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Trends within a triad: comparison between σ-alkyl complexes of nickel, palladium and platinum with respect to association of ethylene, migratory insertion and β-hydride elimination. A theoretical study §

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Density functional B3LYP calculations have been performed for (diimine)(σ-methyl)metal(1+) complexes ($M = Ni^{II}$, Pd^{II} or Pt^{II}), associating ethylene to afford (diimine)(η^2-ethylene)(σ-methyl)metal(1+). All three metals co-ordinate ethylene strongly in the expected order Pt (41.5) > Pd (29.8) > Ni (27.2 kcal mol^{-1}). The co-ordination energies for the corresponding σ-ethyl complexes of Pd and Ni are substantially lower, Pd (16.3) and Ni (10.0 kcal mol^{-1}). This is due to loss of a β-agostic interaction, which in the palladium case is estimated to represent around 10 kcal mol^{-1} and in the case of Ni to around 12 to 14 kcal mol^{-1}. The insertion barriers for the cationic σ-alkyl η^2-alkene complexes are in the order Pt (25.5) > Pd (σ-methyl, 16.4; σ-ethyl, 18.0) > Ni (σ-methyl, 10.4; σ-ethyl, 11.3 kcal mol^{-1}). The insertion step is exothermic for Ni and Pd but slightly endothermic for Pt. For three-co-ordinated (diimine)(σ-propyl)metal(1+) complexes, β-hydride elimination is exothermic for Pt (−6.9) and endothermic for Ni (+11.0 kcal mol^{-1}). The rather low endothermicity to β-hydride elimination of Pd (4.8 kcal mol^{-1}) is consistent with (diimine)(σ-methyl)palladium(1+) being a polymerization catalyst promoting branched polyethylene. The termination for a Pd-catalysed polymerization of ethylene is discussed, and a direct β-hydride elimination from a four-co-ordinated (σ-alkyl)(diimine)(η^2-ethylene)palladium(1+) is excluded due to a barrier of 24.3 kcal mol^{-1}. In all, the calculations agree remarkably well with known energetics and recognized tendencies.

Nickel, palladium and platinum, the elements of the nickel triad, often behave as close relatives in their chemical interactions with alkenes. Thus, all three metals serve as hydrogenation catalysts.[1] In other respects they differ in chemical reactivity as seen for oligo- and poly-merization of alkenes. Homogeneous nickel catalysts are used industrially for oligomerization of ethylene in the Shell Higher Olefin Process (SHOP).[2] On the other hand palladium has been known for a long time as a metal unable to oligomerize or polymerize alkenes under homogeneous conditions. However, just recently cationic (σ-methyl)(1,10-phenanthroline)palladium(II) was shown to oligomerize ethylene.[3] Moreover, Rix and Brookhart[4] demonstrated that well defined cationic (diimine)(σ-methyl)-palladium(II) can afford high-molecular-weight polymers from ethylene. Still, the analogous diiminenickel catalysts are more active.[5] Platinum is yet to polymerize simple olefins.[6] As a whole, this look from the outside continues to support the well known, *qualitative* understanding that migratory insertion of the (η^2-alkene)(σ-alkyl)metal compounds of the nickel triad is more difficult as the triad is declined.

Measurements can provide a *quantitative* understanding, but are laborious to carry out. If a *comparison* between metals, *e.g.* in a triad, is to be performed there may exist a tough synthetic problem to prepare identically ligated complexes of all three metals. Furthermore, direct comparisons of kinetics may be obscured by different rate-determining steps. However, reliable calculations at a reasonable level may be a convenient and valuable tool to disclose chemical tendencies, especially within a triad.

This article focuses on the ground-state energetics and the barriers to insertion for cationic σ-methyl and σ-ethyl η^2-ethylene diimine complexes of the transition metals of the nickel triad. In addition, the β-hydride elimination of some of the intermediates of a polymerization sequence is examined. Special attention is paid to whether three- or four-co-ordinate species are likely to take part in the termination *via* a β elimination.

