Journal of Organometallic Chemistry, 478 (1994) 121–129

The insertion of acetylene into the palladium carbon bond of square planar Pd(II) complexes: a theoretical investigation

P. de Vaal * and A. Dedieu

Laboratoire de Chimie Quantique, UPR 139 du CNRS, Université Louis Pasteur, Strasbourg (France)

(Received October 20, 1993)

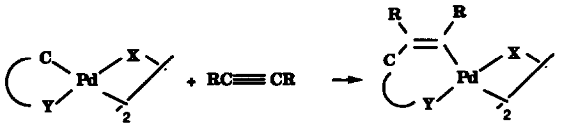
Abstract

Ab-initio SCF, CAS-SCF and CI calculations have been carried out for the acetylene insertion into the Pd–C bond of the $[PdCl(NH_3)(CH_3)(C_2H_2)]$ model system. The acetylene is found to bind quite weakly to the palladium atom and inserts with an activation barrier of 17 kcal mol^{-1}. The geometry of the transition state corresponds to a monohapto coordination of the acetylene. No intermediate seems to be involved on the reaction path, at least for the C_2H_2 system. The effects of substitution of one hydrogen atom by more electron attracting substituents and of a CH group by a metal organic entity are briefly analysed. The stereochemical course of the reaction is also investigated in connection with the geometry of the various isomers known for the isolobal $C_3H_5^+$ organic system.

Key words: Palladium; Alkyne insertion; Ab-initio calculations; Stereochemistry

1. Introduction

The insertion of an alkyne into the palladium carbon bond of square-planar Pd(II) complexes is a well known organometallic reaction and has been used for various synthetic purposes, in particular in cyclopalladated compounds, see eqn. (1) [1]. Yet despite the ready occurrence of this reaction, its intimate mechanism is not known. It is generally believed that the first step involves coordination of the alkyne through its π system, although this type of coordination is rare in organopalladium(II) chemistry [1]. One also expects, by analogy with the coordination of alkenes to Pd, that the alkyne is perpendicular to the coordination plane and should rotate prior to or during the insertion step. Recent kinetic data obtained for dimeric halide-bridged palladacycles also support this traditional view [2]. In particular they exclude the involvement of a five-coordinate complex in which the alkyne would be axially bound and favour instead a pathway with an opening of the bridge and the subsequent coordination of the alkyne in a square-planar environment. Although the above features seem quite reasonable in the light of to our present knowledge of the closely related alkene insertion reaction, they have not been corroborated by any theoretical investigation.



(1)

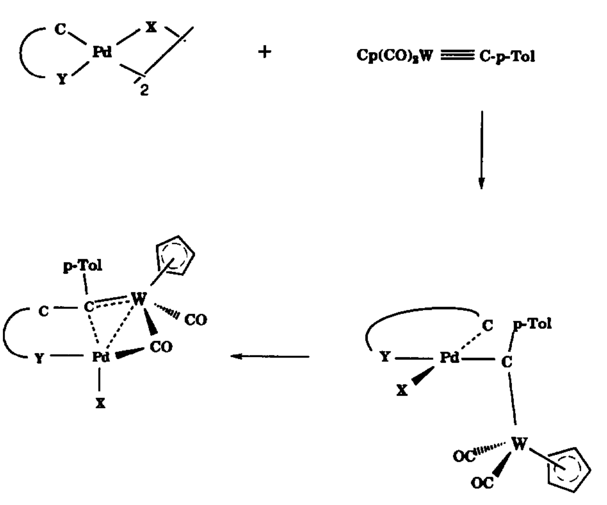
The incentive for the present theoretical study came from the recent synthesis by Engel et al. [3] of metallacarbyne complexes of palladium(II) in which the metallacarbyne is coordinated essentially through the carbyne carbon atom in an η^1 coordination mode, see the Scheme 1. This η^1-metallacarbyne complex can react further by a C–C coupling reaction that is quite similar to an alkyne insertion reaction [3]. The goal of the study was therefore twofold; to investigate the mode of coordination of an alkyne to square-planar Pd(II) complexes, and to assess the reaction mechanism of the alkyne insertion into the Pd-alkyl bond and its stereo-

---

Correspondence to: Prof. A. Dedieu.

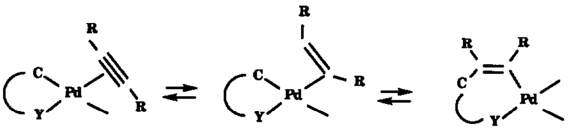
* Present address: SQL Systems B.V., Rotterdam, Netherlands.

0022-328X/94/$7.00
SSDI 0022-328X(94)24427-K



Scheme 1.

chemistry. More specifically, in the light of the experimental results obtained for the metallacarbynes we wanted to check whether a η^1 intermediate is involved in the insertion reaction of alkynes, eqn. (2). Such η^1-Alkyne complexes have been proposed as intermediate structures in the η^2-alkyne-to-vinylidene rearrangement occurring in d^6 ML_5- and T-shaped d^8 ML_3 alkyne complexes [4].



(2)

The results reported here are based on SCF, CAS-SCF and CI *ab-initio* calculations carried out on the $[PdCl(NH_3)(CH_3)(C_2H_2)]$ model system. The various geometries were optimized at the SCF level through an energy gradient technique. Single point calculations were then carried out at the CAS-SCF and CI levels for the reactant, the transition state, the product and some other crucial geometries (*vide supra*), in order to account for the influence of electron correlation. For comparison with the experimental data for $[(C_5H_5)(CO)_2WCC_6H_4\text{-L-Me}]$ [3], calculations were also performed on the $[(C_5H_5)(CO)_2MoCH]$ model system. Finally, the substitution of hydrogen atoms by electron attractiving organic groups (which seem to be necessary for a clean insertion reaction [5]) has been briefly analysed by carrying out calculations on $HCCCF_3$ and $H_3CO(O)C\text{-}CC\text{-}C(O)OCH_3$.

