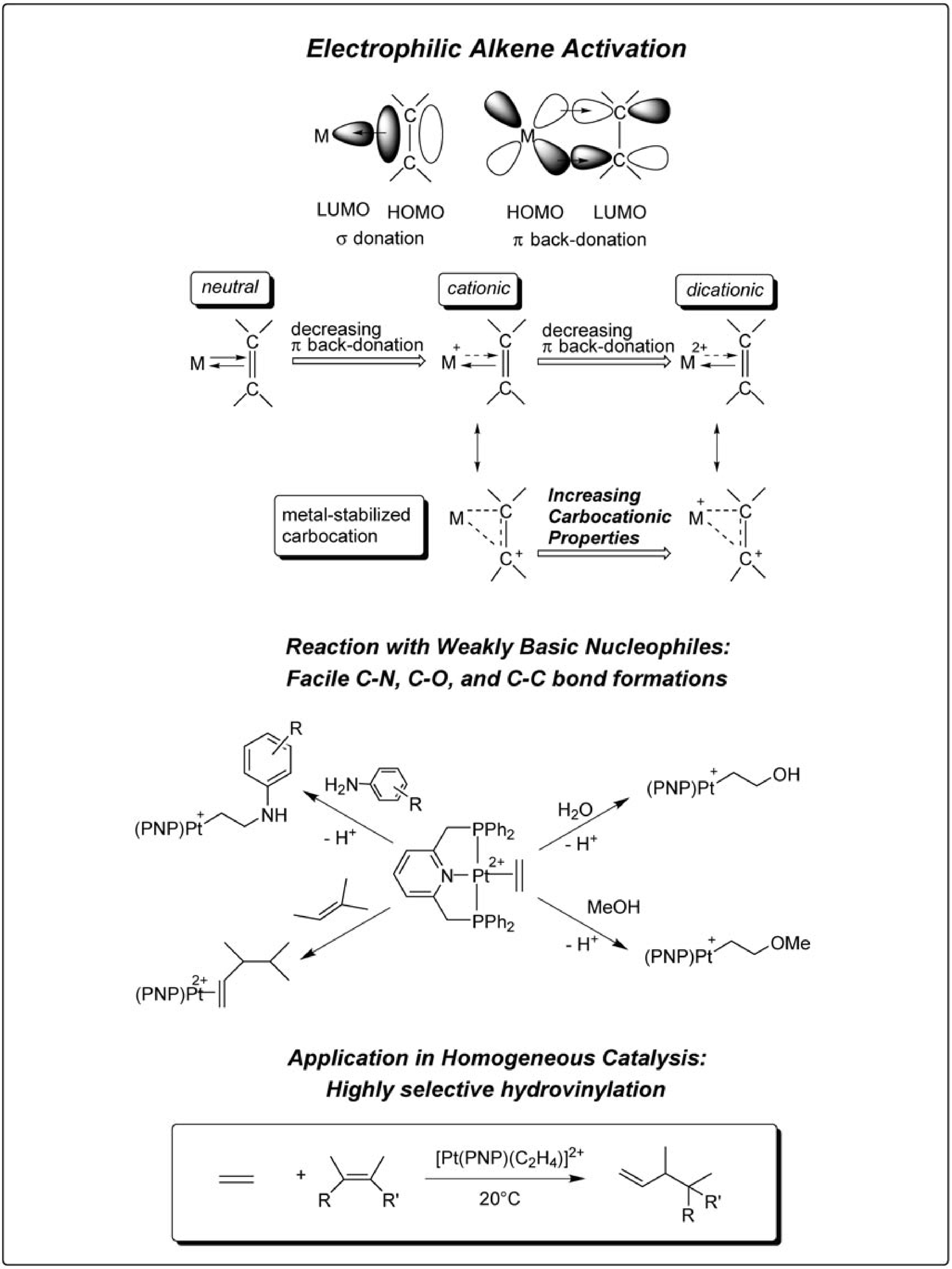

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Enhancing Electrophilic Alkene Activation by Increasing the Positive Net Charge in Transition-Metal Complexes and Application in Homogeneous Catalysis

Christine Hahn*[a]

Abstract: Among a large variety of fine-tuning parameters for homogeneous catalysts the net charge of transition-metal complexes appear to be an interesting factor that considerably affects activation of substrates and catalytic activity in general. The electrophilicity of coordinated alkenes in transition-metal complexes can be strongly enhanced by increasing the positive net charge, resulting in strong carbocationic properties. Theoretical and experimental studies have shown that the alkene in cationic complexes is kinetically and thermodynamically more activated towards nucleophilic addition than in neutral complexes. The concept of increasing the positive complex charge is thought to be useful for the development of new catalysts for reactions in which alkenes or other unsaturated substrates are involved.

Keywords: alkene activation • carbocations • chelating ligands • homogeneous catalysis • transition metals

Introduction

The development of new types of catalysts for organic reactions is a very important field of chemical research, because of the increasing demand for rational organic synthesis under mild conditions, high yields in space and time, and high selectivity; in particular, the economic and environmental benign performance of the catalyst is one of the main goals of green chemistry. Different approaches are being undertaken to find highly efficient catalysts, in particular for new reaction types and organic transformations,[1] for example, in order to shorten multiple step reaction sequences. A common approach in homogeneous catalysis is the creation of new ligand structures[2] in combination with an appropriate transition-metal center. Furthermore suitable activators, additives, and the reaction medium are also important factors that may affect catalytic activities. In any case fine tuning of electronic and steric properties of catalyst complexes, detailed understanding of their structure–reactivity relationship, and principles of substrate activation are key issues for the improvement of catalytic efficiency for a given reaction.

Among the large variety of possible fine-tuning parameters the charge of the complex appears an interesting aspect that has yet to be elucidated in detail. In this paper the concept of enhancement of the electrophilic alkene activation by increasing the positive net charge in transition-metal complexes is described. A case study of dicationic palladium(II)[3] and platinum(II)[4] alkene complexes and their reactivity towards weakly basic nucleophiles will be discussed. A new catalytic pathway for C–C bond formation, which has arisen from those reactivity studies,[5] exhibits a nice example for the benefit of this concept for the development of new homogeneous catalysts.

Enhancing Catalytic Activity by Increasing the Positive Net Charge in Transition-Metal Complexes

Cationic complexes of transition metals in higher oxidation states (+1, +2, or higher) of type **I** [Eq. (1)] display electrophilic properties and can be generated by substitution of an anionic ligand by a neutral one. A common method is halide abstraction by an appropriate reagent (e.g., AgY or Me_3SiY) that provides at the same time a non- (or weakly) coordinating counterion Y^-.[6]

$$[MLX] + L' + AgY \rightarrow [MLL']^+Y^- \ (\mathbf{I}) + AgX \qquad (1)$$

Due to the charge separation, the electronic properties, such as orbital energies and the distribution of electronic density, can be significantly changed. By increasing the positive charge of the complex, the electrophilicity (Lewis acidi-

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[a] Dr. C. Hahn
Friedrich-Alexander Universität Erlangen-Nürnberg
Institut für Organische Chemie, Henkestr. 42
91054 Erlangen (Germany)
Fax: (+49) 9131-85-22960
E-mail: christine.hahn@chemie.uni-erlangen.de

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ty) of the metal center is expected to be enhanced. This considerably affects the activation of substrates and, hence, lowers the activation barriers of further transformation steps; overall it may affect the whole energy profile of a catalytic reaction path.