Computational Details

The calculations were performed in two steps. First, an optimization of the geometry was performed using the B3LYP method,[7] a density functional theory (DFT) type of calculation based on hybrid functionals, and double-zeta basis sets. In the second step the energy was evaluated in the optimized geometry using a large basis set including a polarization function on each atom. The final energy evaluation was also performed at the B3LYP level. In a previous study[8] it has been shown that for the systems studied here the B3LYP method gives excellent results in agreement both with experiments, where available, and with high-level *ab initio* results. All the present calculations were performed using the GAUSSIAN 94 program.[9]

The B3LYP functional used in the present calculations can be written as in equation (1) where F_X^{Slater} is the Slater exchange, F_X^{HF}

$$F^{\text{B3LYP}} = (1 - A)F_X^{\text{Slater}} + AF_X^{\text{HF}} + BF_X^{\text{Becke}} + CF_C^{\text{LYP}} + (1 - C)F_C^{\text{VWN}} \quad (1)$$

the Hartree–Fock exchange, F_X^{Becke} the gradient part of the exchange functional of Becke,[7] F_C^{LYP} the correlation functional of Lee *et al.*[10] and F_C^{VWN} the correlation functional of Vosko *et al.*,[11] *A*, *B* and *C* are the coefficients determined by Becke[7] using a fit to experimental heats of formation. However, it should be noted that Becke did not use F_C^{VWN} and F_C^{LYP} in the expression above when the coefficients were determined, but the correlation functionals of Perdew and Wang[12] instead.

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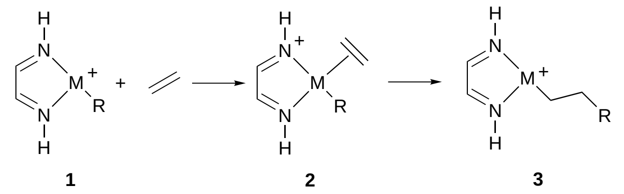
§ *Non-SI unit employed*: cal = 4.184 J.

Table 1 Energies (kcal mol^{-1}) for the reactions between M{(CHNH)$_2$}R$^+$ and ethylene; values in parentheses are derived from an extended basis set

	Ni		Pd		Pt
System	R = Me	R = Et	R = Me	R = Et	R = Me
1 + C_2H_4	27.2	10.0 (9.4)	29.8	16.3 (16.3)	41.5
2	0	0	0	0	0
Insertion transition state	10.4	11.3 (12.6)	16.4	18.0 (19.1)	25.5
3	−11.3	−6.3 (−5.5)	−7.0	−3.9 (−2.3)	2.6



M = Ni, Pd or Pt; R = Me **a** or Et **b**

Scheme 1

In the B3LYP geometry optimizations a rather small basis set, the LANDL2DZ set of the GAUSSIAN 94 program, was used. For nickel a non-relativistic electron core potential (ECP), while for palladium and platinum relativistic ECPs[13] were used. The valence basis set used in connection with these ECPs is of essentially double-zeta quality including a diffuse 3d function. The rest of the atoms were described by standard double-zeta basis sets. The B3LYP energy calculations were made using a larger basis set, in which one set of polarization functions was used for all atoms, but no f function was used on the metals. For the nickel systems, Hessians were also calculated at essentially the same B3LYP level as the geometries were determined. An all-electron basis[14] was used on nickel in order to allow analytic evaluation of the Hessians. For the equilibrium geometries determined there were no imaginary frequencies, and for the C–H activation transition states one imaginary frequency was found as required for true transition states. All energies reported below and in the tables include zero-point vibration. For the palladium and platinum systems these effects were taken from the corresponding nickel systems. Temperature effects were found not to be important for the present qualitative discussion.

Results and Discussion

Initiation of polymerization: association of ethylene and migratory insertion

The first part of the calculations covers the initial stage of a metal-catalysed oligo- or poly-merization of ethylene as shown in Scheme 1. The complexes **1a** (M = Ni or Pd) are very similar to the real catalysts designed by Brookhart.[4,5] (In the latter case bulky aryl substituents are attached to the nitrogens and there may be alkyl substituents at the imine carbons.)