2. Computational details

The SCF calculations were carried out with the ASTERIX system of programs [6] using for the SCF geometry optimization the following basis set (hereafter denoted BSI): (15, 9, 8) contracted to ⟨6, 4, 4⟩ for the palladium and molydenum atoms [7*,8]; (9,5) contracted to ⟨3, 2⟩ for the first row atoms [9]; (11, 7) contracted to ⟨4, 3⟩ for the chlorine atom [9]; and (4) contracted to ⟨2⟩ for the hydrogen atom [10]. The same primitive and contracted functions were used for the CAS-SCF and CI calculations except for the Pd atom where supplemental functions were added to yield a more flexible (16, 11, 9) ⟨7, 5, 5⟩ basis set, hereafter denoted BSII [11*,12]. For the CAS-SCF calculations [13] on $[PdCl(NH_3)(CH_3)(C_2H_2)]$ and $[PdCl(NH_3)(CH{=}CHCH_3)]$ the active space was made of 10 orbitals populated by 10 electrons (10a10e CAS-SCF). These active orbitals, $4d_{xy}$, $4d_{z^2}$, σCH_3 (the lone pair of the methyl group), $\pi \parallel (C_2H_2)$, $\pi \perp (C_2H_2)$, $4d_{x^2-y^2}$, $5d_{xy}$, $5d_z2$ (hybridized with some 5s), $\pi^* \parallel (C_2H_2)$, $\pi^* \perp (C_2H_2)$ account for the main bonding interactions. The CI calculations were multireference contracted CI calculations [14] using as references the configurations which were found to have an expansion coefficient greater than 0.05 in the CAS-SCF wavefunction. Ten electrons were correlated (the same as in the CAS-SCF wavefunction) and single and double excitations to all virtual valence orbitals were included. The CI results reported here include the Davidson correction [15] to provide an estimate of the inclusion of higher-than-double excitations.

The geometry optimization was carried out from analytical energy first derivatives by using an implemented BFGS algorithm [16]. The convergence thresholds for the geometry optimization were set to 0.002 for the gradient norm and for each individual component of the energy gradient. This led in almost every optimized geometry to a value less than 0.001 for the gradient norm. In a few instances some internal coordinates were kept constant so to insure C_s symmetry or to force some specific conformations (which were not true secondary minima on the potential energy hypersurface). The local symmetry of the NH_3 and CH_3 groups was also retained. The search for the reaction path and the associated maximum energy point was done as follows: the $C_{methyl}\text{-}C_{acetylene}$ distance was chosen as reaction coordinate and a gradient optimization was performed for discrete points of this reaction coordinate. The choice of the $C_{methyl}\text{-}C_{acetylene}$ distance as a reaction coordinate was made in line with previous studies on C_2H_4 insertion into the $Ti\text{-}CH_3$ bond [17]. The recent experimental kinetic data also suggest that C-C bond-making plays a major role in the transition

---

[*] Reference number with asterisk indicates a note in the list of references.

state [2]. Thus the geometry obtained for the maximum energy point along the C–C reaction coordinate should be very near to the geometry that one would get from a full gradient geometry optimization of the true transition state. This maximum energy point should be also quite close in energy, although somewhat higher, to the true transition state. We will therefore in the following refer to it as to the transition state.

3. Results and discussion

3.1. Binding of C_2H_2 to $PdCl(NH_3)(CH_3)$

Two orientations of the C_2H_2 have been considered, the in-plane **1** and the out-of-plane **2** orientation (in which the acetylene has been rotated by 90°); see the Fig. 1. In both cases the geometry optimization procedure led invariably to the η^2 coordination mode, even when starting from the η^1 geometry. However, one finds two unequal Pd–C bonds, 2.57 and 2.70 Å, in the in-plane conformation. This might be referred as corresponding to an η^1 coordination mode, but the acute Pd–C–C angle of 82.8° (see the Fig. 1) runs against this interpretation. The most salient and unexpected feature of these two structures is the large values found for the Pd–C bond lengths. This corresponds to a weak binding of acetylene to Pd(II). Indeed the computed binding energy of **1** is 5.8 kcal mol^{-1} [18*–20]. The weak binding of C_2H_2 cannot be attributed to a poor description of the π back donation effects. CAS–SCF calculations, known to account correctly for these non-dynamical correlation effects, were carried out and showed that the π back-donation effects were small. Moreover, moving C_2H_2 from a Pd–C distance of 2.60 Å to a Pd–C distance of 2.15 Å resulted in a parallel increase of the SCF and CAS–SCF energies, 7.5 kcal mol^{-1} at the SCF level and 8.6 kcal mol^{-1} at the CAS–SCF level. Thus the geometry of this system does not seem to depend upon the non-dynamical correlation effects.

To test further our calculations a geometry optimization was performed on the ethylene analog $[PdCl(NH_3)(CH_3)(C_2H_4)]$ with the out-of-plane orientation of C_2H_4. It also yielded a quite long Pd–C bond length, 2.46 Å. This value is in the upper range of, or only slightly exceeds, the theoretical and experimental values observed in Pd(II) ethylene complexes [21–23]. A reason for the rather long Pd–C bond length of 2.70 Å in **1** may well be the repulsion between the chlorine p orbital and the π orbital of the acetylene, see **3**. This repulsion can be partially relieved by an upwards translation of C_2H_2 which in turn would lead to the two unequal Pd–C bond lengths. In support of this proposal, we note that in **2**, where this repulsion is minimized, the two optimized Pd–C bond lengths, although quite large (2.52 Å), are equal. The replacement in **1** of the chloride by a hydride (which has no p orbital) to yield $[PdH(NH_3)(CH_3)(C_2H_2)]$ also suppresses the repulsive interaction **3**. The geometry optimization then led to Pd–C bond lengths of 2.51 and 2.46 Å, long but again quite similar. Thus the long Pd-to-acetylene bond length is probably meaningful. Nevertheless one should be aware that the inclusion of the dynamical correla-