In fact it has been found for several types of reactions that the catalytic activity is enhanced on going from neutral to cationic catalyst complexes; some representative examples are given in Table 1. For the hydrogenation of unsaturated compounds cationic rhodium(I)[7] and iridium(I)[8] complexes $[ML_2S_2]X$ (L_2 = phosphane; S = CH_3OH, cod; X = BF_4, PF_6) show an activity by about two orders of magnitude higher than that of neutral complexes $[MCl(PPh_3)_3]$.

Table 1. Enhanced catalytic activity by cationic catalyst complexes.

Reaction type	Neutral catalyst	Cationic catalyst complex	Factor of enhancement	Ref.
alkene hydrogenation	$[RhCl(PPh_3)_3]$	$[RhL_2(CH_3OH)_2]BF_4$		[7]
		$L_2 = Ph_2P(CH_2)_2PPh_2$	2×10^1	
		$L_2 = Ph_2P(CH_2)_4PPh_2$	1×10^2	
	$[IrCl(PPh_3)_3]$	$[Ir(cod)(PMePh_2)_2]PF_6$	1×10^2	[8]
alkene metathesis	$[Ru(=CHMe)Cl_2(L_2)]$	$[\{Ru(=CHMe)Cl(L_2)\}_2](SO_2CF_3)_2$	1.4×10^2	[9]
	$L_2 = t\mathrm{Bu}_2PCH_2Pt\mathrm{Bu}_2$	$L_2 = t\mathrm{Bu}_2PCH_2Pt\mathrm{Bu}_2$		
1,3-butadiene polymerization	$[\{Ni(C_3H_5)Cl\}_2]$	$[Ni(C_{12}H_{19})]Y$	1.2×10^5	[11]
		Y = PF_6, SbF_6, $B(C_6H_3(CF_3)_2)_4$		

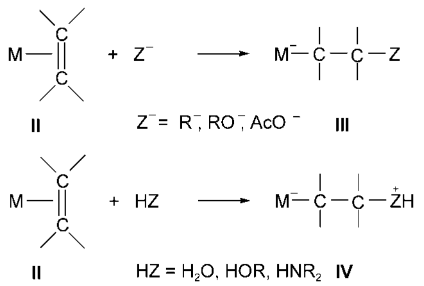
A similar effect was reported by Hofmann,[9] for the ruthenium-catalyzed alkene metathesis. A cationic ruthenium–carbene complex was generated by halide abstraction from the corresponding neutral complex. The turnover frequency of the ring-opening metathetic polymerization (ROMP) of norbonene showed a considerable increase from 60 h^{-1} for the neutral to 8400 h^{-1} for the cationic complex (cf. Table 1).

Furthermore it was found, that cationic complexes of late transition metals of the general formula $[M(NN)(CH_3)L]BArF$ (M = Pd, Ni; NN = α-diimine, BArF = $[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$) are highly active alkene polymerization catalysts, since they provide electrophilic metal centers that allow a rapid alkene insertion.[10] Notable are, for instance, nickel(II) allyl complexes as catalysts for polymerization of 1,3-butadiene; these display a remarkably higher activity when they are cationic, see Table 1.[11]

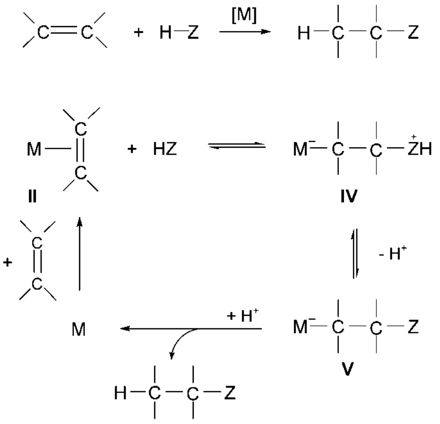
Structural modifications of the ligands of course also affect very sensitively the catalytic activity, for instance the variation of the chelate ring size,[7,12,13] but in general a tendency of enhanced catalytic activity by increased positive complex charge can be noted for several reactions in which alkenes as substrates are involved.

Nucleophilic Addition to Alkenes Coordinated in Transition-Metal Complexes

The nucleophilic addition to alkene transition-metal complexes **II** is an important organometallic reaction type, from which a number of possibilities arises for functionalization of hydrocarbons, see Scheme 1.[14] The stoichiometric addition of anionic and strongly basic nucleophiles like R^-, RO^-, AcO^-, or aliphatic amines to the coordinated C=C double bond is well known and understood in mechanistic details, whereas less basic neutral nucleophiles are less well studied. The addition of protic nucleophiles HZ (e.g., HOR, HNR_2) is of particular interest, because C–Z bond formation exhibits an important step in the general mechanism which may be proposed for catalytic hydrofunctionalization of alkenes, as shown in Scheme 2.[15] This is a highly valuable reaction type due to its 100 % atom economy.

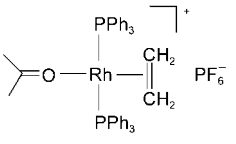


Scheme 1. The addition of nucleophiles to alkene complexes.



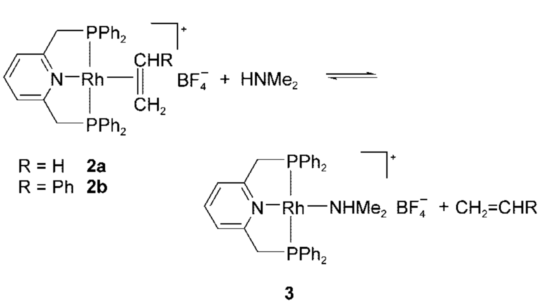
Scheme 2. Proposed mechanism for the hydrofunctionalization of alkenes.[19]

This general mechanism in Scheme 2 was originally proposed for the rhodium(I)-catalyzed hydroamination of alkenes;[16] it is also assumed that palladium(II)[17] and platinum(II)[18] complexes catalyze the reaction according to this pathway by alkene activation.[19] The cationic rhodium(I)–ethylene complex **1** was the first catalyst for the addition of aliphatic amines to ethylene, at room temperature and at-



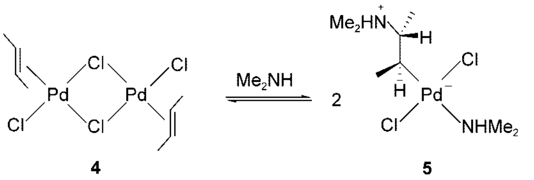
1

mospheric pressure.[20] The neutral Rh^I complex $[\{Rh(C_2H_4)_2Cl\}_2]$ used by Coulson catalyzed the same reaction, but only at elevated temperatures (180 °C).[21] The model complexes **2a**,**b**[22] were prepared in order to trace the proposed mechanism, but no indication for nucleophilic addition of secondary amines to the coordinated alkene was noted under ambient conditions, see Equation (2).



(2)

Alkene complexes of palladium(II)[23] and platinum(II)[24] are known to be very susceptible for addition of amines and other nucleophiles; this has been widely investigated by several research groups,[25,26,27] see Equations (3) and (4).



