Central versus Terminal Attack in Nucleophilic Addition to (π-Allyl)palladium Complexes. Ligand Effects and Mechanism

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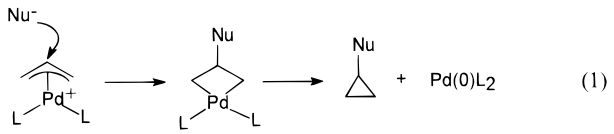
Nucleophilic addition to (η^3-2-chloropropenyl)palladium complexes **1** with stabilized carbanions such as dialkyl malonates was studied. These complexes are used as probes to determine whether nucleophilic attack occurs at the central or terminal carbon of the π-allyl group. Attack at the central carbon leads to substitution of chloride via a palladacyclobutane intermediate. The regiochemistry of the reaction (central versus terminal attack) is controlled by proper choice of ligands. Thus, σ-donor ligands direct the attack of the nucleophile to the central carbon (C-2) of the allyl group whereas π-acceptor ligands direct the attack to the terminal carbons (C-1 or C-3). It was found that there is a correlation between the relative rate of central versus terminal attack and the ^{13}C NMR shifts of the allyl group. The shift difference between the central and terminal carbons, $C_c - C_t$, can be used to predict the site of attack. *Ab initio* calculations were performed on (π-allyl)palladium complexes as well as on the postulated palladacyclobutane. The calculations support the experimental results, and for the π-allyl complexes with the σ-donor ligands the LUMO from the calculations is the symmetrical orbital with a large coefficient at the central carbon.

Introduction

(π-Allyl)palladium complexes are important intermediates in a number of catalytic reactions such as allylic substitution,[1] allylic oxidation,[2] and 1,4-oxidation of conjugated dienes.[3] These reactions involve nucleophilic addition of heteroatom or carbon nucleophiles on the allyl moiety. The ancillary ligands involved, as well as the nature of the nucleophile, play an important role in both the rate and the regiochemical outcome of these reactions.[1,4−6] In general the reaction proceeds faster in the presence of π-acceptor ligands and the nucleophile attacks either terminus (C-1 or C-3) of the allyl moiety. However, with some σ-donor ligands and with less stabilized carbon nucleophiles (pK_a 20−30) nucleophilic attack at the central carbon to yield cyclopropane derivatives has been demonstrated (eq 1).[5,6]



(1)

Hegedus[5] reported the first example of this type of reaction and proposed the mechanism outlined in eq 1, and since then, several other examples have been reported.[6] Hoffmann[6a] has proven this mechanism by isolating and characterizing the proposed palladacyclobutane[7,8] intermediate. In a preliminary communication[6b] we reported that also more stabilized carbon nucleophiles such as branched dialkyl malonates attack the central carbon of (π-allyl)palladium complexes under certain conditions. We now give a full account of the previous study, report additional results on ligand effects, correlate the relative reactivity of central versus terminal attack with ^{13}C NMR shifts,

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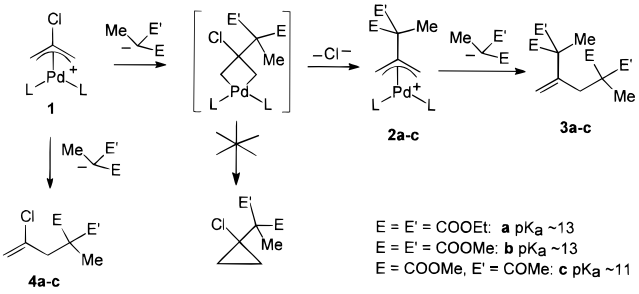
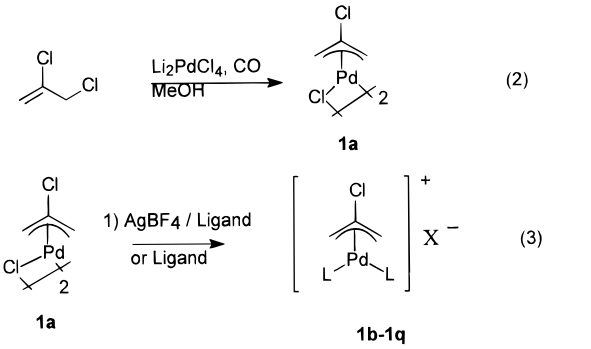
Scheme 1



provide support from theoretical calculations, and discuss the different factors governing whether central or terminal attack occurs.

Results and Discussion

A. Preparation of (π-Allyl)palladium Complexes. The (η^3-2-chloropropenyl)palladium complex **1a** was prepared from 2,3-dichloropropene and palladium chloride in the presence of carbon monoxide (eq 2).[9a]



Complex **1a** is a known compound[9b] for 30 years, and such 2-chloro π-allyl complexes of platiunum and palladium were recently generated in situ in catalytic reactions for studying the site of nucleophilic attack.[8a] The cationic complexes **1b**−**q** were prepared in situ from the chloro dimer **1a** either by treatment with $AgBF_4$ and subsequent addition of the appropriate ligands or just by adding the ligands to the solution of **1a** (eq 3). The cationic tetrafluoroborate complexes were characterized by their ^1H and ^{13}C NMR spectra.