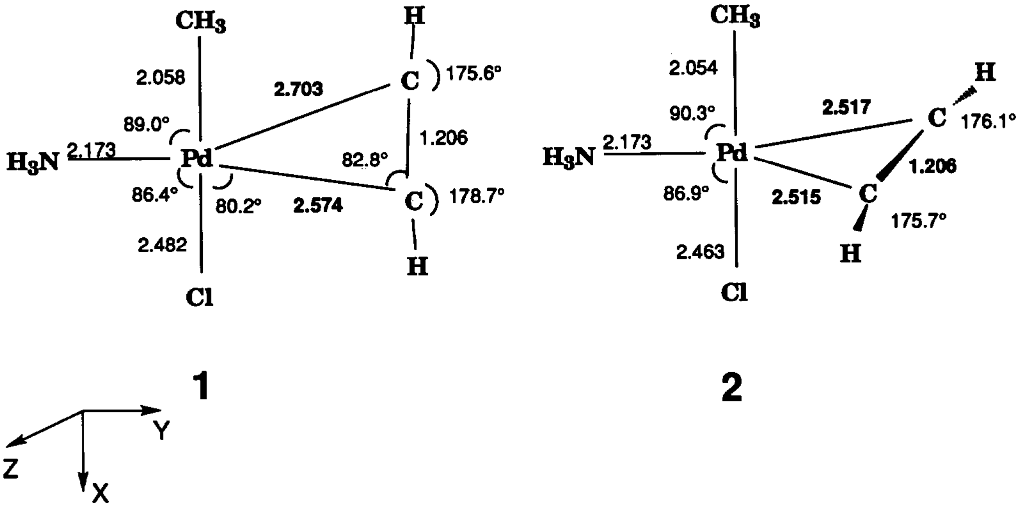
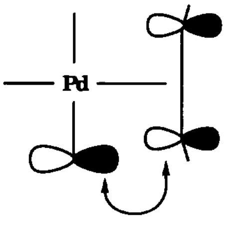


Fig. 1. SCF optimized geometries of the in-plane (1) and out-of-plane (2) of $[PdCl(NH_3)(CH_3)(C_2H_2)]$.

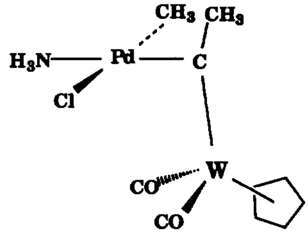
tion effects and of relativistic effects might increase somewhat the binding energy and hence yield shorter Pd–C bond lengths [24*–27].

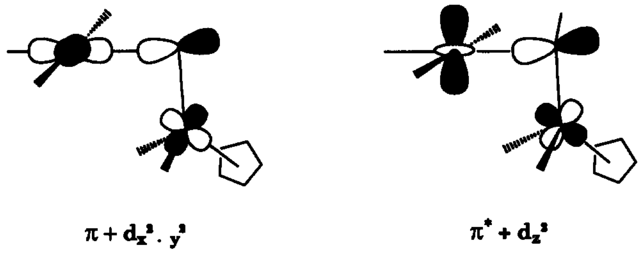


3

In line with the weak binding of C_2H_2 we find a rather small energy difference between the two conformations **1** and **2**. At both the SCF and CAS–SCF levels the in-plane conformation is more stable than the out-of-plane conformation by 1 to 2 kcal mol^{-1} [28a*]. Hence the acetylene will rotate almost freely between these two conformations [28b*]. The influence of the chloride on rotational isomerism was assessed by considering again $[PdH(NH_3)(CH_3)(C_2H_2)]$. Here, too, the planar form is found to be more stable, and to a greater degree, 4 kcal mol^{-1} [29*]. There seems therefore to be an intrinsic preference for the planar conformation in such systems. However, it can be counterbalanced by steric hindrance and the repulsion arising from the lone pairs of the *cis* halide. A few Pt(II) square-planar alkyne complexes are known in which the alkyne adopts an out-of-plane conformation [30,31]. However, in these systems the alkyne is more strongly bonded to the metal atom (the Pt–C bonds are shorter). Since the alkyne has bulkier groups than the hydrogen atom in C_2H_2, minimization of steric repulsion may govern the preference for the out-of-plane conformation. Yet it is noteworthy that in the related $[PdH_2(PH_3)(C_2H_4)]$, Koga and Morokuma [32] found an in-plane conformation to be most stable, at both the SCF and MP2 levels.

We ascribe the weak binding of C_2H_2 to two orbital factors: the poor back-donation ability of Pd(II) which is experimentally found [33] and which we also find here; and the quite strong repulsive interaction between the two π orbitals of C_2H_2 and the d orbitals of palladium (d_{x^2} with $\pi\|$, d_{yz} with $\pi\perp$). This is, of course, a situation that differs completely from the one encountered in bis-(ligand)Pd^0 alkyne complexes where there is a much stronger back donation due to the zero oxidation state of the metal atom and the hybridization of the d_π orbital [34]. It is also interesting to recall that the factors which have been shown to induce isomerisation from square-planar to tetrahedral geometry, a low oxidation state of the metal and a large π back-donation ability [35], are not present in $[PdCl(NH_3)(CH_3)(C_2H_2)]$. Thus the only possibility left to the system is a square planar geometry.

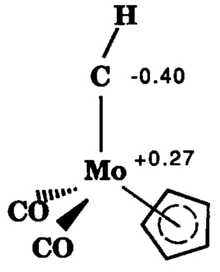




4 **5**

Scheme 2.