The energetics for Scheme 1 are numerically displayed in Table 1 and graphically visualized in Fig. 1. Noteworthy is that all the 14-electron methyl complexes **1a** (M = Ni, Pd or Pt) co-ordinate ethylene strongly, whereas the homologous ethyl complexes **1b** of Ni and Pd are characterized by a considerably weaker co-ordination. The main reason for this large difference is that the (ethyl)metal compounds lose an agostic interaction upon ethylene co-ordination.[8] Just subtracting the co-ordination strengths for methyl and ethyl complexes would suggest that the agostic interaction amounts to 17.8 kcal mol^{-1} for **1b** (M = Ni) and 13.5 kcal mol^{-1} for M = Pd. In reasonable accord, comparison between initial reactants, **1**, and the final products of an insertion **3** reveals that the energy decrease is 17.7 kcal mol^{-1} less for **1b** (M = Ni) compared to **1a** (M = Ni) and 15.5 kcal mol^{-1} less for **1b** (M = Pd) compared to **1a** (M = Pd). These are maximum figures, neglecting other effects like changes in polarization upon addition of one- or two-carbon hydrocarbyl fragments to the ligand sphere. A third, slightly lower and better figure for agostic interaction for palladium can be deduced from Table 2.

Table 2 Bond strengths (kcal mol^{-1}) between palladium(II) and alkyl groups

A	B	Bond strength
Pd^+	Me	52.1
	Et	68.9
	Pr (primary)	72.6
	(secondary)	76.4
	Bu (primary	74.4
	(secondary)	77.4
	(tertiary 3)	80.6
Pd{(CHNH)$_2$}$^+$	Me	37.8
	Et	50.5
	Pr (primary)	53.4
	(secondary)	51.3
	Bu (primary)	53.8
	(secondary)	51.6
	(tertiary)	51.3
PdH^+	Et	54.0
	Pr	59.3
	But-1-ene	61.6
PdH{(CHNH)$_2$}$^+$	Et	36.5
	Pr	38.2
	But-1-ene	38.9
	But-2-ene	41.3

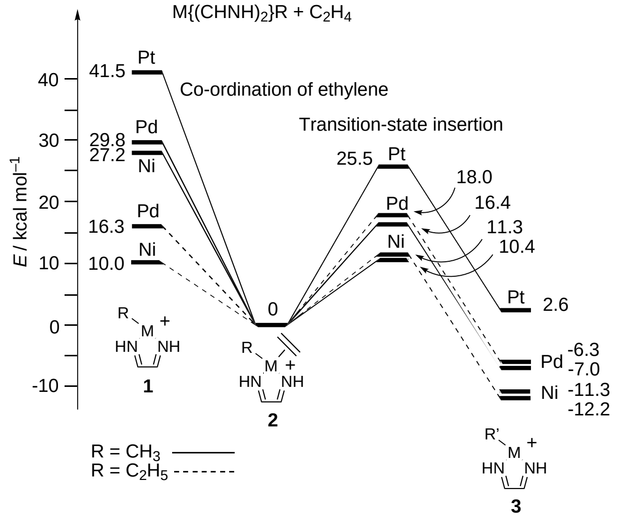


Fig. 1 Initial steps in a polymerization sequence

The bond strength is 12.7 kcal mol^{-1} higher for an ethyl group compared to a methyl group attached to cationic diiminepalladium. For a further one-carbon build-up to a primary propyl group the bond strength increases by a modest 2.9 kcal mol^{-1}. In summary, this indicates that the bond energy of true agostic interaction is in the area of 10 kcal mol^{-1} or slightly less for palladium. It also seems that the agostic interaction is 2 to 4 kcal mol^{-1} stronger for nickel. As the energy release for **1a** (M = Pt) insertion of ethylene is very close to the energy release of the same insertion for **1a** (M = Ni) (38.9 and 38.8 kcal mol^{-1}

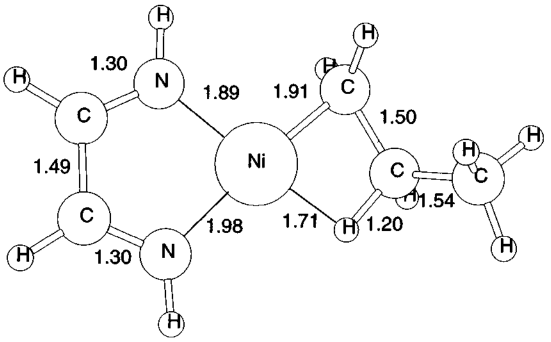


Fig. 2 Optimized geometry (distances in Å) of complex **3a** (M = Ni)

