* **1988**, *27*, 1014.
(158) Liu, S. H.; Lo, S. T.; Wen, T. B.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Organometallics* **2001**, *20*, 667.
(159) Bennett, M. A.; Jin, H.; Willis, A. C. *J. Organomet. Chem.* **1993**, *451*, 249.
(160) Kimmich, B. F. M.; Bullock, R. M. *Organometallics* **2002**, *21*, 1504.
(161) Brown, J. M.; Dayrit, F. M.; Lightowler, D. *J. Chem. Soc., Chem. Commun.* **1983**, 414.
(162) Liu, S. H.; Huang, X.; Lin, Z.; Lau, C. P.; Jia, G. *Eur. J. Inorg. Chem.* **2002**, 1697.
(163) Liu, S. H.; Ng, S. M.; Wen, T. B.; Zhou, Z. Y.; Lin, Z.; Lau, C. P.; Jia, G. *Organometallics* **2002**, *21*, 4281.
(164) Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 195.
(165) Jia, G.; Lee, H. M.; Williams, I. D. *J. Organomet. Chem.* **1997**, *534*, 173.
(166) Katayama, H.; Wada, C.; Taniguchi, K.; Ozawa, F. *Organometallics* **2002**, *21*, 3285.
(167) Li, S.; Hall, M. B. *Organometallics* **2001**, *20*, 2153.
(168) Cao, Z.; Hall, M. B. *Organometallics* **2000**, *19*, 3338.
(169) Ortiz, J. V.; Havlas, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.
(170) Marc, J. M.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1994**, *483*, 213.
(171) Valk, J.-M.; van Belzen, R.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1994**, *1994*, 2293.
(172) del Rio, I.; Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1999**, *583*, 69.
(173) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. *Angew. Chem., Int. Ed.*, in press.
(174) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.*, in press.
(175) Wen, T. B.; Cheung, Y. K.; Yao, J.; Wong, W. T.; Zhou, Z. Y.; Jia, G. *Organometallics* **2000**, *19*, 3803.
(176) Müller, G.; Lutz, M.; Pape, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1.
(177) Cross, R. J.; Kennedy, A. R.; Muir, K. W. *J. Organomet. Chem* **1995**, *487*, 227.
(178) Caruso, F.; Camalli, M.; Rimml, H.; Venanzi, L. M. *Inorg. Chem.* **1995**, *34*, 673.
(179) Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *Tetrahedron Lett.* **1993**, *34*, 3413.
(180) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6.
(181) Creaser, C. S.; Kaska, W. C. *Inorg. Chim. Acta* **1978**, *30*, L325.
(182) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 7085.

(183) Li, R.-X.; Li, X.-J.; Wong, N.-B.; Tin, K.-C.; Zhou, Z.-Y.; Mak, T. C. W. *J. Mol. Catal. A.: Chem.* **2002**, *178*, 181.
(184) Blue, E. D.; Gunnoe, T. B.; Brooks, N. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2571.
(185) Dani, P.; van Klink, G. P. M.; van Koten, G. *Eur. J. Inorg. Chem.* **2000**, 1465.
(186) Beletskaya, I. P.; Chuchurjukin, A. V.; Dijkstra, H. P.; van Klink, G. P. M.; van Koten, G. *Tetrahedron Lett.* **2000**, *41*, 1081.
(187) Gupta, M.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1997**, 461.
(188) Dilworth, J. R.; Zheng, Y.; Vaughan, G. D. *J. Chem Soc., Dalton Trans.* **1999**, 1877.
(189) Yun, J. G.; Seul, J. M.; Lee, K. D.; Kim, S.; Park, S. *Bull. Korean Chem. Soc.* **1996**, *17*, 311.
(190) Cross, R. J.; Kennedy, A. R.; Manojlovic-Muir, L.; Kenneth, W. *J. Organomet. Chem.* **1995**, *493*, 243.
(191) Liu, F.; Goldman, A. S. *Chem. Commun.* **1999**, 655.
(192) Park, S. *Bull. Korean Chem. Soc.* **2000**, *21*, 1251.
(193) Park, S. *Bull. Korean Chem. Soc.* **2001**, *22*, 15.
(194) Park, S. *Bull. Korean Chem. Soc.* **2001**, *22*, 1410.
(195) Hahn, C.; Sieler, J.; Taube, R. *Chem. Ber./Recueil* **1997**, *130*, 939.
(196) Seul, J. M.; Park, S. *J. Chem Soc., Dalton Trans.* **2002**, *6*, 1153.
(197) Park, S. *Bull. Korean Chem. Soc.* **2002**, *23*, 132.