Although we do not find any indication of a local minimum corresponding to the η^1 coordination mode, it is worth noting that the potential energy hypersurface is quite flat around the ground state η^2 structure. For instance, we have already mentioned that bringing the acetylene to a Pd–C distance of 2.15 Å led to a moderate destabilisation (7.5 kcal mol^{-1} at the SCF level). Even more interesting is the fact that for that distance the optimization of the remaining geometrical parameters led to η^1 coordination. This result clearly implies that there may be some instances in which η^1 coordination is preferred, or is at least a local minimum on the full potential energy surface. A representative example is given by $[(C_5H_5)(CO)_2WCC_6H_4\text{-4-Me}]$ where the alkyne has been replaced by a metallacarbyne, see Scheme 1. We have previously shown [3] through an extended Höckel analysis of the model system $[(C_5H_5)(CO)_2WCCH_3][PdCl(NH_3)(CH_3)]$ that two stablizing interactions **4** and **5** are at work, see Scheme 2. Interaction **4** takes place between the $d_{x^2-y^2}$ orbital of palladium and the π orbital of the $WCC_6H_4\text{-4-Me}$ metallacarbyne; **5** is between the d_{z^2} orbital of palladium and the π^* orbital of $(C_5H_5)(CO)_2WCCH_3$. SCF calculations carried out on the model $[(C_5H_5)(CO)_2MoCH]$ **6** indicate that its LUMO is quite low in energy and highly polarized on the carbon atom (the weight of the carbon atom is 52% whereas the weight of the molybdenum atom is 14%). This should therefore give rise to a strong d_{z^2}/π^* two electron interaction. In addition, the polarization of the metallacarbyne, see **6**, should also contribute greatly to the binding of the negatively charged carbon atom to the positively charged Pd atom through a favourable electrostatic interaction. Preliminary SCF calculations performed on $[(C_5H_5)(CO)_2MoCH][PdCl_2(NH_3)]$ seem to confirm this binding scheme [36].



6

3.2. *The various isomers of* $[PdCl(NH_3)(CH=CHCH_3)]$

Before examining the insertion reaction in detail it might be useful to look more carefully at the product of this reaction, the alkenyl complex $[PdCl(NH_3)(CH=CHCH_3)]$. More specifically, we are concerned with the stereochemistry of this system, since this may have some relevance to the course of the reaction. A guide for our investigation was provided by the isobal analogy between $[PdCl(NH_3)(CH=CHCH_3)]$ and the $C_3H_5^+$ cation. This concept was used already by Silvestre and Hoffmann [4] to infer the occurrence of an η^1 acetylene intermediate structure in the rearrangement leading from the η^2 alkyne complex to the vinylidene complex. Figure 2 sketches the various organic oraganometallic isomers which have been computed by Pople and coworkers [37] and their organometallic analogues as obtained from a geometry optimization procedure using the BSI basis set. The analogue of the η^2 acetylene complex is the corner protonated cyclopropene whereas the various isomers of the alkenyl complex correspond to the allyl (planar or perpendicular) or to the cyclopropyl cation. The η^1 alkenyl isomers **6** and **8** are more stable than the alkyne complex **1**, thus making the insertion reaction quite exothermic. We note that the out-of-plane isomer is as stable as the in-plane isomer, in sharp contrast with the organic situation where the perpendicular allyl cation is destabilized by more than 33 kcal mol^{-1} with respect to the planar allyl cation. In these two isomers the Pd–C bond does not bisect the N–Pd–Cl angle to yield a Y-shape geometry. One gets instead a T-shape geometry. The two above features point clearly to a preference for a σ type 2e stabilizing interaction, see **10**, rather than for a π type 2e stabilizing interaction, see **11**. The organometallic structures therefore lack the π conjugation (which for instance stabilizes strongly the planar form of the allyl cation) and cannot be considered as strict isolobal analogs of the organic structures. One should also point out that the η^2 coordination of the alkenyl **9** does not correspond to a true intermediate (*i.e.* a stationary point) since it could be obtained only by freezing the dihedral angles of the two H's and of CH_3 in $CH=CHCH_3$. Relaxing these angles led directly to the planar alkenyl system **8**.

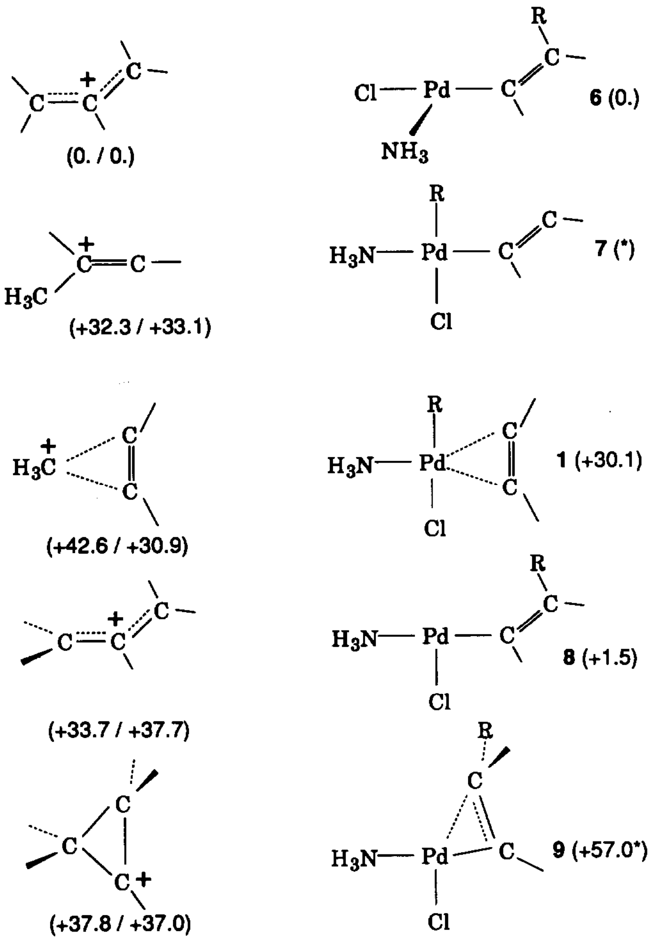
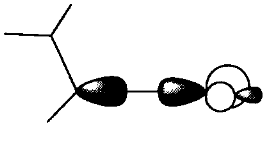
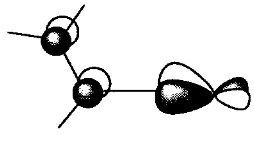


Fig. 2. Some isomers of $C_3H_{5^+}$ and their organometallic analogues (R=CH_3). For the $C_3H_5^+$ systems the relative energies (in kcal mol^{-1} SCF/MP2) energies are given [37]. For the organometallic system the relative energies (in kcal mol^{-1}) are SCF energies computed with the BSI basis set. The asterisk denotes a structure which is not a local minimum on the potential energy hypersurface.