B. Reaction of (π-Allyl)palladium Complexes 1 with Carbon Nucleophiles. The (π-allyl)palladium complexes **1** were reacted with sodium diethyl methylmalonate, sodium dimethyl methylmalonate, or sodium methyl methylacetoacetate, in the presence of different ligands (Scheme 1).

Attack by the nucleophile at the terminal carbon leads to the monoalkylated product **4**, which can be isolated and characterized. On the other hand, an initial attack at the central carbon, followed by the elimination of the chloride and subsequent addition to the terminal carbon, yields the doubly alkylated product **3**. Cyclopropane formation from the 2-chloropalladacyclobutane intermediate is unlikely and has not been observed under the reaction conditions employed in this study.

Table 1. Variation of Ligands and Nucleophiles[a]

entry	complex	ligand (equiv)	nucleophile	products **3**:**4**[b]
1	**1b**	TMEDA (2)	$NaC(Me)(CO_2Et)_2$	>99:<1
2	**1c**	bipy (2)		>99:<1
3	**1d**	TMPDA		95:5
4	**1e**	TMMDA[c]		2:98
5	**1f**	TMBDA[c]		2:98
6	**1g**	dppb (2)		10:90
7	**1h**	$P(OPh)_3$ (6)		<1:>99
8	**1j**	PPh_3 (4)		<2:>98
9	**1k**	dppf (2)		<1:>99
10	**1l**	PBu_3 (4)		13:87
11	**1m**	dppe (2)		25:75
12	**1n**	COD		2:98
13	**1o**	DMSO		2:98
14	**1p**	$BuS(CH_2)_2SBu$		2:98
15	**1q**	phenyl-BIP[10]		2:98
16	**1b**	TMEDA	$NaC(Me)(CO_2Me)_2$	>99:<1
17	**1d**	TMPDA		>99:<1
18	**1j**	PPh_3		3:97
19	**1b**	TMEDA	Na(Me)C(COMe)(CO2Me)	<1:>99

[a] Abbreviations: TMEDA: *N,N,N′,N′*-tetramethylethylenediamine. TMPDA: *N,N,N′,N′*-tetramethyl-1,3-propanediamine. TMMDA: *N,N,N′,N′*-tetramethylmethanediamine. TMBDA: *N,N,N′,N*-tetramethyl-1,4-butanediamine. COD: 1,5-cyclooctadiene. dppf: 1,1′-bis(diphenylphosphino)ferrocene. dppe: 1,2-bis(diphenylphosphino)ethane. dppb: 1,4-bis(diphenylphosphino)butane. bipy: 2,2′-bipyridine. Phenyl-BIP: (*Z,Z*)-9,10-bis(phenylimino)-9,10-dihydrophenanthrene. [b] The isolated yields of products were in the range 75−95%. [c] Yield not determined.

1. Central versus Terminal Attack: Ligand Effects. Several different ligands were tried in combination with the variation of nucleophiles. It was found that the regioselectivity of the reaction can be controlled to a great extent by a proper choice of ligands and the nucleophile (Table 1). The influence of the ligands on the regioselectivity is related to their σ-donor versus π-acceptor properties. Thus, σ-donor nitrogen ligands such as TMEDA, TMPDA, or bipy (entries 1−3) gave mainly **3a**, arising from an initial central attack. Nitrogen ligands such as TMMDA and TMBDA, which are not able to form stable bidentate complexes with the (π-allyl)palladium fragment, gave rise to product **4a** (entries 4 and 5). π-Acceptor ligands, on the other hand, like PPh_3, $P(OPh)_3$, dppf, phenyl-BIP, or COD, gave only **4a** (entries 7−9, 12, and 15) indicating an initial terminal attack. Using the more σ-donating phosphine ligand PBu_3 resulted in a significant drop in the regioselectivity (entry 10). Sulfoxide or sulfide ligands gave mainly product **4** (entries 13 and 14). These sulfur ligands have considerable π-acceptor character which drives the reaction to terminal attack. It is particularly interesting that DMSO, which is a potential solvent in palladium chemistry, is capable of directing the nucleophile to the terminal carbon.

Very similar results were obtained with sodium methyl dimethylmalonate as a nucleophile, though it was only tested for some representative ligands which give either clean central or terminal attack (entries 16−18). Reaction of complexes **1** with a considerably more stabilized carbon nucleophile, such as sodium methyl methylacetoacetate ($pK_a \sim 11$),[11] afforded product **4c**

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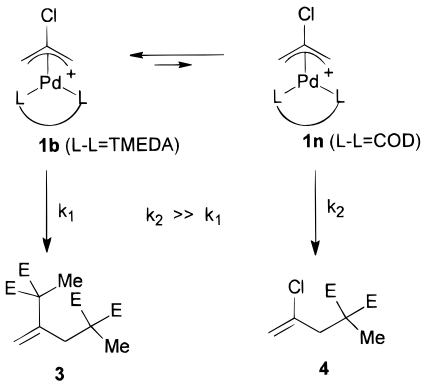
Table 2. Competitive Experiments with π-Acceptor vs σ-Donor Ligands

entry	ligand (ratio)	product ratio **3**:**4**
1	TMEDA:PPh_3 (1 equiv:0.5 equiv)	2:98
2	TMEDA:PPh_3 (0.8 equiv:0.4 equiv)	5:95
3	TMEDA:COD (0.5 equiv:0.5 equiv)	5:95

Scheme 2



from terminal attack *even if TMEDA was used as a ligand* (entry 19).