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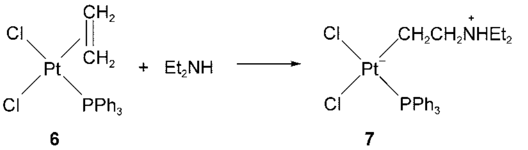
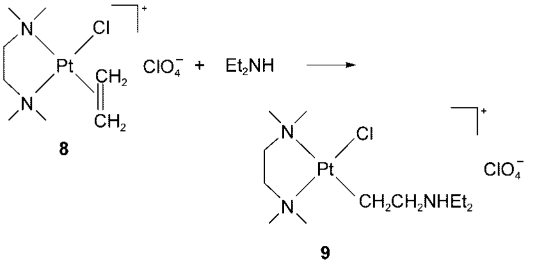


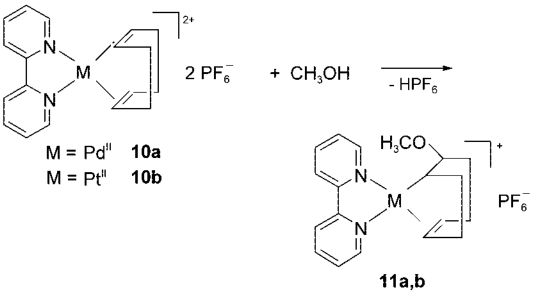
(4)

An important fact which has been revealed experimentally by Natile and co-workers is that cationic platinum(II) alkene complexes [e.g. **8**, Eq. (5)] undergo nucleophilic addition more readily in comparison to anionic or neutral complexes, and the addition products (such as **9**) display a higher stability.[28,29] A simple explanation is that neutral alkene complexes form anionic or zwitterionic addition products **III** and **IV** (cf. Scheme 1, or **5** and **7**) in which the M–C σ bond can not be stabilized due to the formal negative charge remaining at the metal center. In anionic complexes this would destabilize the product even more. On the other hand it is reasonable to expect that the higher the positive charge on the complex the higher the stability of the σ-alkyl complex.



(5)

While a number of monocationic palladium(II)[30] and platinum(II)[31] alkene complexes are known, there are only very few examples of dicationic alkene complexes of Pd^{II} and Pt^{II} described for which the effect of enhanced reactivity was investigated experimentally. Pietropaolo et al. reported that dicationic cyclooctadiene complexes **10a**,**b** added methanol at the C=C double bond even in the absence of any auxiliary base, see Equation (6).[32]



(6)

Not only is the thermodynamic stability of the addition product influenced by the complex charge, also the activation barrier of the nucleophilic attack is strongly affected. Sakaki et al. investigated the nucleophilic attack of ammonia to ethylene Pd^{II} complexes by ab initio MO calculations, see Figure 1.[33] While for the anionic and neutral complexes **12** and **13** no transition state could be identified (in terms of strong destabilization of these systems), the calculations for the cationic complexes **14** and **15** came to a relatively low activation barrier of around 30 kJ mol^{-1}.

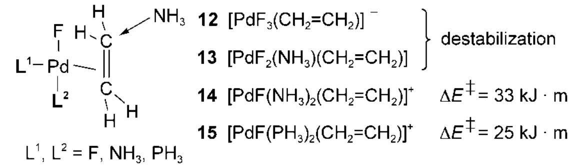
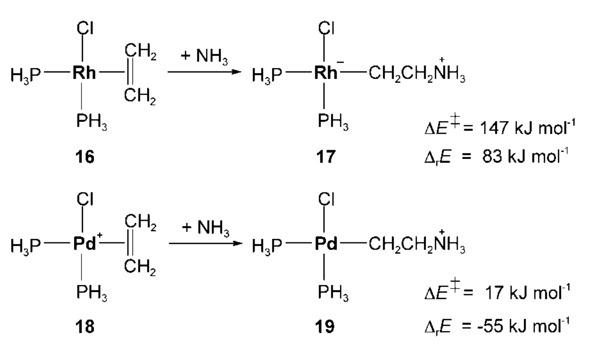


Figure 1. Results from theoretical studies on the nucleophilic attack.[33]

Further theoretical studies by Senn et al. on the catalytic reaction mechanism of the hydroamination of ethylene with Group 9 and 10 d^8 metals have shown quite similar trends, see Scheme 3.[34] Going, for example, from the neutral rho-



Scheme 3. Results from a part of the theoretical studies on the mechanism of alkene hydroamination.[34]

dium(I) complex **16** to the isostructural and isoelectronic cationic palladium(II) complex **18** (i.e., the increase of the nuclear charge of the central metal atom by one unit) the activation energy $\Delta E^{\neq}$ for the nucleophilic addition drops significantly from 147 to 17 kJ mol^{-1}.

The Dewar–Chatt–Duncanson Model of the Metal–Alkene Bond

The Dewar–Chatt–Duncanson model[35,36] provides a general description for the metal–alkene bond and reasonably explains the principle of the electrophilic alkene activation. The strength of σ donation and π back-donation depends on the specific σ-acidic and π-basic properties of the transition-metal atom M. Considering the complex charge as a variable parameter for a constant metal center M, the electronic properties of the coordinated alkene should, in principle, be tunable between two extreme cases as shown in Figure 2.

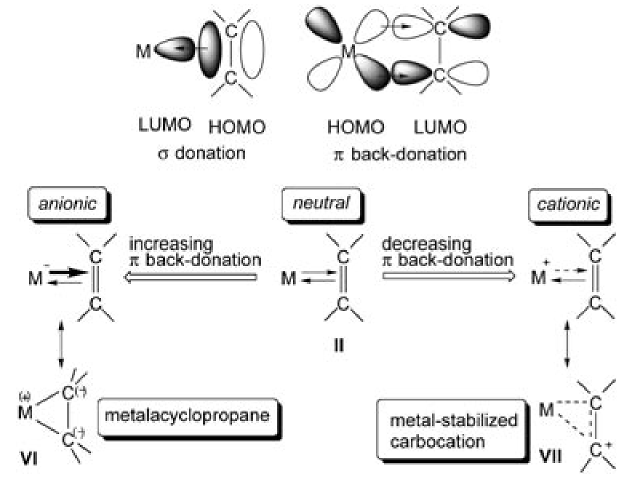


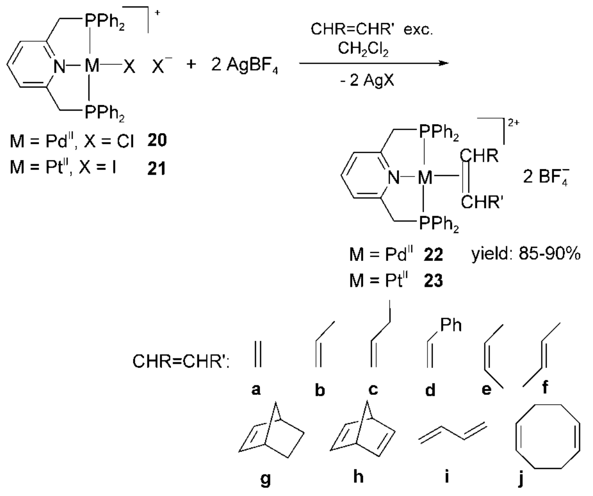
Figure 2. The Dewar–Chatt–Duncanson model[35,36] and considerations on complex charge.

In the case of a highly negative net charge the extreme of metallacyclopropane **VI** could be approached. Due to the relatively high electronic density at the metal center the π back-donation is so strong that the double-bond character of the coordinated alkene is considerably reduced, and the alkene undergoes formal oxidative addition to the metal center. On the other hand by increasing the positive charge of the metal complex the π back-donation can be strongly decreased, and thus the coordinated alkene becomes more electrophilic and enhanced in its reactivity toward donor molecules. In this extreme case the coordinated alkene can be seen as a metal-stabilized carbocation[37] (**VII**) by slipping from an η^2 to η^1 coordination mode (especially when a nucleophile approaches).[38] The fractional charge at the carbocation would increase with increasing positive charge at the metal center. It should be noted, that the "slipping" of the coordinated alkene should be seen as a dynamic process by which the carbocationic property is more or less averaged on both olefinic carbon atoms, depending essentially on further substituents at the alkene (see discussion below).