10



11

Finally, as far as the conformation of the alkenyl ligand is concerned, a slight thermodynamic preference (0.5 kcal mol^{-1}) is found for the *trans* isomer of **8** (not

TABLE 1. Relative energy values (in kcal mol^{-1} BSII basis set [38*]) of the reactant, transition state and product for C_2H_2 insertion into the Pd–C bond of $[PdCl(NH_3)(CH_3)(C_2H_2)]$. The values in parentheses refer to the SCF calculations with the BSI basis set.

	$[PdCl(NH_3)$ $(CH_3)(C_2H_2)]$	TS	$[PdCl(NH_3)$ $(CH{=}CHCH_3)]$
SCF	0	+20.5 (+19.7)	−26.0 (−28.6)
CAS-SCF	0	+22.6	−19.3
CI	0	+17.1	−22.4

represented on Fig. 2). However, when the alkenyl ligand lies out of the Pd–Cl–N plane, the *cis* conformation **6** is the most stable (by 0.7 kcal mol^{-1}). These values are however very small and the order might well be reversed if a better basis set were used or if electron correlation were taken into account.

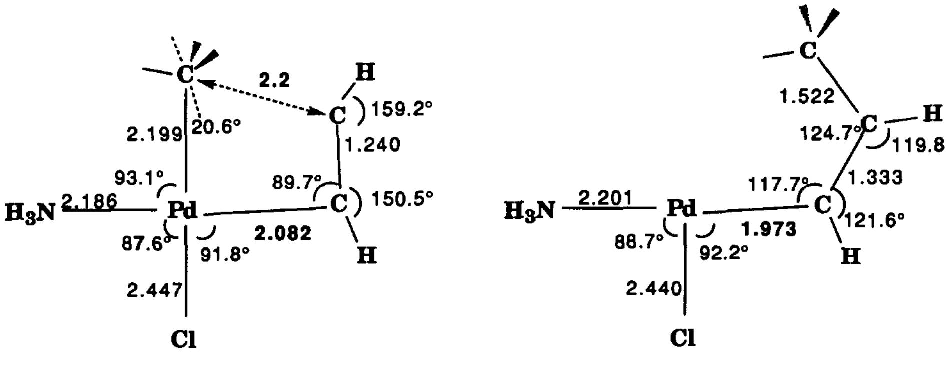
3.3. *The insertion reaction*

The energies for the C_2H_2 insertion reaction into the Pd–C bond of **1** are given in the Table 1 and the corresponding geometries of the transition state (TS) and of the alkenyl product **8** are shown schematically in the Fig. 3.

The comparison between the SCF and the CAS–SCF or CI values (see Table 1) indicates that the conclusions reached from the SCF calculations are not altered by the inclusion of correlation effects. The reaction is found to be quite exothermic (by about 22 kcal mol^{-1}) with an energy barrier of 17 kcal mol^{-1}. This value, although still rather high, is reasonable, considering that we are dealing here with an unsubstituted acetylene, in contrast to the experimental situation where electron-attracting substituents are necessary to produce an insertion (*vide infra*). One should also not forget, as mentioned before, that the reaction-coordinate method may exaggerate the energy barrier slightly.

In the transition state the acetylene has η^1 coordination and its geometrical parameters are not very much altered: the C–C bond length has increased by only 0.03 Å and the bending back of the hydrogen atoms remains quite limited, especially for the β hydrogen atoms. However, the Pd–C methyl bond length has been appreciably elongated (by 0.14 Å). This transition state appears to be less advanced towards the alkenyl product than the transition state computed by Nakamura *et al.* [32] for the addition of CH_3Cu to C_2H_2 [39]. In this reaction the O–C and Cu–C_{methyl} bond lengths increased by 0.07 and 0.17 Å respectively. The hydrogen atoms also bend back to a greater extent. The coordination of C_2H_2 is still η^2 and the two Cu–$C_{acetylene}$ bond distances are 2.14 and 2.26 Å. This dihapto coordination is even more pronounced in the transition state for the addition of $(CH_3)_2Cu^-$ to C_2H_2 [39]. In contrast in the transition state of the Pd insertion reaction the two Pd–C distances are 2.08 and 2.42 Å, thus suggesting η^1 coordination, which appears to be a property of the transition state rather than corresponding to an intermediate.

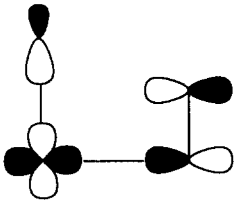
It is interesting to compare the above results with the results obtained by Koga *et al.* [23] for the insertion of ethylene into the Pd–H bond of $[PdH_2(PH_3)(C_2H_4)]$. There is a similarity in the geometries of the transition states. In each case the geometry of the unsaturated ligand is still on the reactant side: the C–C elongation is 0.06 Å in the ethylene case and 0.03 Å in the acetylene case, the Pd–C bond length is shortened by 0.26 Å in the ethylene case and by 0.49 Å in the acetylene case. However, the energetics of the two reactions differ somewhat. Ethylene insertion in the Pd–H bond is endothermic by 3 kcal mol^{-1} with a moderate energy barrier of 5.1 kcal mol^{-1} (MP2 values) [23]. Acetylene insertion in the Pd–C bond is much more exothermic but has to overcome a higher energy barrier.