2. Competitive Experiments. Competitive experiments were made with both π-acceptor and σ-donor ligands present in the reaction mixture, and the results are summarized in Table 2. In all cases the major product is that from initial terminal attack on the allyl moiety. It is interesting to note that even in the case of COD, which has a much smaller complexation constant with Pd(II) than TMEDA, product **4** is formed in about 95% relative yield. Thus, the major product of the reaction is obtained via terminal attack on the less stable COD complex (Scheme 2). This may be explained by the significantly larger rate constant (k_2) for the reaction of the COD complex compared to that of the TMEDA complex (k_1). Here k_1 refers to the nucleophilic attack at the middle carbon, which is an irreversible process. The results show that the rate of the nucleophilic addition to the π-allyl systems is always faster in the case of π-acceptor ligands. Therefore, if both types of ligands are present in the reaction mixture, even a weakly coordinating π-acceptor ligand can direct the reaction toward terminal attack.

3. Effect of the Concentration. Another important factor determining the regiochemical outcome of the reaction is the concentration of the reaction mixture. We observed that, on dilution, the TMEDA complex **1b** showed a decreased selectivity for central attack. Thus, on 10 times dilution the ratio of central attack to terminal attack changed from 99:1 to 66:34 in the reaction of **1b** with sodium diethyl methylmalonate. A likely explanation of this result is that the reaction partially proceeds via the asymmetric monocoordinated TMEDA complex which give rise to terminal attack to give product **4**.

C. Correlation with ^{13}C NMR. A simple way of measuring the influence of a ligand on the π-allyl system is to look at the ^{13}C NMR shifts of the allyl moiety. Cationic tetrafluoroborate complexes **1b**,**d**,**h**,**j**,**n**,**p** were obtained from the chloro dimer **1a** as described above, and their ^{13}C NMR spectra were recorded. The results are given in Table 3.

A comparison of π-allyl complexes having σ-donor ligands like TMEDA (**1b**) or TMPDA (**1d**) with the unreactive chloro dimer **1a** shows that the central carbon is shifted downfield about 7 ppm for the former complexes while the terminal carbon shift is essentially unchanged. In the reactions, these ligands direct the first nucleophilic attack to the middle carbon of the π-allyl moiety. On the other hand, the effect of π-acceptor ligands on the central carbon shift is about the same as for the σ-donors, but there is a dramatic increase in the shift of the terminal carbons (16 ppm for **1j**). These complexes gave products arising from initial terminal attack on the π-allyl moiety. An inspection of the data shows that the shift difference between the central and terminal carbon, $C_c - C_t$, can be used to predict the regiochemistry of the attack; a small difference (<61 ppm) is indicative for terminal attack while a large difference (>67 ppm) is indicative for central attack.

Table 3. ^{13}C NMR Shifts in $CDCl_3$ of the (η^3-2-Chloropropenyl)palladium Tetrafluoroborate Complexes[a]

		chem shifts in ppm		
complex	ligand	C_c	C_t	$C_c - C_t$
1a	Cl dimer	123.90	62.6	61.3
1b	TMEDA	130.01	61.31	68.7
1d	TMPDA	130.56	63.29	67.27
1h	$P(OPh)_3$	133.32	74.11	59.21
1j	PPh_3	131.29	78.72	52.57
1n	COD	133.06	76.43	56.63
1p	$BuS(CH_2)_2SBu$	129.96	69.02	60.94

[a] The complexes were prepared according to eq 3, employing $AgBF_4$ followed by addition of the appropriate ligand.

D. Theoretical Calculations. To gain further insight into the mechanism of the experimental results, theoretical calculations were undertaken. These calculations involve (π-allyl)palladium complexes and palladacyclobutanes.

1. π-Allyl Complexes. *Ab initio* calculations at the Hartree−Fock (HF) level as well as at the second-order Møller−Plesset (MP) perturbation theory were performed on (π-allyl)palladium complexes **5**. Four different types of ligands, ammonia, phosphine, ethylene, and TMEDA, were employed for the simple π-allyl complex **5a**. To estimate the effect by the chloride sustituent on the properties of the π-allyl group we also made a calculation on the 2-chloro π-allyl complex **5b**.