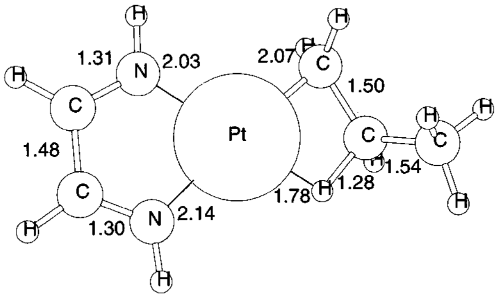


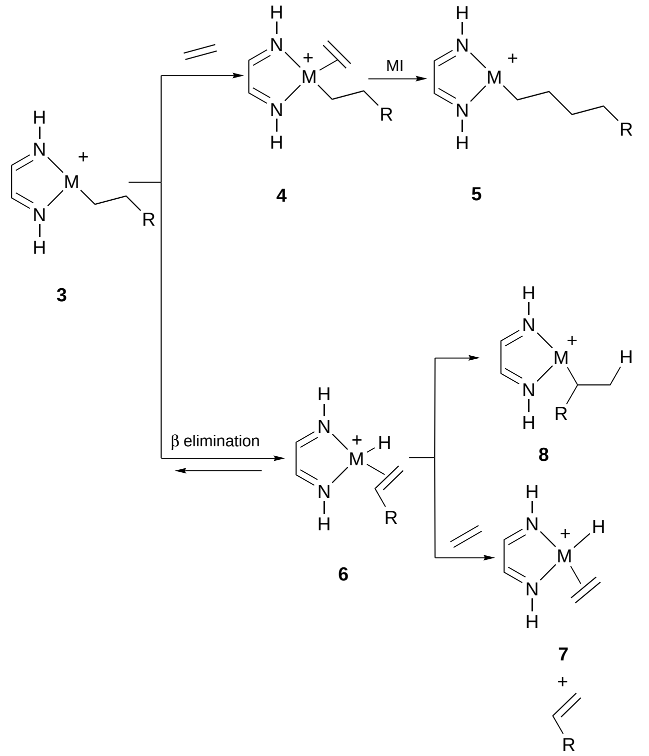
Fig. 3 Optimized geometry of complex **3a** (M = Pt)

respectively) it is a reasonable assumption that platinum achieves an agostic interaction of the same strength as that of nickel. Agostic interactions for nickel and platinum are shown for **3a** (M = Ni) (Fig. 2) and **3a** (M = Pt) (Fig. 3). A corresponding figure for palladium has been published.[8]

The common view that the alkene co-ordination ability is in the order Pt^{II} > Pd^{II} > Ni^{II} receives support from Fig. 1, as far as the ligand surroundings are identical.[15] The migratory insertion (MI) step shows moderate exothermicity for nickel and palladium, but slight endothermicity for platinum. More importantly, the insertion barrier is low for nickel, moderate for palladium and high for platinum.

The barrier (18.0 kcal mol^{-1}) calculated for the insertion in complex **2a** (M = Pd) is close to that observed (18.5 kcal mol^{-1}) by Rix and Brookhart.[4] The low insertion barrier of nickel is in accordance with the high activity for nickel polymerization catalysts.¶ Finally, the figure found for platinum (25.5 kcal mol^{-1}) indicates that ethylene, at best, slowly inserts at room temperature.[6] In all, a common qualitative opinion about insertion aptitudes that has never been proven till now is supported by systematic figures for all three metals.

As far as we look vertically upon a triad, *i.e.* methyl or ethyl complexes are considered independently, Table 1 lends support to the suggestion that a weak co-ordination of an alkene is related to a low insertion barrier.[3a] This seems not to be the case when ethyl complexes are compared with methyl complexes for nickel and palladium separately. A substantial decrease in co-ordination strength correlates with a small increase of the barrier; 0.9 kcal mol^{-1} for nickel and 1.6 kcal mol^{-1} for palladium. However, the calculated bond strength between an ethylene ligand and an ethyl complex sums the energies of two events: loss of a β-agostic interaction and co-ordination of alkene. As the strength of the β-agostic interaction roughly makes up for the difference in bond strength between ethyl and methyl complexes, the terms related to just the co-ordination are rather similar. The β-agostic interaction, lost upon co-ordination of ethylene, is not regained in the transition state, and therefore the barriers should be similar for ethyl and methyl complexes. In conclusion, relations between co-ordination strengths and insertion barriers are relevant as long as only sheer co-ordination terms are compared.