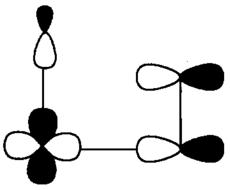
TS **8**

Fig. 3. SCF optimized geometries of the transition state and of the product of the C_2H_2 insertion reaction.

One of the reasons for the greater exothermicity of the acetylene insertion certainly lies in the poorer binding of acetylene to the palladium atom (*vide supra*) and to the smaller Pd–CH_3 bond energy as compared with the Pd–H bond energy. The greater energy barrier may be ascribed to the directionality of the methyl sp hybrid orbital. As in the ethylene insertion reaction [23], the transition state is characterized by two charge-transfer interactions, one between σ_{Pd-C} and $\pi^*_{C_2H_2}$ see **12**, and the other one between σ^*_{Pd-C} and $\pi_{C_2H_2}$ see **13**. Here the methyl sp hybrid orbital cannot interact with both the metal d and acetylene π^* orbitals in the transition state as efficiently as the spherical s hydride orbital would. A similar explanation has been given previously for the CO insertion reaction into either the Pd–H or the Pd–CH_3 bond to account for the fact that in the transition state region CO insertion into the Pd–H bond (which is in fact best viewed as a hydride migration) is more favourable [32].



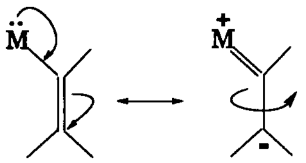
12



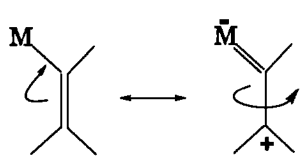
13

Another factor which can contribute to the greater energy barrier for acetylene insertion is the higher energy of the π^* orbital of the bound C_2H_2. For instance the π^* orbital energy is 3.23 eV in [PdCl(NH_3)(CH_3)(C_2H_2)] and 2.66 eV in [PdCl(NH_3)(CH_3)(C_2H_4) [40*]. A low π^* orbital energy also accounts for the fact that electron attracting substituents in the acetylene make the reaction easier [1]. Calculations carried out on CF_3CCH and [$H_3CO(O)C$ $-CC-C(O)OCH_3$] yield lowerings of the π^* orbital energy of 1.6 and 4.1 eV respectively. Similarly the LUMO of [(C_5H_5)$(CO)_2$MoCH] is quite low (3.4 eV lower than the $\pi^*_{C_2H_2}$ orbital). One therefore easily understand that a metallacarbyne will undergo an easy insertion reaction [3]. The reason why this insertion gives rise to a C–C coupling rather than a Mo–C coupling is probably thermodynamic in nature, the C–C bond energy being greater than a Mo–C bond energy. Calculations are in progress on this interesting reaction.

A recurrent question about the insertion mechanism deals with the stereochemistry of the product. Although alkyne insertion reactions generally proceed in a *cis* manner there are several known examples of an overall *trans* insertion [41]. It has been proposed that the reaction might start by a *cis* insertion followed by a *cis–trans* isomerization which would take place through some dipolar form of the alkenyl, either **14** or **15** depending on the nature of the metal.

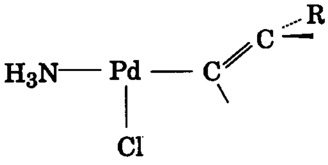


14



15

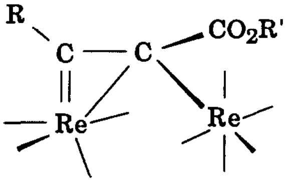
In the case of [Ni(acac)(PPh_3)(CH_3)]/alkyne Bergman proposed that the rotation depicted in **15** might be assisted by nucleophilic addition of a group to the β alkenyl carbon atom [5]. However, Nakamura and Otsuka [42] pointed out that it is difficult to describe the mechanistic details purely in terms of ionic or radical character and that even the geometry of the transition state may vary from planar to skewed according to subtle stereoelectronic effects. For the system under study the *trans* isomer is found to be slightly more stable than the *cis* isomer (by 0.5 kcal mol^{-1} at the SCF level with both geometries fully optimized). Nevertheless, a CAS–SCF calculation with a 5a6e active space designed to take account of possible delocalization of the C=C double bond over the Pd–C bond fails to show it [43*]. This precludes a facile rotation of the $CHCH_3$ moiety in the *monohapto* alkenyl product **8**. Indeed a calculation carried out for **16** (at the SCF level, with the geometrical parameters of **8**) yields a rotational barrier of 71.8 kcal mol^{-1}.



16

However, **16** was found through the geometry optimization procedure to relax to **9** (see the Fig. 2). In **9** the values of the Pd–C_α and C_α–C_β bond lengths (1.90 and 1.40 Å, respectively) clearly show the partial double-bond character of the Pd–C_α bond, at the expense of the C_α–C_β bond. A 5a6e CAS–SCF calculation also confirms this and puts **9** 43.1 kcal mol^{-1} above the alkenyl product **8**, *i.e.* in the vicinity of the transition state of the insertion reaction [44*]. One may therefore expect that a change in the alkyne or in the transition metal complex might make this skewed structure **9** more stable than the planar four-centred transition state. The acceptor orbital for nucleophilic addition on C_β is also lower in **9** than in **16**. Thus should the rotational process be assisted by a nucleophilic ligand as suggested by Huggins and Bergman [5], this again should occur more easily in a skewed form such as **9**.

Finally, in this context we note the mechanism recently proposed [45] for the insertion of activated alkynes $RC\equiv CCO_2R'$ into the metal–metal bond of a dirhenium complex $[Re_2L_{10}]$ to yield dimetallated olefin complexes that have a *trans* stereochemistry at the C=C double bond In this mechanism a key intermediate is **17**. If one now uses the isolobal analogy between ReL_5 and CH_3 on one hand, and between ReL_4 and CH_2^+ or $PdCl(NH_3)$ on the other hand, one easily sees that this intermediate is nothing else than the analogue of **9**.