In fact carbocationic reactivity has been proposed to be involved for reactions like enyne, diene cyclization, skeleton rearrangements,[39] and alkene oligomerization/polymerization[40,41,42] catalyzed by cationic transition-metal complexes. However, highly positively charged alkene complexes are very unstable. Due to the strongly reduced π back-donation the metal–alkene bond is correspondingly weakened, and their isolation or detection is very difficult and only possible in a narrow range of conditions. Chelating ligands play an important role in stabilization of the coordination sphere of the highly electrophilic metal center, as for instance in the case of the dicationic cyclooctadiene Pd^{II} and Pt^{II} complexes **10 a**,**b**[32] [Eq. (6)].

Synthesis and Characterization of New Dicationic Monoalkene Complexes of Palladium(II) and Platinum(II)

The synthesis of dicationic monoalkene complexes of palladium(II) and platinum(II) was recently successful with the use of 2,6-bis(diphenylphosphanylmethyl)pyridine (PNP) as a stabilizing tridentate co-ligand.[3,4] Halide abstraction from [M(PNP)X]X (**20**, **21**: M = Pd, Pt; X = Cl, I) with two equivalents of $AgBF_4$ in the presence of an excess of the alkene gave the respective alkene complexes **22** and **23** in high yields, see Scheme 4. They are stable enough as solids and in solution, and could be characterized by NMR spectroscopy and X-ray crystal structure analysis. These complexes are the first examples of dicationic monoalkene complexes that have been isolated.



Scheme 4.

The ^{13}C NMR shift is a useful parameter for the characterization of the metal–alkene bond.[43] Upon coordination of an alkene to a transition metal a certain upfield shift Δδ of the ^{13}C NMR signal, relative to that of the free alkene, is generally observed. The extent of the upfield shift gives an estimate of the electronic density around the olefinic carbon nuclei. The chemical shifts of the coordinated ethylene in isostructural PNP complexes **2a**, **22a**, and **23a** are depicted in Figure 3. The signal of the coordinated ethylene is shifted upfield to much lesser extent for the dicationic Pd^{II} and Pt^{II} complexes **22a** and **23a**[3,4] ($\Delta\delta = -34$ and -45 ppm) relative to that of the monocationic Rh^{I} complex **2a**[22] ($\Delta\delta = -64$ ppm). This is consistent with the reduced electronic density due to the weaker π back-donation.

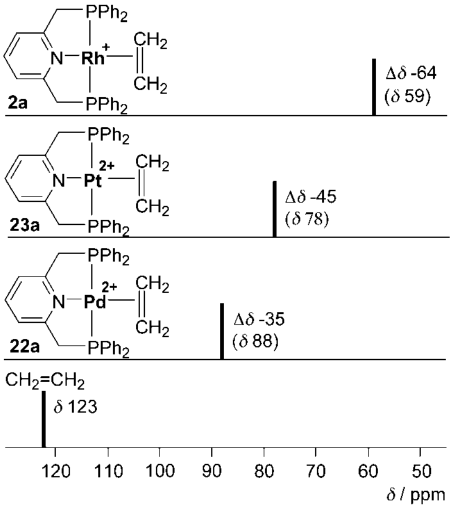


Figure 3. ^{13}C NMR shift of the coordinated ethylene in **2a**, **22a**, and **23a**, $\Delta\delta = \delta_{coord} - \delta_{free}$.

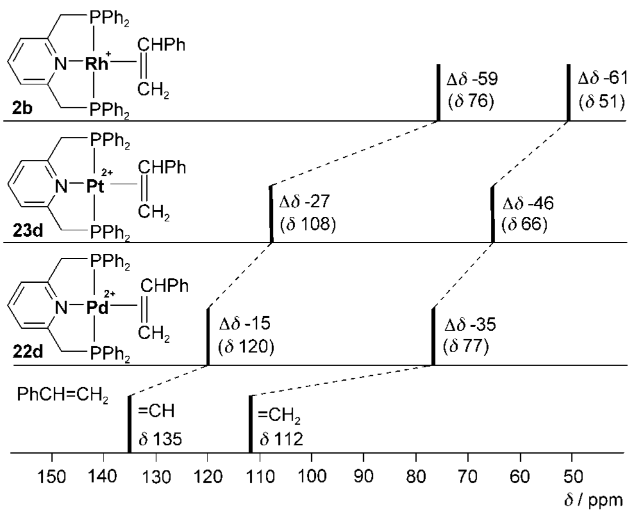


Figure 4. ^{13}C NMR shift of the coordinated styrene in **2b**, **22d**, and **23d**, $\Delta\delta = \delta_{coord} - \delta_{free}$.

The influence of the increasing positive charge of the complex on the coordination of monosubstituted alkenes $CH_2{=}CHR$ is particularly notable. In Figure 4 the ^{13}C NMR data of isostructural styrene complexes are compared. While in the monocationic Rh^{I} complex **2b**[22] for both olefinic carbon atoms (=*C*H$_2$ and =*C*HPh) roughly the same Δδ is observed ($\Delta\Delta\delta \approx 2$ ppm), in the dicationic complexes **22d** and **23d** a significant difference of the upfield shifts ($\Delta\Delta\delta \approx 20$ ppm) can be noted. It is assumed that with lower degree of the π back-donation the difference $\Delta\Delta\delta = \Delta\delta(CH_2) - \Delta\delta(CHR)$ increases[43] indicating a higher polarization of the C=C double bond. Since in the dicationic complexes the signal for the =*C*HR carbon atom is shifted much less upfield than that for the =*C*H$_2$, the lower electronic density can be supposed to be at the substituted carbon atom. Or in other words the fractional positive charge, that is, the incipient carbocation, seems to be localized more at the substituted olefinic carbon atom, which is therefore supposed to be preferably attacked by the nucleophile.

This polarization effect on the C=C double bond in the dicationic complexes can be also explained by the different strength of interaction of the two carbon atoms =*C*H$_2$ and =*C*HR with the central metal atom. While the two coupling constants $J_{C\text{-}Rh}$ in the monocationic rhodium(I) styrene complex **2b** are rather similar (cf. Table 2), for the isostructural dicationic platinum(II) complex **23d** $J_{C\text{-}Pt}(CHPh)$ is significantly smaller than $J_{C\text{-}Pt}(CH_2)$. The lower value of $J_{C\text{-}Pt}(CHR)$ relative to $J_{C\text{-}Pt}(CH_2)$, also observed for other alkene complexes $[Pt(PNP)(CH_2{=}CHR)][BF_4]_2$ (**23b**,**c**: R = Me, Et),[4] indicates a reduced interaction for Pt–*C*HR than Pt–*C*H$_2$.