L = NH_3, PH_3, CH_2=CH_2, TMEDA

The frontier orbitals of importance for the reactivity are shown in Scheme 3. In particular the two lowest unoccupied orbitals 2a′ and 2a″ (Figure 1) will play an important role in determining the regioselectivity of the nucleophilic attack, *i.e.* central versus terminal attack. The HF calculations show that the orbitals 2a′ and 2a″ are close in energy, the difference being in the range 0.1−0.6 eV (Table 4). With ammonia and TMEDA as ligands the LUMO of complex **5a** is the symmetrical 2a′ type MO whereas for phosphine and ethylene the LUMO is the antisymmetrical 2a″ type MO. Interestingly, the largest difference between the orbitals 2a′ and

Scheme 3

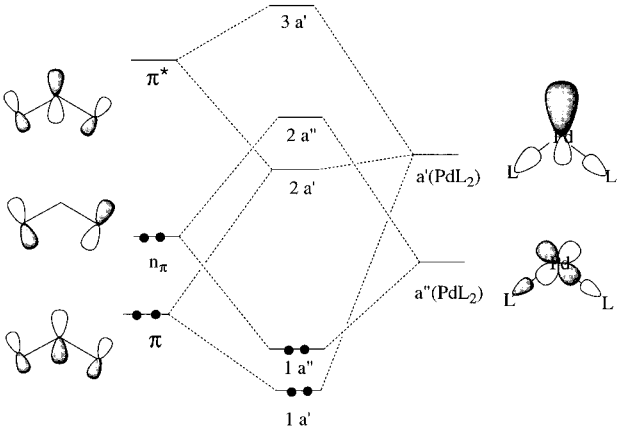


Table 4. Lowest Unoccupied MO's for Complexes 5[a]

L	2-subsituent	$E_{2a'}$ (eV)	$E_{2a''}$ (eV)	LUMO
NH_3	H	−1.8	−1.4	2a′
NH_3	Cl	−1.9	−1.6	2a′
TMEDA[b]	H	−1.2	−0.6	2a′
PH_3	H	−1.8	−1.9	2a″
$CH_2{=}CH_2$[c]	H	−2.1	−2.4	2a″

[a] For orbitals 2a′ and 2a″ see Figure 1 and Scheme 3. [b] The C_s symmetry of the complex is lowered by the distortion of the TMEDA ligand; however, the local C_s symmetry of the allyl−Pd fragment is well preserved and the LUMO is a 2a′ type MO. [c] The C_s symmetrical form does not represent a minimum on the PES (cf. ref 4a).

2a″ was obtained for TMEDA, which is in line with the experimental observations.

Although the difference between the 2a′ and 2a″ levels is small, the calculations predict that for a frontier orbital controlled nucleophilic attack, σ-donor ligands direct the attack to the central carbon whereas π-acceptor ligands direct the attack to the terminal carbon. It is important to note, however, that for a nucleophile with a low HOMO energy, the reaction may become charge controlled.[12] For a cationic (π-allyl)-palladium complex a charge-controlled nucleophilic attack is expected to occur at the terminal carbon (vide infra).[13]

According to Scheme 3 the energy of the two low-lying virtual orbitals 2a′ and 2a″ can vary depending on the ligands.[4a,6b] Strong σ-donor ligands raise and slightly lower the a″(PdL_2) and a′(PdL_2) levels, respectively. As a consequence, the 1a″−2a″ splitting is increased and 2a′ is slightly decreased and becomes the LUMO (cf. entry 1, Table 4). On the contrary, coordination of π-acceptor ligands involves charge transfer from the metal to the ligand through back-donation that leads to orbital contraction and as a consequence a lowering of the 2a″ level. The ligand effects on the MO interactions are reflected, for example, by the Pd−C bonding: in (π-allyl)PdL_2 complexes with σ-donor ligands the Pd−C bond lengths are 2.08−2.15 Å, while with π-acceptor ligands the Pd−C bonds are much longer and weaker, 2.19−2.22 Å.[4a,14] This is consistent with the higher reactivity toward nucleophiles of the (π-allyl)-palladium complexes with π-acceptor ligands compared to those with σ-donor ligands.

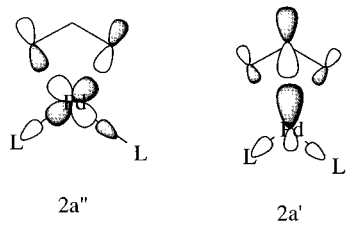


Figure 1. Low-lying unoccupied MO's in a (π-allyl)PdL_2 complex (see also Scheme 3).

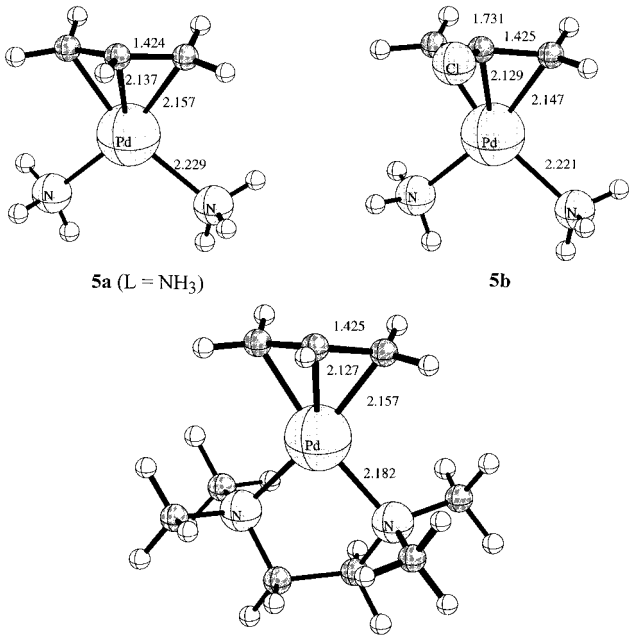


Figure 2. MP2 geometries of selected (π-allyl)PdL_2 complexes (L = NH_3, TMEDA). The bond lendths are given in Å.