(198) Farrington, E. J.; Martinez, V. E.; Williams, B. S.; van Koten, G.; Brown, J. M. *Chem. Commun.* **2002**, 308.
(199) Hughes, R. P.; Williamson, A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2001**, *20*, 4741.
(200) Liu, S. H.; Lo, S. T.; Wen, T. B.; Williams, I. D.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Inorg. Chim. Acta* **2002**, *334*, 122.
(201) Morales-Morales, D.; Cramer, R. E.; Jensen, C. M. *J. Organomet. Chem.* **2002**, *654*, 44.
(202) Morales-Morales, D.; Redón, R.; Wang, Z.; Lee, D. W.; Yung, C.; Magnuson, K.; Jensen, C. M. *Can. J. Chem.* **2001**, *79*, 823.
(203) Reinhart, B.; Gusev, D. G. *New. J. Chem.* **1999**, *23*, 1.
(204) Koelle, U.; Pasch, R. *Inorg. Chem. Commun.* **1998**, *1*, 395.
(205) Thompson, D. T. *Plat. Met. Rev.* **1998**, *42*, 71.
(206) Krogh-Jespersen, K.; Czerw, M.; Zhu, K.; Singh, B.; Kanzelberger, M.; Darji, N.; Achord, P. A.; Renkema, K. B.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 10797.
(207) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1984**, *260*, C52.
(208) Evans, D. R.; Huang, M.; Seganish, W. M.; Chege, E. W.; Lam, Y.-F.; Fettinger, J. C.; Williams, T. L. *Inorg. Chem.* **2002**, *41*, 2633.
(209) Dedieu, A.; Strich, A. *Inorg. Chem.* **1979**, *18*, 2940.
(210) Silverstre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.
(211) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fisher, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844.
(212) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Öfele, K.; Beller, M. *Chem. Eur. J.* **1997**, *3*, 1357.
(213) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23.
(214) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 481.
(215) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.
(216) Beller, M.; Zapf, A. *Synlett* **1998**, *12*, 792.
(217) Ben-David, Y.; Portnoy, M.; Gozin, M.; Milstein, D. *Organometallics* **1992**, *11*, 1995.
(218) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665.
(219) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organometallic Chemistry*, University Science Books, 2nd ed.; 1987.
(220) Canty, A. J. *Handbook of Organopalladium Chemistry for Organic Synthesis*; John Wiley & Sons: Hoboken, NJ, 2002.
(221) Böhm, V. P. W.; Herrmann, W. A. *Chem. Eur. J.* **2001**, *7*, 4191.
(222) van Strijndonck, G. P. F.; Boele, M. D. K.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1999**, 1073.
(223) Shaw, B. L. *New. J. Chem.* **1998**, 77.
(224) Shaw, B. L.; Perera, S. D.; Staley, E. A. *Chem. Commun.* **1998**, 1361.
(225) Brunel, J. M.; Hirlemann, M.-H.; Heumann, A.; Buono, G. *Chem. Commun.* **2000**, 1869.
(226) Sundermann, A.; Uzan, O.; Martin, J. M. L. *Chem. Eur. J.* **2001**, *7*, 1703.
(227) Ohff, M.; Ohff, A.; Milstein, D. *Chem. Commun.* **1999**, 357.
(228) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981.
(229) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.
(230) Moravsky, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182.
(231) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1985**, *286*, C13.
(232) Catellani, M.; Frignani, F.; Rangomi, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 119.
(233) Lewis, J.; Hill, M. N. S.; Johnson, B. F. G. *J. Chem. Soc. A.* **1971**, 2341.
(234) Tomita, K.; Caires, A. C.; DeLucca, N.; Vincente, A.; Mauro, A. E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, *C50*, 1872.
(235) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201.
(236) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700.
(237) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485.
(238) Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 11504.
(239) Weissmann, H.; Milstein, D. *Chem. Commun.* **1999**, 1901.
(240) Beller, M.; Fisher, H.; Herrmann, W. A.; Öfele, K.; Bromssmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1847.
(241) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599.
(242) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994.
(243) Maguire, J. A.; Petrillo, A.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 9492.
(244) Gérard, H.; Eisenstein, O.; Lee, D.-H.; Chen, J.; Crabtree, R. H. *New. J. Chem.* **2001**, 1121.
(245) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788.
(246) Braustein, P.; Chauvin, Y.; Nahring, J.; DeCian, A.; Fisher, J.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1996**, *15*, 1532.
(247) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738.
(248) Reetz, M. T.; Haderlein, G.; Angermund, K. *J. Am. Chem. Soc.* **2000**, *122*, 996.
(249) Belli, J.; Jensen, C. M. *Organometallics* **1996**, *15*, 1532.