In addition, the C–C bond length of the coordinated alkene is thought to be diagnostic for the strength of the M–alkene bond. It has been widely discussed particularly for those alkene complexes in which the double-bond character is weakened due to the relatively strong π back-donation. In these cases the C–C distance is somehow lengthened relative to the free alkene,[44] and the structures tend more or less to the metallacyclopropane type. For the extreme opposite structural type, that is, the masked carbocation, the dicationic Pt^{II}–ethylene and Pd^{II}–styrene complexes **23a** and **22d**, respectively, are so far precedents which could be characterized by X-ray crystal structure

Table 2. Selected ^{13}C NMR, X-ray, and Raman data of the coordinated alkene in PNP complexes.[3,4,22,45,47]

$[M(PNP)(CH_2{=}CHR)][BF_4]_n$		$J_{C\text{-}M}(CH_2)$ [Hz]	$J_{C\text{-}M}(CHR)$ [Hz]	M-CH$_2$ [Å]	M-CHR [Å]	C=C [Å]	Raman ν(C=C) [cm^{-1}]
$[Rh(PNP)(CH_2{=}CH_2)]BF_4$	**2a**	–	–	2.142(6)	2.157(6)	1.351(11)	1514
$[Rh(PNP)(CH_2{=}CHPh)]BF_4$	**2b**	12.2	11.4	2.144(5)	2.201(4)	1.383(7)	1516
$[Pd(PNP)(CH_2{=}CH_2)][BF_4]_2$	**22a**						1530
$[Pd(PNP)(CH_2{=}CHPh)][BF_4]_2$	**22d**			2.165(7)	2.273(7)	1.292(10)	1528
$[Pt(PNP)(CH_2{=}CH_2)][BF_4]_2$	**23a**	116		2.180(6)	2.181(8)	1.359(10)	
$[Pt(PNP)(CH_2{=}CHMe)][BF_4]_2$	**23b**	138	108				
$[Pt(PNP)(CH_2{=}CHEt)][BF_4]_2$	**23c**	131	113				
$[Pt(PNP)(CH_2{=}CHPh)][BF_4]_2$	**23d**	137	81				

analysis.[4,45] In the Pt^{II}–ethylene complex **23a**, however, no particular influence of the twofold positive charge on the C–C bond length could be noted; it is practically the same as that observed in the monocationic Rh^{I}–ethylene complex **2a**[22] (see Table 2) and also very similar to that in the anionic Zeise's salt $[PtCl_3(CH_2{=}CH_2)]^-$ (1.37 Å).[46] However, in the Pd^{II}–styrene complex **22d**[45] the C–C distance is significantly shorter than in the isostructrural Rh^{I} complex **2b**,[22] and is no longer than the C=C double bond in the free styrene. For palladium(II) a stronger influence of the increasing positive net charge is observed than for platinum(II).

Furthermore, comparing the different M–C distances in the styrene complexes **22d** and **2b**, the Pd–*C*HPh bond is 0.108 Å longer than the Pd–*C*H$_2$ bond, while in the Rh^{I} complex a much less pronounced prolongation by 0.057 Å is observed (see Table 2). The structural data of these complexes are quite in accordance with the $J_{\text{M-C}}$ coupling constants observed respectively for the Pt^{II}– and Rh^{I}–styrene complexes **23d** and **2b** (see above) and support the general picture of the incipient slipping of the alkene from η^2 to η^1 coordination mode (cf. **VIII** and **IX** in Figure 5). These considerations illustrate the overall enhancement of alkene activation in dicationic complexes, in which the structure of the transition state of the nucleophilic attack is approached (cf. Scheme 1, the overall transformation **II→III/IV** is $\eta^2 \rightarrow \eta^1$).

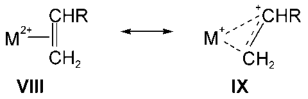
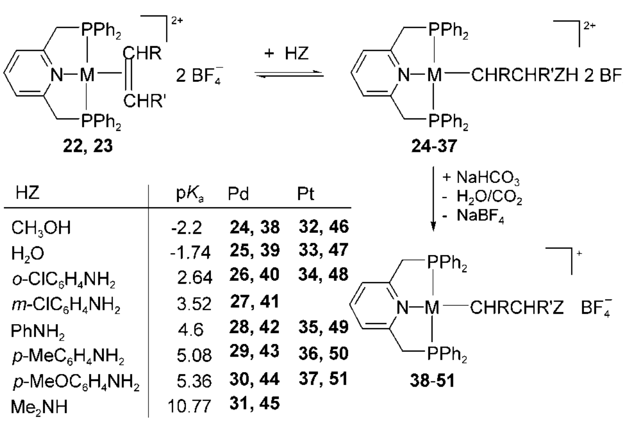


Figure 5. The incipient "slipping" from η^2 to η^1 coordination mode.

Micro Raman measurements of the ν(C=C) stretching frequencies were found to be higher for the Pd^{II} complexes **22a,d** than for the isostructural Rh^{I} complexes **2a,b**, providing further evidence for the overall weakening of the metal–alkene bond in the dicationic complexes in comparison with the monocationic alkene complexes.[47]

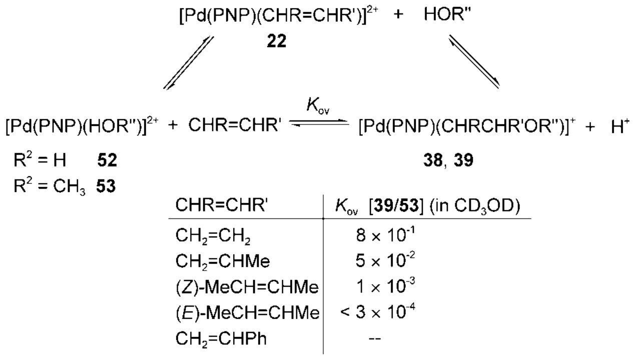
Reaction Studies of Dicationic Alkene Complexes of Palladium(II) and Platinum(II)



HZ	pK_a	Pd	Pt
CH_3OH	-2.2	**24, 38**	**32, 46**
H_2O	-1.74	**25, 39**	**33, 47**
o-$ClC_6H_4NH_2$	2.64	**26, 40**	**34, 48**
m-$ClC_6H_4NH_2$	3.52	**27, 41**	
$PhNH_2$	4.6	**28, 42**	**35, 49**
p-$MeC_6H_4NH_2$	5.08	**29, 43**	**36, 50**
p-$MeOC_6H_4NH_2$	5.36	**30, 44**	**37, 51**
Me_2NH	10.77	**31, 45**	

Scheme 5. Addition of different nucleophiles.