Scheme 2 Different fates of alkyl metals in the presence of ethylene. M = Ni, Pd or Pt; R = Me **a** or Et **b**

Chain growth, branching and termination: continued migratory insertion, β-hydride elimination, readdition of hydride and displacement of olefin

The immediate fate of the primary insertion products **3** is essentially two-fold (see Scheme 2). (1) Further association of ethylene to complex **3** generates **4** and consecutive migratory insertions will continue the growth of an oligomer, ultimately affording a linear polymer. The rather low to moderate insertion barriers for nickel and palladium would allow facile polymerization. In all, the situation would be similar to that already discussed for **1b**, M = Ni or Pd respectively. In the platinum case a high barrier is preventive to chain growth. (2) Alternatively, the 14-electron complexes **3** may undergo β-hydride elimination, affording the (η^2-alkene)(hydride)metal complex **6**. Such a reaction for **3a** and **3b** (M = Ni) would be endothermic by about 11 kcal mol^{-1} (Table 3 and Fig. 4).

For the corresponding palladium complexes **3a** and **3b** the endothermicity would be less, *i.e.* 4.8 and 4.5 kcal mol^{-1}, respectively. In the platinum case the elimination is exothermic by 6.9 kcal mol^{-1}.

We are unable to detect specific transition states for these eliminations. The endothermicity suggests a late, hydride-like transition state for nickel and palladium. The β-hydrogen elimination product **6** contributes a new point of bifurcation as exemplified in Scheme 3.

Displacement of the co-ordinated olefin terminates the chain growth (see below).[4,5] Alternatively, the hydride may readd either back to **3** or to **8**. In case of the latter readdition two possibilities for a β-agostic interaction will appear (Scheme 3). An agostic interaction involving an internal hydrogen seems to be

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¶ The DFT calculations by Ziegler have provided somewhat different values for the barriers when cationic (σ-alkyl)(π-ethylene)(chelate ligand)nickel complexes undergo insertion: (*a*) 15.5 kcal mol^{-1}, alkyl = Et, chelate = 1,2-diphosphinoethylene;[16a] (*b*) 11.1 kcal mol^{-1}, alkyl = Me, chelate = diimine; 17 kcal mol^{-1}, alkyl = Pr^n, chelate = diimine;[16b] (*c*) a combined DFT, quantum mechanics and molecular mechanics model has most recently been applied to calculate the insertion barrier for a Brookhart-type polymerization catalyst giving 11.8 kcal mol^{-1}, alkyl = Pr^n, chelate = *N*,*N*′-diaryldiimine, aryl = $C_6H_3Pr^i_2$-2,6.[16c]

Table 3 Energetics (kcal mol^{-1}) for (diimine)(σ-propyl)metal compounds undergoing β-hydride elimination and reinsertion of hydride

System	Ni	Pd	Pt
3a	0.0	0.0	0.0
6a	11.0	4.8	−6.9
8a	−0.9	−1.9	0.4

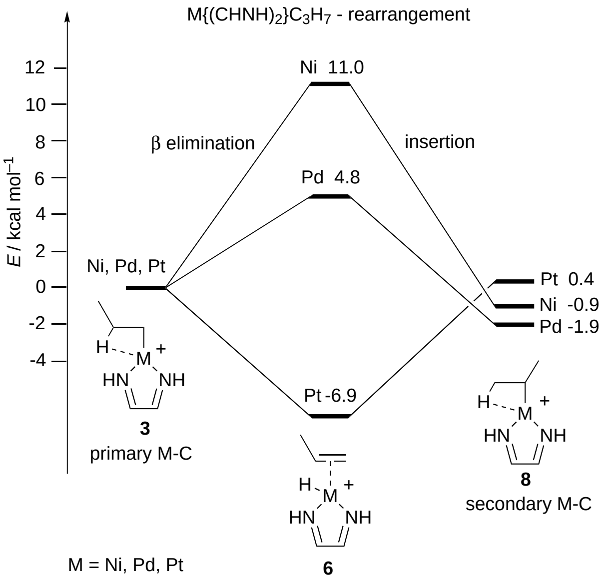
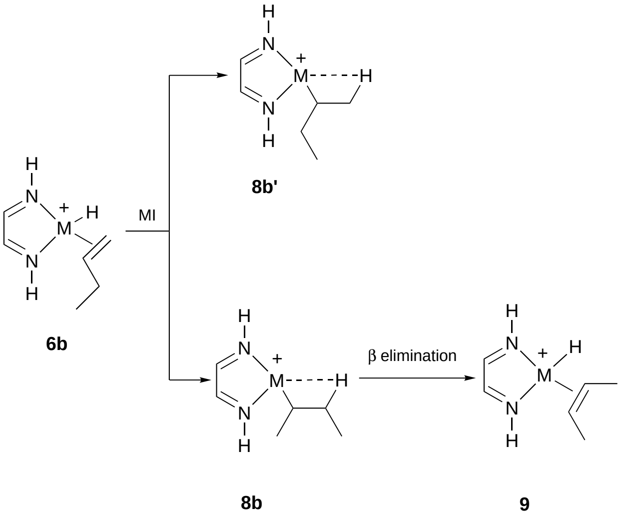