The calculated structures for **5a** (L = NH_3 and TMEDA) and **5b** are shown in Figure 2. It is interesting to note that in all three structures the C−C bond lengths of the π-allyl are the same (1.424−1.425 Å). Also there are only minor variations in the Pd−C^1 bond (2.147−2.157 Å) and Pd−C^2 bond (2.129−2.139 Å) between the three different structures. The most significant difference in bond length between the structures is found in the Pd−N bond. Whereas for **5a** (L = NH_3) and **5b** the Pd−N bond is 2.229 and 2.221 Å, respectively, for **5a** (L = TMEDA) it is 2.182 Å. Importantly, there are no significant differences in bond lengths between the π-allyl complex **5a** (L = NH_3) and the corresponding 2-chloro-π-allyl complex **5b**. Also the lowest unoccupied orbitals 2a′ and 2a″ for these complexes are not very different (Table 4, entries 1 and 2). Thus, the 2-chloro-π-allyl complexes should be good probes for the mechanistic studies done in this work.

2. Palladacyclobutanes. The calculations were carried out at the MP2 level of theory assuming C_s symmetry for the complexes. Geometry optimization of the 2-chloro-substituted complex leads to equilibrium

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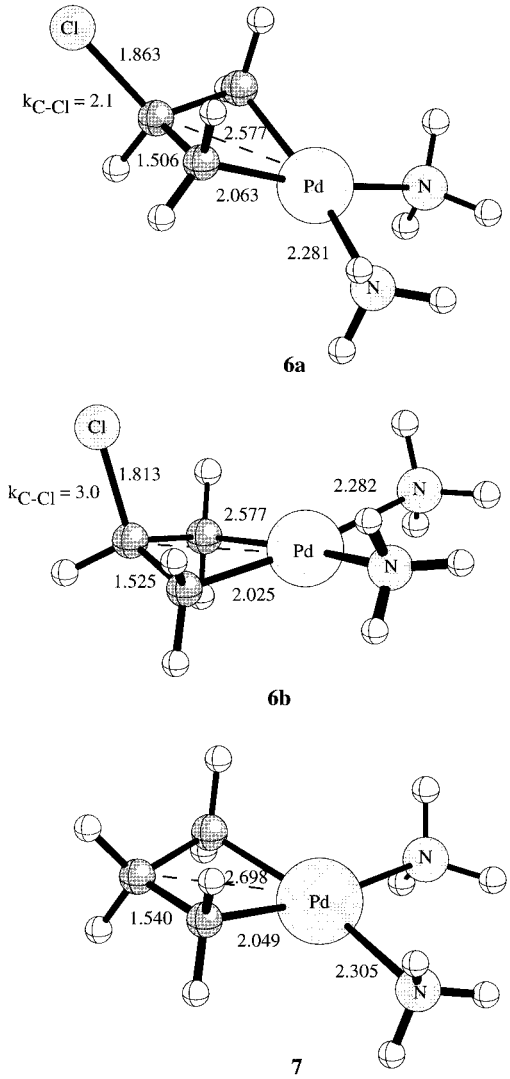

Figure 3. MP2 geometries and C−Cl force constants (k_{C-Cl}) of palladacyclobutane complexes **6** and **7**. The bond lengths are given in Å and the force constants in mdyn/Å.

structure **6a** (Figure 3), which shows some remarkable geometrical features. The C^2−Cl bond (1.86 Å) is 0.07 Å longer than the calculated C−Cl bond length in CH_3Cl (1.79 Å, MP2), and the C^1−C^2 bond (1.50 Å) is considerably shorter than a normal C−C single bond (1.54 Å). When the Cl substituent of **6a** is replaced by a H (**7**), the C^1−C^2 bond is lengthened by 0.04 Å. Weakening of the C^2−Cl bond in **6a** is also reflected by its low stretching force constant (k_{C-Cl} = 2.1 mdyn/Å), which is smaller than the C−Cl stretching force constant in CH_3Cl (k_{C-Cl} = 3.5 mdyn/Å, MP2) by about 40%.

In **6a** the Cl and Pd atoms are on the opposite sides of the C^1−C^2−C^3 plane; i.e., these atoms are in a *trans* position. The *cis* arrangement (**6b**) does not represent a minimum on the MP2 potential energy surface. However, a *cis* structure **6b** can be obtained by freezing the C^2−Pd distance at 2.577 Å, which is the C^2−Pd distance in **6a**. In **6b** the C−Cl bond (1.813 Å) is considerably shorter, while the C^1−C^2 bond (1.525 Å) is longer than in **6a**. The total energy of **6b** is 8.3 kcal/mol higher than that of **6a**.