(250) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649.
(251) Howk, B. W.; Little, E. L.; Scott, S. L.; Whitman, G. M. *J. Am. Chem. Soc.* **1954**, *76*, 1899.
(252) Pez, G. P.; Galle, J. E. *Pure Appl. Chem.* **1985**, *76*, 1899.
(253) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770.
(254) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *Organic Lett.* **2001**, *3*, 3091.
(255) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.
(256) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716.
(257) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.
(258) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z.-I. *J. Am. Chem. Soc.* **1988**, *110*, 3994.
(259) Fukuda, Y.; Utimoto, K.; Nozaki, H. *Heterocycles* **1987**, *25*, 297.
(260) Brunet, J.-J.; Neibecker, D.; Philippot, K. *Tetrahedron Lett.* **1993**, *34*, 3877.
(261) Furlani, A.; Napoletano, C.; Russo, M. V. *J. Polym. Sci. A* **1989**, *27*, 75.
(262) Tang, B. Z.; Poon, W. H.; Leung, S. M.; Leung, W. H.; Peng, H. *Macromolecules* **1997**, *30*, 2209.
(263) Katayama, H.; Yamamura, K.; Miyaki, Y.; Ozawa, F. *Organometallics* **1997**, *16*, 4497.
(264) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, R.; Noyori, J. *J. Am. Chem. Soc.* **1999**, *121*, 12035.
(265) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92.
(266) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016.
(267) Fujimura, T.; Aoki, S.; Nakamura, E. *J. Org. Chem.* **1991**, *56*, 2809.
(268) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780.
(269) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771.
(270) Murakami, M.; Takahashi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9307.
(271) Murkami, M.; Ito, Y. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer-Verlag: Berlin, Heidelberg, 1999; Vol. 3.
(272) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
(273) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.
(274) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 1763.
(275) Shvo, Y.; Abed, M.; Blum, Y.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1986**, 267.
(276) Shvo, Y.; Laine, R. M. *Chem. Commun.* **1980**, 753.
(277) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.
(278) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.
(279) Heinekey, D. M.; Oldham, J., W. J. *Chem. Rev.* **1993**, *93*, 913.
(280) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577.
(281) Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632.
(282) Coalter, J. N., III.; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569.
(283) Yoshida, T.; Okana, T.; Thorn, D. L.; Tulip, T. H.; Osuka, S.; Ibers, J. A. *J. Organomet. Chem* **1979**, *181*, 183.

(284) Leigh, G. *Acc. Chem. Res.* **1992**, *25*, 177.
(285) Allen, A. D.; Bottomley, F. *Acc. Chem. Res.* **1968**, *1*, 360.
(286) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.
(287) Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828.
(288) van Gaal, H. L. M.; Moers, F. G.; Steggerda, J. J. *J. Organomet. Chem* **1974**, *65*, C43.
(289) Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; Dubois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.
(290) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.
(291) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.
(292) van der Ent, A.; Onderderlinden, L. *Inorg. Chim. Acta* **1973**, *7*, 203.
(293) de Buin, B.; Peters, T. P. J.; Thewissen, S.; Blok, A. N. J.; Willing, J. B. M.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2135.
(294) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394.
(295) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.
(296) Dorta, R.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2002**, *124*, 188.
(297) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **2002**, *124*, 11456.
(298) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 141.
(299) Dorta, R.; Togni, A. *Organometallics* **1998**, *17*, 3423.
(300) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875.
(301) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387.
(302) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem Soc., Dalton Trans.* **1976**, 1853.
(303) Tani, K.; Iseki, A.; Yamagata, T. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3381.
(304) Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. G. *Inorg. Chim. Acta* **1997**, *259*, 5.
(305) Rep, M.; Kaagman, J.-W. F.; Elsevier, C. J.; Sedmera, P.; Hiller, J.; Thewalt, U.; Horacek, M.; Mach, K. *J. Organomet. Chem* **2000**, *597*, 146.
(306) Ohff, A.; Zipperl, P.; Arndt, O.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 1649.
(307) Zimniak, A.; Bakalarski, G. *J. Mol. Struct.* **2001**, *597*, 211.
(308) Kiplinger, J. L.; Morris, D. E.; L., S. B.; Burns, C. J. *Organometallics* **2002**, *21*, 3073.
(309) Zipperl, T.; Arndt, P.; Ohff, A.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 4429.
(310) Fryzuk, M. D.; MacNeil, O. *Organometallics* **1983**, *2*, 682.
(311) Immirzi, A.; Musco, A.; Carturan, G.; Belluco, U. *Inorg. Chim. Acta* **1975**, *12*, L23.
(312) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138.
(313) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.