The reactions of the dicationic Pd^{II} and Pt^{II} complexes have been investigated toward different protic O and N donor nucleophiles as shown in Scheme 5.[3,4] It was found that addition of very weakly basic nucleophiles such as MeOH, H_2O, and aromatic amines (cf. pK_a (H_2Z^+), Scheme 5) proceed readily at room temperature. Proton abstraction from the intermediates $[M(PNP)(CHRCHR'ZH)]^{2+}$ **24–37** by $NaHCO_3$ as auxiliary base drove the equilibrium quantitatively to the β-functionalized alkyl complexes $[M(PNP)(CHRCHR'Z)]^+$ **38–51**, which are very stable compounds as solids and in solution. The unusually high stability of the Pd^{II}–σ-alkyl complexes **38–45** is remarkable; they are very resistant towards β-hydrogen elimination due to the strong stabilizing influence of the PNP chelate ligand, with the phenyl groups in the ligand periphery. Detailed ^{1}H NMR studies could be performed directly in solution to follow the nucleophilic addition and have been carried out for the first time for palladium(II) complexes. The palladium(II)–alkene complexes **22** reacted with an excess of H_2O or CH_3OH *without* any auxiliary base immediately under nucleophilic addition and partial alkene substitution (cf. formation of **38**, **39** vs **52**, **53** in Scheme 6). These two competitive reactions are fast and reversible; this was proven by a ^{1}H magnetization transfer experiment and by reverse reaction studies.[3] For the reaction of the dicationic palladium(II)–alkene complexes **22** with methanol (CD_3OD), overall equilibrium constants were determined which reflect the relative stabilities between the methanol complex and the deprotonated addition product [M(PNP)(CHRCHR'Z)]. A value $K_{\text{ov}} = 0.8$ was found for C_2H_4, and the overall equilibrium constants decrease for alkenes CHR=CHR' with larger substituents R/R'; this means the substitution becomes more competitive. In contrast the isostructural platinum(II) alkene complexes **23a–d** reacted immediately at room temperature with an excess of water or methanol resulting in complete nucleophilic addition. No substitution was observed, presumably due to the strong kinetic inhibition, and thus for the Pt^{II}–alkene complexes the nucleophilic addition is *kinetically* favored over the substitution [Eq. (7)]. In all cases exclusively Markovnikov addition products **46** and **47** were obtained as suggested by the ^{13}C NMR shifts of the coordinated alkene (see discussion above).



CHR=CHR'	K_{ov} **[39/53]** (in CD_3OD)
$CH_2{=}CH_2$	8×10^{-1}
$CH_2{=}CHMe$	5×10^{-2}
(*Z*)-MeCH=CHMe	1×10^{-3}
(*E*)-MeCH=CHMe	$< 3 \times 10^{-4}$
$CH_2{=}CHPh$	--

Scheme 6. Overall equilibrium system with O-donor nucleophiles.

$$\underset{\textbf{23a-d}}{[Pt(PNP)(CH_2{=}CHR)]^{2+}} + HOR' \rightleftharpoons \underset{\textbf{46, 47}\ (R'{=}H, Me)}{[Pt(PNP)(CH_2CHROR')]^{+}} + H^{+} \quad (7)$$

From these reaction studies a general reaction principle for alkene complexes and any protic nucleophile HZ can be derived. There are three reversible thermodynamic individual equilibria: 1) the substitution of the alkene by the nucleophile [Eq. (8)], which shows a strong kinetic inhibition in the case of $M = Pt^{II}$; 2) the nucleophilic addition [Eq. (9)]; and 3) the deprotonation equilibrium [Eq. (10)] has to be taken into consideration when there is more than one equivalent of the nucleophile HZ present in solution, since the nucleophile itself also works as a Brønsted base. The equilibria in Equations (9) and (10) are closely related and thought to be associated to the pK_a of the H_2Z^+. It is reasonable to expect that the deprotonated addition product $[(L)M(CHRCHR'Z)]^+$ in Equation (10) is favored due to enhanced Brønsted acidity of the highly positive charged complex.

$$[M(L)(ZH)]^{2+} + CHR{=}CHR' \xrightleftharpoons{K_{sub}} [M(L)(CHR{=}CHR')]^{2+} + ZH \quad (8)$$

$$[M(L)(CHR{=}CHR')]^{2+} + ZH \xrightleftharpoons{K_{add}} [M(L)(CHRCHR'ZH)]^{2+} \quad (9)$$

$$[M(L)(CHRCHR'ZH)]^{2+} + ZH \xrightleftharpoons{K_{dep}} [M(L)(CHRCHR'Z)]^{+} + ZH_2^{+} \quad (10)$$

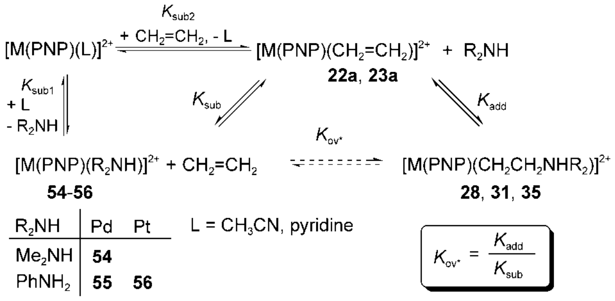
$$[M(L)(ZH)]^{2+} + CHR{=}CHR' + ZH \xrightleftharpoons{K_{ov}} [M(L)(CHRCHR'Z)]^{+} + ZH_2^{+} \quad (11)$$

The equilibria in Equations (8)–(10) consitiute a well-defined overall equilibrium [Eq. (11)], and a number of important conclusions can be drawn. Firstly, higher concentrations of both alkene *and* nucleophile shift the overall equilibrium to favor the addition product; that is, suppressing the alkene substitution [Eq. (8)] and promoting the nucleophilic addition [Eqs. (9) and (10)]. In addition the irreversible removal of the proton (e.g., by an auxiliary base) drives the reaction in Equation (11) to completion. Thus a new carbon–heteroatom bond (C–Z) can be formed in quantitative yield, providing a very interesting and attractive example for the functionalization of hydrocarbons.

Returning to the question of the degree of electrophilic alkene activation in dicationic complexes, the equilibrium constant of the nucleophilic addition K_{add} is sought as a parameter to give a direct correlation. In order to access a K_{add} value, the deprotonation equilibrium [Eq. (10)], needs to be strictly excluded. The equilibria in Equations (8) and (9) give the overall equilibrium in Equation (12), with the thermodynamic constant defined by $K_{ov*} = K_{add}/K_{sub}$ expressing the pure ratio of nucleophilic addition and substitution.

$$[M(PNP)(ZH)]^{2+} + CHR{=}CHR' \xrightleftharpoons{K_{ov}*} [M(PNP)(CHRCHR'ZH)]^{2+} \quad (12)$$

Since water and methanol are weakly basic nucleophiles, which did not afford detectable β-oxonioalkyl species $[M(PNP)(CHRCHR'OHR'')]^{2+}$ (**24**, **25**) in the presence of only one equivalent of HOR″, stronger basic nucleophiles HZ were sought. It was found that ^{1}H NMR investigations were feasible by using amines (see Scheme 7). The equilibrium reactions were started from the isolated amine complexes **54**–**56** (ensuring an exact nucleophile/metal ratio of 1:1) by treating it with an excess of alkene. Mechanistically, the reaction proceeds through the substitution of the amine by the alkene, resulting in the π-complexes **22** and **23**. The free amine then externally attacks the coordinated double bond, forming the β-ammonioalkyl complexes **28**, **31**, or **35** (Scheme 7). The equilibration of these system was fast for palladium (<1 h), while in the case of platinum the reaction was only observed when CH_3CN was added to accelerate the amine/alkene substitution; thus the equilibrium was achieved within 10 days. In addition, it should be noted that the alkene complex is the most reactive species in this system and hence it is not detectable. The K_{sub} value was determined independently by auxiliary substitution equilibria K_{sub1} and K_{sub2} by using CH_3CN or pyridine (see Scheme 7).



Scheme 7. Equilibrium studies for determination of K_{add}.