Appearance of the above structural effect can be attributed to a homoconjugative interaction between a low-lying σ^*(C−Cl) orbital and a filled d_σ orbital of palladium. This interaction involves charge transfer from the d_σ orbital to the antibonding σ^*(C−Cl) orbital. As a consequence, the C−Cl bond is weakened and C^2 is partially coordinated to palladium, which lends C^1−C^2−C^3 similarity to an η^3-allyl moiety. When the chloro substituent is replaced by a hydrogen (**7**) the energy level of the σ^* orbital is raised;[15] thereby, the homoconjugative interaction is suppressed. Because of the homoconjugative interactions, **6a** can easily be decomposed to a (π-allyl)PdL_2 complex and a chloride ion. Thus the reactivity of the proposed palladacyclobutane intermediate in Scheme 1 is supported by the theoretical results.

We note that electronic interactions between Pd and (C^2)═O in 2-palladacyclobutanones have previously been described by Kemmit and co-workers[16] designating them as transannular interactions. However, these interactions do not influence considerably the stability of 2-palladacyclobutanones due to the strong carbon−oxygen double bond. Furthermore, it is probable that homoconjugative interactions between polar C^2−X bonds and metal atoms in metallocyclobutanes are not restricted to palladium complexes. Tjaden and Stryker,[8b,17] for instance, have described transannular interactions in iridacyclobutane derivatives.

E. Mechanism. As shown in Scheme 1, nucleophilic attack on **1** may give rise to three different products: alkenes **3** and **4** as well as a cyclopropane derivative. Cyclopropane formation is not observed since in the palladacyclobutane intermediate (Scheme 1) the activation energy for reductive elimination is considerably higher than that for elimination of chloride. The above experimental findings clearly indicate that the ratio **3**:**4** can be controlled by the ligands on palladium. Phosphorus ligands with distinct π-acceptor character (PPh_3, $P(OPh)_3$) favor terminal attack, whereas σ-donor ligands (e.g. TMEDA, bipy) favor C-2 attack (Table 1). Obviously, the σ-donor and π-acceptor ligands exert different electronic effects on the π-allyl moiety, which influence the regioselectivity of the nucleophilic attack. These electronic effects have an influence on the energy levels of the frontier orbitals as well as on the charges at the different carbons of the π-allyl group. These effects are nicely reflected by the ^{13}C NMR shifts (Table 3).

Previous theoretical calculations have been made on (π-allyl)palladium complexes in an effort to study central versus terminal attack by nucleophiles.[6h,18] These calculations were made at the extended Hückel (EHMO) level. Curtis and Eisenstein[18] made a careful analysis of different (π-allyl)metal complexes and proposed that the nucleophilic addition is frontier orbital controlled. For the (π-allyl)palladium case[19] their calculation indicated that antisymmetric 2a″ (cf. Figure 1) is the only energetically accessible LUMO. As a consequence, they concluded that nucleophilic attack at the central carbon of (π-allyl)palladium complexes is unlikely.

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(19) In their calculation chlorides were used as ligands.

In another EHMO calculation[6h] it was concluded that the symmetrical 2a′ level (cf. Figure 1) competes with the 2a″ level to be the LUMO of the system and as a result central attack would be possible.

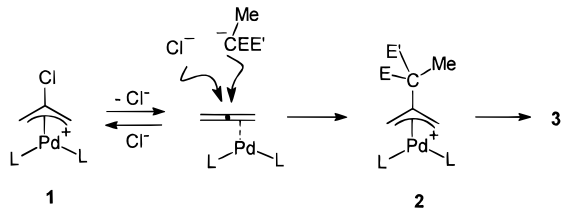
Our calculations indicate that with σ-donating ligands, such as TMEDA, the symmetric orbital 2a′ (Scheme 3, Figure 1) is indeed the LUMO. This is in line with frontier orbital control in the nucleophilic attack at the central carbon and confirms the experimental observation that a σ-donor ligand is necessary for such an attack.

For a frontier orbital controlled reaction the rate will depend inversely on the difference $E_{LUMO} - E_{HOMO}$,[12,20] where in our case we have the LUMO of the π-allyl complex and the HOMO of the nucleophile. If we consider a case with a given (π-allyl)palladium complex and vary the nucleophile, the E_{LUMO} will be constant whereas the E_{HOMO} will vary. For a nucleophile with a high-lying HOMO the reaction will therefore be fast, but for a nucleophile with a low-lying HOMO the reaction will be slow. This is consistent with the observations that strong carbon nucleophiles with a high pK_a easily undergo attack at the central carbon and that examples from more stabilized carbanions are scarce. The former nucleophiles should have a higher HOMO compared to the latter.