17

4. Conclusion

We have shown in this study that acetylene seems to be quite weakly bound to Pd in square-planar Pd(II) complexes. This is due in part to weak π back donation from Pd to the π^* orbital of C_2H_2. Replacement of the hydrogen by an electron structure group or of a CH end by a metal organic entity such as $MoCp(CO)_2$ (or $W(Cp(CO)_2)$ appreciably lowers the π^* orbital and should lead to stronger binding.

The insertion of C_2H_2 is a relatively easy process, quite exothermic and with a rather moderate energy barrier. No monohapto intermediate seems to be involved, at least in the C_2H_2 case. The transition state displays monohapto coordination of the acetylene. A structure characterized by a rotation of 90° around the C_β atom is found to lie in the vicinity of the transition state and may be involved when the insertion leads to a *trans* alkenyl product.

We have restricted our analysis to monomeric square-planar palladium complexes. A real reaction starts most often from a dinuclear complex in which the two palladium atoms are bridged by two halides. The experimental evidence produced so far favours cleavage of one of the two Pd–Cl–Pd bridges opening coordination site to the incoming alkyne. Thus the reacting system can be viewed as having a $[Pd(\overset{\frown}{C\,N})Cl_2]^-$ ligand instead of the Cl^- of our model system. It would be interesting to assess the influence of this metal organic ligand on the course of the reaction. Calculations along these lines are currently planned.

Acknowledgements

The calculations were carried out on the IBM 3090 computer of the Centre de Calcul de Strasbourg Cronenbourg and on the CRAY2 computer of the CCVR in Palaiseau. We thank the staffs of these two computer centers for their cooperation. The stay of P.d.V. at the Laboratoire de Chimię Quantique was made possible through a grant of the European Community (Science Program, Contract No. SC1-0319-C(GDF)).

References and notes

1 For a review, see for instance: M. Pfeffer, *Recl. Trav. Chim. Pays Bas*, *109* (1990) 567.
2 A.D. Ryabov, R. van Eldik, G. Le Borgne and M. Pfeffer, *Organomet. 12* (1993) 1386.
3 P.E. Engel, M. Pfeffer, J. Fischer, and A. Dedieu, *Chem. Comm.* (1991) 1294.
4 J. Silvestre and R. Hoffmann, *Helv. Chim. Acta, 68* (1985) 1461.
5 See for instance: J.M. Huggins and R.G. Bergmann, *J. Am. Chem. Soc., 103* (1981) 3002.
6 (a) R. Ernenwein, M.-M. Rohmer and M. Bénard, *Comp. Phys. Commun., 58* (1990) 305; (b) M.-M. Rohmer, J. Demuynck, M. Bénard and R. Wiest, *Comp. Phys. Commun., 60* (1990) 127; (c) R. Wiest, J. Demuynck, M. Bénard, M.-M. Rohmer and R. Ernenwein, *Comp. Phys. Commun., 62* (1991) 107.
7 The original (14,9,8) basis set [8] was modified by the addition of a p function of exponent 0.15 for Mo and 0.08386 for Pd.
8 A. Veillard and A. Dedieu, *Theoret. Chim Acta, 65* (1984) 215.
9 S. Huzinaga, Technical Report, University of Alberta, Edmonton, 1971.
10 S. Huzinaga, *J. Chem. Phys., 42* (1965) 1293.
11 The (15,9,8) basis set was modified by the addition of an s primitive of exponent 0.3056 to suppress the gap between the functions needed to describe the widely separated 4s and 5s shells and two p functions of exponents 0.2356 and 0.08386 to describe the 5p shell and one d function of exponent 0.07890. These exponents were chosen according to the even tempered criterion [12].
12 R. Raffenetti, R.D. Bardo and K. Ruedenberg, in D.W. Smith, W.B. Mc Rae (eds.), *Energy Structure and Reactivity*, Wiley, New York, 1973, p. 164.
13 (a) B.O. Roos, P.R. Taylor and P.E.M. Siegbahn, *Chem. Phys., 48* (1980) 157; (b) P.E.M. Siegbahn, J. Almlöf, A. Heiberg and B.O. Roos, *J. Chem. Phys., 74* (1981) 2384; (c) B.O. Roos, *Int. J. Quantum Chem. Symp., 14* (1980) 175.
14 P.E.M. Siegbahn, *Int. J. Quant. Chem., 23* (1983) 1869.
15 E.R. Davidson, in R. Daudel and B. Pullman (eds.), *The World of Quantum Chemistry*, Reidel, Dordrecht, 1974, p. 17.
16 P. de Vaal, M. Bénard and C. Pouchan, to be published.
17 C.A. Jolly and D.S. Marynick, *J. Am. Chem. Soc., 111* (1989) 7968.
18 The corresponding total energies (BS I) are −5558.6689 (1 a.u. = 627.5 kcal mol^{-1} for $[PdCl(NH_3)(CH_3)(C_2H_2)]$ in its optimum in-plane geometry, −5481.9069 a.u. and −76.7432 a.u. for $PdCl(NH_3)(CH_3)$ and C_2H_2 in their optimum geometries. The energy difference −11.8 kcal mol^{-1} is corrected by the basis set superposition error [19] which is computed to be 6.0 kcal mol^{-1} by the counterpoise method [20].
19 For a review, see W. Kolos, *Theor. Chim. Acta, 51* (1979) 219.

20 (a) S.F. Boys and F. Bernardi, *Mol. Phys.*, *19* (1970) 553; (b) N.S. Ostlund and D.L. Merrifield, *Chem. Phys. Lett.*, *39* (1976) 612.