The overall equilibrium constant $K_{ov*} = 3\times10^4\,L\,mol^{-1}$ for the reaction of the dimethylamine complex **54** with ethylene was determined, and the substitution constant $K_{sub} = 6\times10^8$, the addition constant $K_{add} = 1.8\times10^{13}\,L\,mol^{-1}$ could be estimated. This shows that the nucleophilic addition of dimethylamine to the dicationic palladium(II) ethylene complex **22a** is a thermodynamically highly favored process. This is in large contrast to the isostructural monocationic rhodium(I) complex **2a**, for which only the alkene substitution was the observed under similar conditions [see Eq. (2)]. In the case the reaction of the palladium ethylene complex **22a** with the less basic aniline, the nucleophilic addition is still a highly favored reaction, $K_{add} = 2\times10^5\,L\,mol^{-1}$ (see Table 3), while the substitution becomes more competitive. Interestingly, it was found that ethylene in the platinum(II) complex **23a** is thermodynamically somehow more activated $K_{add} = 3\times10^6\,L\,mol^{-1}$ than in the palladium(II) complex **22a**, while at the same time the substitution is also thermodynamically less competitive (see above; Table 3).

Comparable equilibrium studies reported by Green et al. in 1979 on nucleophilic addition were performed with neutral platinum(II) alkene complexes such as

Table 3. Equilibrium constants for the reaction of ethylene complexes with H_2NPh (Scheme 7).

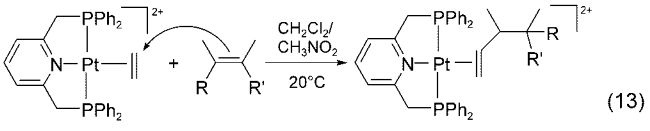
$[M(L_x)(CH_2{=}CH_2)]^{n+}$		K_{add} $[L\,mol^{-1}]$	K_{sub}	$K_{ov*} = K_{add}/K_{sub}$ $[mol^{-1}]$	Ref.
$[Pd(PNP)(CH_2{=}CH_2)]^{2+}$	**22a**	2×10^5	2×10^5	1	[3]
$[Pt(PNP)(CH_2{=}CH_2)]^{2+}$	**23a**	3×10^6	3×10^4	10^2	[4]
$[Pt(H_2NPh)(CH_2{=}CH_2)Cl_2]$		<0.1	–	–	[48]

$[Pt(H_2NPh)(CH_2{=}CH_2)(Cl_2)]$; the addition of aniline and other aromatic amines with $pK_a < 5$ was reported to be not detectable ($K_{add} < 0.1\,L\,mol^{-1}$, see Table 3).[48] Substitution of the alkene by the amine were noted with those Pt^{II} complexes to start after 30 min, and in the case of similar neutral palladium(II) alkene complexes *trans*-[Pd(amine)(alkene)(Cl_2)], the alkene substitution was found to be irreversible.[49]

In summary, considering the thermodynamic alkene activation in the dicationic complexes toward nucleophilic addition, it can be stated that a 2 unit increase in the positive charge of the complex results in an increase of the thermodynamic equilibrium constant K_{add} by a factor of at least 10^7. These experimental data are quite consistent with the calculated values of the reaction energies $\Delta_r E$, which correspond to the relative thermodynamic stabilities of the individual species,[34] see Scheme 3.

Discovery of a New Catalytic Pathway for Hydrovinylation

During the reaction studies it was discovered that internal alkenes, such as *Z*-2-butene, 2-methyl-2-butene or 2,3-dimethyl-2-butene, which are moderately electron-rich, even added to the platinum(II)–ethylene complex **23a** under C–C bond formation. Successive hydride and alkyl shifts gave isolable complexes of the corresponding heterodimers **57a–c** [Eq. (13)].[5] Notably, a similar reaction was reported by Rosenblum et al. in which the allylic ligand of $[Fe(Cp)(CO)_4(CH_2CH{=}CH_2)]$ added as a nucleophile to the coordinated ethylene in $[Fe(Cp)(CO)_4(CH_2{=}CH_2)]$.[50] However, other examples of a reaction between an alkene complex and a free alkene giving an isolable complex, to the author's knowledge, are not described to date.



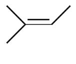
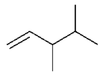
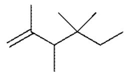
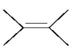
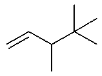
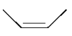
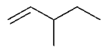
(13)

23a

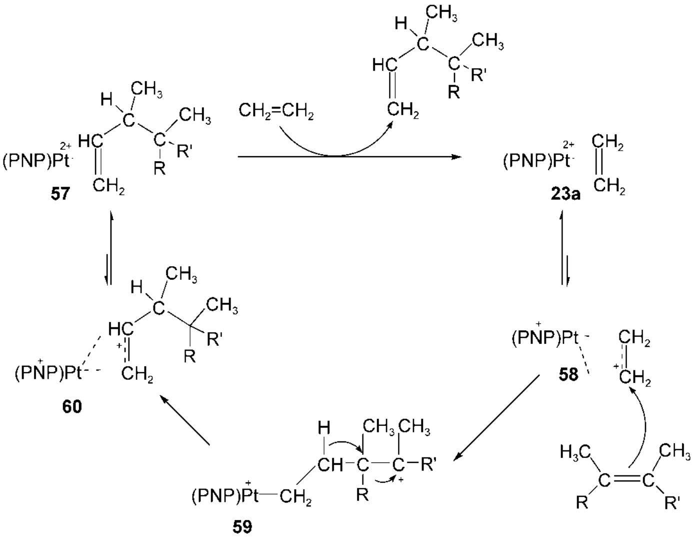
57a-c
(**a**) R = R' = H
(**b**) R = H, R' = Me
(**c**) R = R' = Me

Interestingly, complexes of higher substituted alkenes than ethylene, for example, propene or 1-butene did not react with the internal alkenes; these prevent side reactions such as oligomerization. Thus a highly selective catalytic process could be achieved simply by displacement of the coordinated heterodimeric product by free ethylene.[5] Under atmospheric pressure of ethylene at 20 °C and an excess of the internal alkene ([Pt]:[alkene] = 1:300; see Table 4), turnover numbers (TONs) of 170–200 (4 h) were observed for 2,3-dimethyl-2-butene and 2-methyl-2-butene. The reaction with *Z*-2-butene was found to be much slower with TON = 5 (24 h). In the case of 2-methyl-2-butene a homodimer was formed as the only by-product (see discussion below).

Table 4. Catalytic hydrovinylation of internal alkenes, [alkene]:[**23a**] = 300:1, $T = 20\,°C$, atmospheric pressure ethylene, in CH_3NO_2.[5]

Entry	Alkene	Product	Remarks
1			TON = 200(4 h)
			homodimer 10 %
2			TON = 170(4 h)
3			TON = 5(24 h)

The proposed mechanism for the Pt^{II}-catalyzed hydrovinylation is shown in Scheme 8. The "slipping" coordinated ethylene in **58** is nucleophilically attacked by the internal alkene forming the carbocationic intermediate **59**. Subsequent alkyl and hydride shift affords the generation of the terminal C=C double bond via the delocalized carbocationic intermediate **60**. The displacement of the heterodimer by free ethylene and regeneration of the ethylene complex **23a** is straightforward and thermodynamically favored ($K = 4 \pm 1$).



Scheme 8. Proposed mechanism for the Pt^{II}-catalyzed hydrovinylation.