The observed central attack by dialkyl malonates (pK_a ≈ 13) on complex **1b** shows that the difference $E_{LUMO} - E_{HOMO}$ is still in the range to give a frontier orbital controlled reaction. However, for the reaction of methyl methylacetoacetate (pK_a ≈ 11) with complex **1b** the difference $E_{LUMO} - E_{HOMO}$ has further increased, because of the lower energy of the nucleophile orbital (HOMO), and we have reached the point where a frontier orbital controlled reaction turns into a charged controlled reaction.[20,21]

When the ligands are changed from σ-donor ligands to π-acceptor ligands, the order of 2a′ and 2a″ is changed and now the antisymmetric 2a″ is below 2a′. Thus, with these ligands terminal attack is predicted with a frontier orbital controlled reaction. These ligands would also increase the charge on the π-allyl carbons and increase the rate of a charge-controlled reaction. In their analysis of nucleophilic attack on polyenes coordinated to transition metals, Davies, Green, and Mingos[13] employed a simplified model based on complete charge control. Their analysis predicts attack at the terminal carbon on (π-allyl)palladium complexes.[22] With an electron-accepting ligand such as PPh_3 significant carbonium character is developed at the allyl moiety. The complex can be viewed as an allyl cation coordinated to Pd(0), and the positive charge would be located on terminal carbons of the allyl group. The conclusion is that for the (π-allyl)palladium complexes with π-acceptor ligands *both* frontier orbital control and charge control predict nucleophilic attack at the terminal carbon, and the energy level of the nucleophile orbital will determine whether one or the other predominates.

Scheme 4



In the reaction of e.g. complex **1b** with the dialkyl methylmalonate anion the attack is directed to the central carbon (C-2). Because of the presence of a chloride in the 2-position of the palladacyclobutane produced, the latter will be transformed to π-allyl complex **2** (Scheme 1). An alternative mechanism for the formation of **2** from **1** is possible and would involve the formation of an allene followed by addition of the carbanion to the central carbon atom (Scheme 4).[23]

This mechanism, however, can be ruled out on the basis of the following reasons: (1) When **1b** (L = TMEDA) was stirred with AgOTf in THF, no AgCl precipitation was observed. (2) It is known that kinetic nucleophilic attack on (allene)palladium(II) complexes takes place at the terminal carbon.[23,24] (3) During preparation of the complexes **1a**−**q** allene formation was only observed for **1m** (dppe as ligand). (4) When the dppe complex **1m** was allowed to decompose to allene and Pd(dppe)Cl^+, followed by the addition of the malonate, no reaction took place.

Conclusion

In conclusion we have shown that the regiochemistry of nucleophilic attack on (π-allyl)palladium complexes can be controlled by the choice of the ligands. Thus, bidentate σ-donor ligands favor attack at the central carbon whereas π-acceptor ligands favor attack at the terminal carbon of the π-allyl moiety. In this paper we have demonstrated that stabilized carbon nucleophiles such as dialkyl malonates (pK_a ∼13) indeed can attack the middle carbon of a (π-allyl)palladium complex and, furthermore, that ^{13}C NMR of the different (π-allyl)-palladium complexes can be used to predict whether attack at the central or terminal carbon will occur. Theoretical MO calculations confirm the experimental results and give an explanation for the variation in the regiochemistry observed. The 2-chloro substituent in the π-allyl group does not significantly change the energy of the frontier orbitals of importance for nucleophilic attack, and thus, the (2-chloro-π-allyl)palladium complexes should be reliable models for probing the reactivity of unsubstituted (π-allyl)palladium complexes.

Computational Details

For hydrogens the primitive (4s)[25] basis was used contracted to [2s]. For carbon, nitrogen, and chlorine atoms the (9s,5p) basis of Huzinaga[25] was used, augmented with one d-function

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(21) Mealli and Musco[6h] showed that when weak nucleophiles, such as largely stabilized carbanions, attack the central carbon atom, four electron repulsive interactions are induced between the occupied s-hybrid orbital of the carbanion and a 1a′ type orbital of the complex. It was concluded that in this case the nucleophile is redirected toward the terminal position, where such repulsive interactions have not been observed.

(22) In their analysis they treated cationic 18-electron complexes.

(23) The allene mechanism (cf. Scheme 4) was previously considered by Murai[8a] and was ruled out on the ground that amines are known to attack the terminal carbon of allene−metal complexes.

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and contracted to [3s,2p,1d], with the chlorine core replaced by an ECP.[26] For palladium a relativistic ECP according to Hay and Wadt[27] was used. The 4s and 4p semicore orbitals are described by a single-ζ contraction, the valence 5s and 5p orbitals are described by a double-ζ basis, and the 4d orbital is describned by a triple-ζ basis, including one diffuse d-function. The geometries of **6a**,**b**, **7**, and CH_3Cl were optimized employing second-order Møller−Plesset (MP2) perturbation theory.[28]

Experimental Section

NMR spectra were recorded for $CDCl_3$ solutions (^1H at 400 MHz and ^{13}C at 100.5 MHz) using chloroform-*d* (7.26 ppm, ^1H, 77.0 ppm, ^{13}C) as an internal standard. Coupling constants were evaluated using the *J*-doubling[29] routine. THF and dichloromethane were dried according to standard procedures. TMEDA was distilled over CaH_2 and was stored in a dark place under nitrogen. Commercially available malonates were passed through a short column of $MgSO_4$ and silica gel. $PdCl_2$ was obtained from Johnson Matthey; all other chemicals were bought from Lancaster or Aldrich and were used without further purification. In the ^1H NMR spectra of **1b**,**d**,**j**,**h**,**p**,**n** the shifts of the ligands vary slightly with the concentration.