Fig. 4 β-Hydride elimination from three-co-ordinated metals



Scheme 3 Reinsertion of hydride and isomerization of butene

slightly preferred (Table 4). Readditions that move the metal to secondary carbons will eventually result in a branched polymer. In summary, it is evident that nickel will be the most prone of the metals to catalyse the formation of linear polymers, whereas platinum will be extremely reluctant to promote any polymerization at all. Palladium fulfils prerequisites to provide branched polyethylene.

Moreover, Table 4 and Fig. 5 illustrate that such a branching is thermodynamically slightly favored for palladium. [In contrast, neutral (σ-alkyl)palladium complexes thermodynamically prefer primary metal–carbon bonds.][17] The low-energy route to secondary (σ-alkyl)palladium intermediates is consistent with extensive branching found for palladium-catalysed polymerization.[4,5]

Table 4 Energetics (kcal mol^{-1}) for (σ-butyl)(diimine)metal complexes undergoing β-hydride elimination and reinsertion of hydride

System	Ni	Pd
3b	0.0	0.0
6b	11.3	4.5
Migration transition state	10.6	5.3
8b′	−0.1	−1.1
8b	−1.9	−2.9
β-Elimination transition state	7.0	2.1
9	7.0	0.7

Further hydride eliminations may cause formation of internal alkenes co-ordinated to the metal. As seen from Table 4 and in Fig. 5 the rearrangement from (but-1-ene)(diimine)hydridometal **6** to (*Z*-butene)(diimine)hydridometal **9** corresponds to an energy decrease of 3.8 kcal mol^{-1} for palladium and 4.3 kcal mol^{-1} for nickel. Free *Z*-but-2-ene is thermodynamically favored by 2 kcal mol^{-1} compared to but-1-ene.[18] Accordingly the but-2-ene possesses about a 2 kcal mol^{-1} stronger co-ordination to nickel and palladium than does but-1-ene. This is noteworthy since less-substituted alkenes are commonly considered to co-ordinate better than more substituted ones.[15a]

It is known that neutral monoalkylpalladium 16-electron complexes are able directly to β eliminate, but the major route to β-hydride elimination for such complexes is by way of a prior dissociation of a co-ordinated counter-ion and a subsequent β-hydride elimination from a cationic three-co-ordinate intermediate, and independently such complexes have been shown to decompose rapidly.[19] With this in mind a most probable termination for palladium seems to be a two-step sequence: (*i*) β elimination from a three-co-ordinate species like homologs to **3** or **8**, and (*ii*) a consecutive associative displacement.‖ Still, a β elimination from a cationic four-co-ordinated (σ-alkyl)(diimine)-(η^2-ethylene)palladium complex followed by dissociation cannot be ruled out.