(314) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodrîquez, L. *Organometallics* **1996**, *15*, 3670.
(315) Harris, M. C. J.; Hill, A. F. *J. Organomet. Chem.* **1992**, *438*, 209.
(316) Tomaszewksi, R.; Hyla-Kryspin, I.; Mayne, C. L.; Arif, A. M.; Gleiter, R.; Ernst, R. *J. Am. Chem. Soc.* **1998**, *120*, 2959.
(317) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokurna, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105.
(318) Stegmann, R.; Frenking, G. *Organometallics* **1998**, *17*, 2089.
(319) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831.
(320) Borowski, A.; Donnadieu, B.; Daran, J. C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 1697.
(321) Borowski, A. F.; Donnadieu, B.; Daran, J. C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 543.
(322) Smith, K. T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473.
(323) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314.
(324) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800.
(325) Amouri, H.; Vaissermann, J.; Rager, M. N.; Grotjahn, D. B. *Organometallics* **2000**, *19*, 1740.
(326) Amouri, H.; Besace, Y.; Le Bras, J.; Vaissermann, J. *J. Am. Chem. Soc.* **1998**, *120*, 6171.
(327) Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 6581.
(328) Rabin, O.; Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 7119.
(329) Rabin, O.; Vigalok, A.; Milstein, D. *Chem. Eur. J.* **2000**, *6*, 454.
(330) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 3.
(331) Huck, W. T. S.; Snellink-Ruël, B.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Organometallics* **1997**, *16*, 4287.
(332) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.
(333) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
(334) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305.
(335) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 421.
(336) Taylor, R. *Electrophilic Aromatic Substitution*; John Wiley & Sons: New York, 1990.
(337) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* **1986**, *5*, 168.
(338) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.
(339) Crabtree, R. H.; Hamilton, D. G. *Organomet. Chem.* **1998**, *28*, 299.
(340) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1998**, *36*, 1.
(341) Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406.
(342) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180.
(343) Weissman, H.; Song, X.-P.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 337.
(344) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826.
(345) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437.
(346) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090.
(347) Renkema, K. B.; Bosque, R.; Streib, W. E.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1999**, *121*, 10895.
(348) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.
(349) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371.
(350) Herrmann, W. A.; Cornils, B. *Angew. Chem. Int. Ed.* **1997**, *35*, 22615.
(351) Burdeniuc, J.; Jedlicak, B.; Crabtree, R. H. *Chem. Ber./Recueil* **1997**, *130*, 145.
(352) Bonanno, J. B.; Henry, T. P.; Neithamer, D. R.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1996**, *118*, 5132.
(353) Yamamoto, A. *Adv. Organomet. Chem.* **1992**, *34*, 111.
(354) van der Boom, M. E.; Ben-David, Y.; Milstein, D., unpublished observations.
(355) Aizenberg, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1994**, 411.
(356) *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press: Boca Raton, FL, 2002−2003.
(357) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.
(358) Lavin, M.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 99.
(359) Perera, S. D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1995**, 3861.
(360) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santasiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
(361) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222.
(362) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.
(363) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227.
(364) Khumtaveeporn, K.; Alper, H. *Acc. Chem. Res.* **1995**, *28*, 414.
(365) Aye, K.-T.; Colpitts, D.; Ferguson, G.; Puddephatt, R. *Organometallics* **1988**, *7*, 1454.
(366) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Am. Chem. Soc.* **1990**, *112*, 6411.
(367) Chaudret, B. *Bull. Soc. Chim. Fr.* **1995**, *132*, 268.
(368) Poignant, G.; Nlate, S.; Guerchais, V.; Edwards, A. J.; Raithby, P. R. *Organometallics* **1997**, *16*, 124.
(369) Dunbar, K. R.; Haefner, S. C.; Uzelmeier, C. E.; Howard, A. *Inorg. Chim. Acta* **1995**, *240*, 524.
(370) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.
(371) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.
(372) VanCheesan, S.; Kuriacose, J. C. *J. Sci. Ind. Res.* **1983**, *42*, 132.
(373) Sun, J.-S.; Uzelmeier, C. E.; Ward, D. L.; Dunbar, K. R. *Polyhedron* **1998**, *17*, 2049.
(374) Gordon, A. J.; Ford, A. *The Chemist's Companion*; Wiley: New York, 1972.
(375) Caldwell, T. E.; Abdelrehim, I. M.; Land, D. P. *J. Am. Chem. Soc.* **1996**, *118*, 907.
(376) Rybtchinski, B.; Konstantinovsky, L.; Shimon, L. J. W.; Vigalok, A.; Milstein, D. *Chem. Eur. J.* **2000**, *17*, 3287.

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