When the reaction was performed with $CD_2{=}CD_2$, in all cases the product $CD_2{=}CD{-}CD(CH_3)C(CH_3)RR'$ contained one deuterium atom at the adjacent carbon atom to the vinyl group; this remained deuterated, supporting the proposed subsequent alkyl and hydride shift. The occurrence of homodimer can be also rationalized by a proton loss from the carbocationic intermediate **59**. This proton is able to catalyze the homodimerization; however, no other side reactions which carbocations could likely undergo were observed.[5]

The catalytic heterodimerization/hydrovinylation with nickel(II) catalyst precursors is a well-established reaction.[51,52] However, the general features differ considerably from those of the recently discovered Pt^{II}-catalyzed reaction, which are compared in Table 5. For the Ni^{II}-catalyzed reaction, a cationic nickel hydride species $[Ni(H)(L)]^+Y^-$ is proposed to be the catalytically active complex, which could not be directly detected. It is generated in situ by treatment of allylic Ni^{II} precursors with phosphane ligands and Lewis acidic co-activators. In contrast, the dicationic platinum(II)–ethylene complex **23a** was isolated as a stable compound, which is well characterized by NMR spectroscopy and X-ray structure analysis (see above); moreover, it is an intermediate of the catalytic cycle (see Scheme 8), that is, the metal–substrate complex. No activators or any pre-equilibria are necessary, hence the Pt^{II}–ethylene complex can be considered a single component catalyst.

The mechanism of the $[Ni(H)(L)]^+$-catalyzed reaction differs considerably from that of Pt^{II}. In the case of $[Ni(H)(L)]^+$ the cycle starts with insertion of one alkene (e.g. styrene) into the Ni–H bond followed by the insertion of the other alkene (e.g., ethylene) into the Ni–C bond under C–C bond formation. A β-hydrogen elimination process liberates then the heterodimer and regenerates the nickel hydride species. In the case of the Pt^{II} catalyst, the C–C bond formation step proceeds by external nucleophilic addition of the alkene to the highly activated ethylene, and carbocationic intermediates are involved in the further transformation steps.

Since the hydrovinylation proceeds by means of considerably different mechanisms, it is expected that also the scopes of these two types of catalyst are somehow different. In fact for the nickel(II) catalysts aryl alkenes, 1,3-dienes and strained alkenes are typical substrates, while with the dicationic platinum(II) complex internal alkenes were successfully coupled with ethylene; this type of alkene, to the authors knowledge, was not applied so far for any catalytic hydrovinylations.

Due to the different mechanistic pathways for the $[Ni(H)(L)]^+$ and Pt^{II} catalysts, the type of occurring side reactions are also different. For nickel(II) catalysts often oligomerization to higher alkenes and double-bond isomerization of the product are common problems limiting their selectivity. These side reactions were not observed with the Pt^{II} catalyst. Although the homodimerization was found to be a side path, there should be certainly possibilities to suppress it by further fine-tuning of the catalyst structure and/or the reaction medium and conditions. In summary, the Pt^{II}-catalyzed hydrovinylation exhibits a high potential as a new alternative method to the known $[Ni(H)(L)]^+$-catalyzed reaction with a complementary scope of applications.

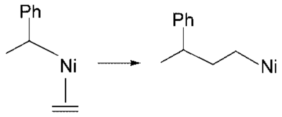
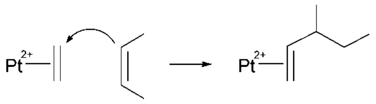
Conclusion and Perspectives

In conclusion the electrophilic activation of coordinated alkenes can be strongly enhanced by increasing of the positive net charge as was shown in case study on stable dicationic Pd^{II}– and Pt^{II}–alkene complexes. The Dewar–Chatt–Duncanson model of the metal–alkene bond shows that increasing the positive charge in the complex leads to the increase in the positive fractional charge on the coordinated C–C double bond, and hence the carbocationic reactivity is enhanced. In fact these theoretical assumptions have been illustrated by spectroscopic and X-ray structural data of the dicationic Pd^{II}– and Pt^{II}–alkene complexes. In addition, a remarkable influence on polarization of C=C double bond in coordinated monosubstituted alkenes $CH_2{=}CHR$ was noted with higher positive net charge. This resulted in high regioselectivity of the nucleophilic attack.

The reaction studies with the dicationic Pd^{II}– and Pt^{II}–alkene complexes toward protic nucleophiles revealed a reversible thermodynamic overall equilibrium between alkene substitution and addition at the C=C double bond. Important insights into the degree of alkene activation in the dicationic complexes were given with the quantitative estimation of the equilibrium constants for the nucleophilic addition K_{add}, which have been shown to be enhanced by several orders of magnitude compared to that of neutral Pt^{II}–alkene complexes.

The electrophilic activation of the alkene in the dicationic complexes is so strong that even moderately electron-rich

Table 5. Comparison of general features of the $[Ni(H)(L)]^+$- and Pt^{II}-catalyzed hydrovinylation.

Feature	$[Ni(H)(L)]^+$	$[Pt]^{2+}$
catalyst formation	allylic Ni precursor + Lewis acid activator in situ formation of $[Ni(L)(H)]^+$; active species not detectable	$[Pt(PNP)(CH_2{=}CH_2)][BF_4]_2$ isolated and characterized (NMR, X-ray); single component catalyst
C–C bond formation	alkene insertion 	nucleophilic addition 
substrates	aryl alkenes, 1,3-dienes, strained alkenes	internal alkenes
side reactions	product isomerization, oligomerization	homodimerization

alkenes can add to the Pt^{II}–ethylene complex. In addition it has been discovered that an excess of substrates resulted in a highly selective catalytic hydrovinylation process. The proposed mechanism differs considerably from that suggested for the well-known $[Ni(H)(L)]^+$-catalyzed reaction. Certainly the asymmetric version of the new Pt^{II}-catalyzed method would be worthy of further investigations in order to introduce the vinyl group stereoselectively into unsaturated hydrocarbons.

It is worth noting that a similar enhancement of electrophilic reactivity with the carbonyl ligand toward weakly basic protic nucleophiles was observed with dicationic cobalt(III) complexes $[Co(Cp)(dppe)(CO)]^{2+}$ reported by Brill and co-workers.[53] The concept of enhancement of electrophilic activation by increase of the positive complex charge is certainly not limited to alkenes; it can be naturally extended to any other unsaturated substrates, since the π back-donation would be more or less strongly decreased in the metal–substrate bond. There is a high potential of this concept for the discovery of new catalytic reaction pathways for C–C or C–hereoatom bond formations[54,55] as well as for C–H activation of alkanes, which remains to be further elucidated.

For the generation of cationic transition-metal complexes the choice of a suitable counterion Y^- also plays an important role. The pK_a of the conjugate acid HY and the nucleophilic properties of Y^- can be further fine-tuning parameters for increasing the catalytic activity of a cationic transition-metal complex.[56] In fact increasing interest for the development of non- or weakly coordinating anions[57] in homogeneous catalysis exists.[58] For instance $BArF^-$ has become very common counterion for cationic polymerization catalysts.[59] Carboranes $(CB_{11}H_6X_6)^-$ are among the least coordinating anions; recently these anions have gained increasing interest in synthesis of cationic transition-metal complexes,[60] displaying very weakly nucleophilic properties and the stabilization of carbocations.[61,62]

The investigation of activation of unsaturated substrates in transition-metal complexes with positive net charge higher than 2+ would be quite interesting to explore a new range of electrophilicity, but at the same time it seems to be very challenging. Due to certain limits in stability of these systems, and probable limits in their solubility in organic solvents, some restrictions in spectroscopic characterization and homogeneous reaction conditions may occur. However, the application of alternative solvents for these systems, such as ionic liquids or supercritical CO_2 could open new field in development of novel types of superelectrophilic cationic catalysts.

Acknowledgement

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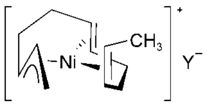

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