In Fig. 6 the situation is visualized together with the chain-building migratory insertion. There are two points of concern. (*a*) If the barrier in the formation of complex **4** from **3** is insignificant, the β-hydride entrance *via* **6** to both low-molecular-weight chain-transfer products and branched polymers should be closed. However, in practice diffusion-controlled bimolecular processes are associated with a barrier of around 3 kcal mol^{-1}.[20] Consequently, at room temperature β-hydride elimination from **3** would take place roughly every 10th to 100th insertion even if this reaction is diffusion controlled. Furthermore, rupture of a β-agostic interaction in **3b** and/or disruption of solvent co-ordination to **3** may contribute an enthalpy to the barrier. The calculations concern the gas phase. In solution a ‘non-co-ordinating’ counter ion actually may co-ordinate, more or less, or appear in the proximity of **3** delaying the ethylene trapping.** In all, Fig. 6 does not take into account some circumstances that may make β-hydride elimination possibly competing with co-ordination of ethylene to **3**. (*b*) If we disregard the above discussion and assume that association of ethylene to **3** *is* much faster than β-hydride elimination, the migratory insertion path to unbranched polymers from **4** should have a lower barrier than chain termination *via* combined dissociation back to **3**, β-hydride elimination to **6** and associative displacement to **7**. The difference in barrier heights from the resting state **4** is rather small but significant, around 2–3 kcal mol^{-1}. In consequence, cationic (σ-alkyl)(diimine)-

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‖ As all three metals strongly co-ordinate ethylene in the four-co-ordinate hydrido(π-alkene) complexes a dissociative route is excluded as a reasonable termination step. Data concerning the bond strength of ethylene to Ni^{II}, Pd^{II} and Pt^{II} is scarce. Our group is currently investigating this.

** Maybe the dramatic enhancements of polymerization capacity seen with the cocatalyst MAO (monomethylaluminoxane) are in part a result of removal of the counter ion and making it a distant, non-interfering deportee.