21 See for instance: S. Sakaki, K. Maruta and K. Ohkubo, *Inorg. Chem.*, *26* (1987) 2499 and references therein.

22 Note also that the complete geometry optimization of the $PdH_2(PH_3)(C_2H_4)$ in-plane system by Koga *et al.* led to a Pd–C bond of 2.49 Å [23].

23 N. Koga, S. Obara, K. Kitaura and K. Morokuma, *J. Am. Chem. Soc.*, *107* (1985) 7109.

24 In $[PtCl_3(C_2H_4)]^-$ the inclusion of the correlation effects strengthens the binding of C_2H_4 by 9 to 15 kcal mol^{-1} depending on the method used [25]. One would not expect effects of the same magnitude in the Pd system because in the Pt system π back donation effects are at work and need a post-SCF treatment to be accounted for. Calculations performed by Blomberg *et al.* [26] on $Pd(C_2H_4)$ and $PdH_2(C_2H_4)$ have shown that relativistic corrections increase the binding energy by about 10 kcal mol^{-1} [26,27].

25 S. Sakaki and M. Ieki, *Inorg. Chem.*, *30* (1991) 4218.

26 M. Blomberg, J. Schüle and P.E.M. Siegbahn, *J. Am. Chem. Soc.*, *111* (1989) 6156.

27 M. Blomberg, P.E.M. Siegbahn and M. Svensson, *J. Phys. Chem.*, *96* (1992) 9794.

28 (a) The corresponding total energies are: for **1**, −5558.6689 a.u. and −5558.8892 a.u. with the basis set BS I and BS II respectively. For **2** −5558.6658 a.u. and −5558.8881 a.u. with the basis sets BSI and BSII respectively. This gives an energy difference of 1.9 kcal mol^{-1} with the smaller basis set and 0.7 kcal mol^{-1} with the larger basis set at the SCF level. The corresponding CAS–SCF values (obtained with the BS II basis set) are −5559.0252 a.u. and −5559.0233 a.u. for **1** and **2** respectively, thus giving an energy difference of 1.2 kcal mol^{-1}. (b) For an intermediate conformation corresponding to a 45° rotation of the acetylene ligand, the optimization of the geometry led to a total energy of −5558.6679 a.u. (BSI calculation), i.e. between the energies obtained for **1** and **2**. We therefore do not expect any barrier between **1** and **2**.

29 The corresponding SCF total energies (BSI) are: for the in-plane geometry −5100.2462 a.u.; for the out-of-plane geometry −5100.2450 a.u.

30 G.R. Davies, W.H. Hewerston, R.H.B. Maise, P.G. Owston, and C.G. Patel, *J. Chem. Soc.* (1970) 1873.

31 A.L. Beauchamp, F.R. Rochon and T. Theophanides, *Can. J. Chem.*, *51* (1973) 126.

32 N. Koga and K. Morokuma, in A. Dedieu (ed.), *Transition Metal Hydrides*, VCH, New York, 1991, p. 185.

33 F. Calderazzo and D.B. Dell'Amico, *Inorg. Chem.*, *20* (1981) 1310.

34 See for instance: T.A. Albright, *J. Organomet. Chem.*, *198* (1980) 180.

35 G. Marinelli, W.E. Streib, J.C. Huffman, K.G. Caulton, M.R. Gagné, J. Takats, M. Dartiguenave, C. Chardon, S.A. Jackson and O. Eisenstein, *Polyhedron*, *9* (1990) 1867.

36 P. Engel, A. Dedieu and M. Pfeffer, to be published.

37 K. Raghavachari, R.A. Whiteside, J.A. Pople and P.v.R. Schleyer, *J. Am. Chem. Soc.*, *103* (1981) 5649.

38 The corresponding total SCF energies (in a.u.) are: $[PdCl(NH_3)\text{-}(CH_3)(C_2H_2)]$ −5558.8892; TS −5558.8566; $[PdCl(NH_3)(CH{=}CHCH_3)]$ −5558.9306. The corresponding total CAS–SCF energies (in a.u.) are: $[PdCl(NH_3)\text{-}(CH_3)(C_2H_2)]$ −5559.0252; TS −5558.9892; $[PdCl(NH_3)(CH{=}CHCH_3)]$ −5559.0559. The corresponding total CI energies (in a.u.) are: $[PdCl(NH_3)(CH_3)(C_2H_2)]$ −5559.0529; TS −5559.0256; $[PdCl(NH_3)(CH{=}CHCH_3)]$ −5559.0886.

39 E. Nakamura, Y. Miyachi, N. Koga and K. Morokuma, *J. Am. Chem. Soc.*, *114* (1992) 6686.

40 For an out of plane conformation of either C_2H_2 or C_2H_4.

41 See D. Zargarian and H. Alper, *Organomet.* *10* (1991) 2914 and references therein.

42 A. Nakamura and S. Otsuka, *J. Mol. Cat.* (1976) 285.

43 This CAS–SCF wave function used five active orbitals populated by six electrons, distributed as given by the computed occupation numbers: π_{alkenyl} (1.909); $4d_{x^2-y^2}+p_{C_\alpha}$ (1.882); $4d_{yz}$ (1.996); $4d_{x^2-y^2}-p_{C_\alpha}$ (0.178); π^*_{alkenyl} (0.095). The high population of the $4d_{yz}$ orbital indicates that there is no π bonding between $4d_{yz}$ and the π^*_{alkenyl} orbital. The computed total energy of **8** with this 5a6e active space is −5559.0048 a.u.

44 The total CAS–SCF 5a6e energy of **9** is −5558.9361 a.u. We were not able to obtain a stable 10a10e CAS–SCF wavefunction for **9** which could give an energy directly comparable with the energy of **1**. However putting together the 43.1 kcal mol^{-1} (5a6e CAS value) energy difference between **9** and **8** and the 41.9 (10a10e CAS value) energy difference between TS and **8** (see the Table 1) indicates that **9** and the TS are close to each other.

45 R.D. Adams, L. Chen and W. Wu, *Organomet.*, *12* (1993) 1257.