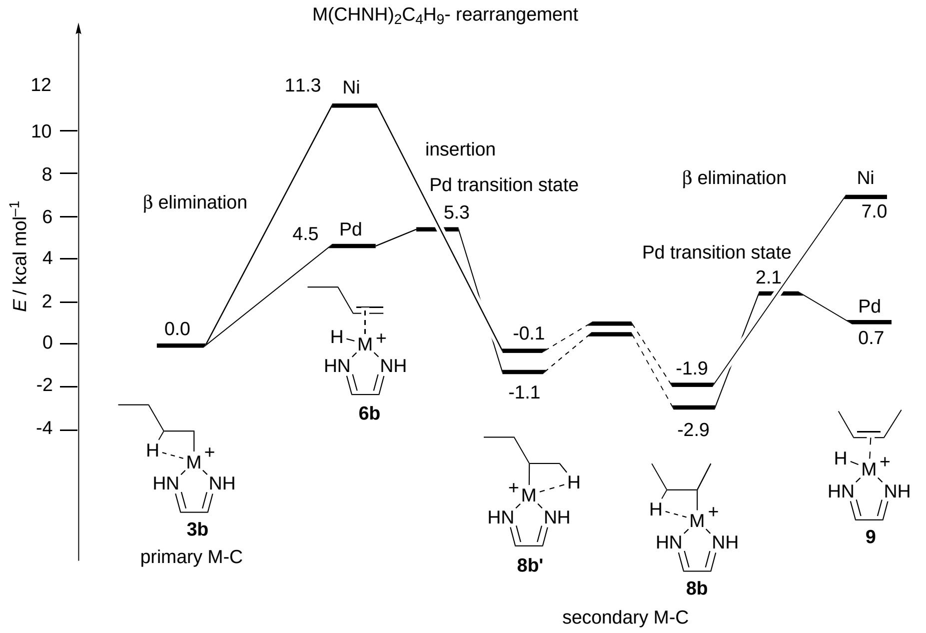

Fig. 5 Different reaction routes for complex **3b**

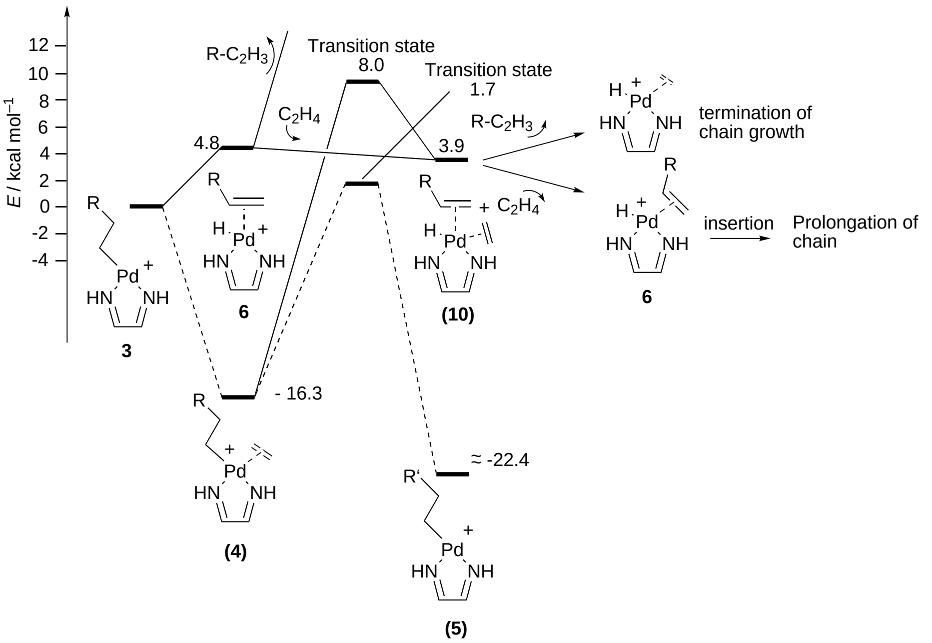

Fig. 6 Comparison of different fates of a (σ-alkyl)(diimine)palladium complex in the presence of ethylene. Parentheses around a compound number show that no value has been calculated for that specific compound. Instead an estimation is made with the help of the value for a homolog

palladium should be able to provide at least rather long straight-chain oligomers in the presence of ethylene, which is inconsistent with observation.[4,5] Without aryl substituents on nitrogen no poly- or oligo-mers (higher than butenes) will be formed. The discrepancy has a simple explanation. Calculations mainly derive changes of enthalpic character (ΔH). The entropy drop upon co-ordination of ethylene to **3** has to be considered in order to estimate the change in free energy (ΔG). In a bimolecular process, two molecules combining to one, the loss of translational freedom may correspond to an increase in free energy of as much as 8 kcal mol^{-1} at room temperature.[21] This means that if we estimate the free-energy changes, the level of **4** and its transition state for insertion would be significantly raised in comparison with the level of complex **3**, and a β-hydride elimination may appear much more probable accordingly.

In the case of nickel ligated with non-substituted diimines it is evident that polymerization would be possible also in solution, unless a termination step other than β-hydride elimination is operative. In fact, Ziegler and co-workers[22] have illustrated such a facile decomposition path involving β-hydrogen transfer to an incoming ethylene.

Conclusion

(1) The calculations show that the bond strength between metal and ethylene is in the order $Pt^{II} > Pd^{II} > Ni^{II}$.

(2) β-Agostic interaction for (σ-alkyl)(diimine)metal(1+) is substantial for Ni and Pt (≈12–14) and Pd (≈9–10 kcal mol^{-1}).

(3) β-Agostic interactions are lost in (σ-alkyl)(diimine)-metal(1+) upon co-ordination of ethylene. This is the main reason why ethylene binds much more strongly to methyl complexes than to higher homologs.

(4) The barrier to migratory insertion of cationic (σ-alkyl)-(η^2-ethylene)metal(1+) is in the order $Pt^{II} > Pd^{II} > Ni^{II}$.

(5) The low barrier to β-hydride elimination for three-co-ordinated alkylmetal complexes explains why Pd affords branched polyethylene.

(6) β-Hydride elimination from four-co-ordinated cationic (diimine)(σ-ethyl)(η^2-ethylene)palladium(1+), directly affording a five-co-ordinated hydride corresponds to a high barrier (≈24.3 kcal mol^{-1}) and is therefore an unlikely termination reaction. Such a five-co-ordinated hydride is a reasonable model for transient associative displacement intermediates but formed *via* displacement from (diimine)(σ-ethyl)(η^2-ethylene)palladium(1+), in accordance with Brookhart's proposal for chain termination.

In summary, the calculated activities of complexes of Ni, Pd and Pt are in nice accordance with qualitative and quantitative knowledge in the field. It is our firm belief that calculations at reasonable levels, as in this study, will evolve as an efficient and convenient method to explore chemistry.

Acknowledgements

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