Bis(*μ*-chloro)-bis(η^3-2-chloro-propenyl)palladium (1a). The procedure of ref 9a was employed. $PdCl_2$ (1 g) and LiCl (0.8 g) was dissolved in 1.5 mL of hot water. Methanol (30 mL) and 2,3-dichloropropene (2.0 g, excess) were added, and carbon monoxide was bubbled through the stirred solution until the color changed from dark brown to light yellow (30−60 min depending on the CO rate). The reaction mixture was then poured into 800 mL of water and extracted with chloroform (3 × 150 mL). The combined organic phases were dried over $MgSO_4$ and evaporated. The remaining solid was collected and recrystallized from a dichloromethane−ether mixture to give 1 g (90%) of yellow, needle-shaped crystals; decomposition point 162−164 °C (lit.[9b] 176−78 °C). ^1H NMR: δ 3.24 (dd, 2H, J = 1.98 Hz, J = 0.84 Hz), 4.25 (dd, 2H, J = 1.98 Hz, J = 0.84 Hz). ^{13}C NMR: δ 123.9 (C_c), 62.6 (C_t).

Reaction of 1 with Dialkyl Malonates. General Procedure. A solution of 21.7 mg (0.05 mmol) of dimer **1** and the ligand in the proper ratio in 2.5 mL of THF was cooled to −78 °C under nitrogen. After 5−10 min of stirring a freshly prepared sodium dialkyl malonate solution (0.25 mmol in 2.5 mL of THF) was injected, and the reaction was allowed to warm to room temperature overnight. The solvent was evaporated, the residue was dissolved in $CDCl_3$, and the product ratio was determined by ^1H NMR. Alternatively the reaction mixture was extracted with ether and washed with brine, and the products were isolated by column chromatography (75−95% yield). The ^1H NMR spectra of compounds **3** and **4** were identical to those previously published.[8a]

5,8-Dithiadodecane.[30] A 1.55 g (0.025 mol) amount of 1,2-ethanedithiol and 2 g of NaH (60% in mineral oil, 0.05 mol) were mixed in 20 mL of THF at 0 °C. To this mixture was added 9.2 g of butyl iodide (0.05 mmol), and the reaction was stirred overnight. Ether (200 mL) was added, and the organic phase was washed with water (2 × 50 mL), 2 M NaOH (2 × 25 mL), water, and brine. The organic phase was collected, dried (Na_2SO_4), and concentrated under vacuum. The product obtained was 99% pure according to GC. ^1H NMR: δ 2.72 (s, 4H), 2.58 (app t, 4H, J = 7.5 Hz), 1.6 (quint, 4H, J = 7.6 Hz), 1.42 (sext, 4H, J = 7.6 Hz), 0.94 (t, 6H, J = 7.6 Hz). ^{13}C NMR: δ 32.17, 31.9, 31.8, 21.98, 13.67.

***(N,N,N′,N′*-Tetramethylethylenediamine)(η^3-2-chloropropenyl)palladium Tetrafluoroborate (1b).** A 21.7 mg amount of **1a** (0.05 mmol) was mixed with 19.4 mg of $AgBF_4$ (0.1 mmol) in chloroform. After 10 min of stirring at room temperature the solution was centrifuged, the precipitate was removed, and 30 μL of TMEDA (0.2 mmol) was added. After a few minutes ether was added to the solution until precipitation appeared, and the compound was allowed to crystallize at −18 °C. The mixture was centrifuged again, and the crystals were collected, washed with ether, and dried in vacuum. ^1H NMR: δ 3.85 (m, 2H), 3.53 (m, 2H), 3.06 (s, 6H), 2.94−3.03 (m, 2H), 2.89 (s, 6H), 2.76−2.85 (m, 2H). ^{13}C NMR: δ 130.01 (C_c), 61.31 (C_t), 60.88, 52.86, 51.98.

***N,N,N′,N′*-Tetramethylpropanediamine)(η^3-2-chloropropenyl)palladium tetrafluoroborate (1d)** was prepared using the procedure for **1b**, but 2 equiv of TMPDA was added. ^1H NMR: δ 3.83 (dd, 2H, J = 1.7 Hz, J = 0.8 Hz), 3.67 (m, 2H, J = 1.7 Hz, J = 0.8 Hz), 3.12 (app. t, 2H), 2.95 (s, 6H), 2.68 (s, 6H), 2.32 (ddd, 2H, J = 13.1 Hz, J = 5.8 Hz, J = 2.25 Hz), 1.76−1.94 (m, 2H). ^{13}C NMR: δ 130.56 (C_c), 63.29 (C_t), 62.56, 55.79, 52.1, 23.25.

Bis(triphenylphosphine)(η^3-2-chloropropenyl)palladium tetrafluoroborate (1j) was prepared as **1b**, but the reaction was done at 0 °C and only 2 equiv of triphenylphosphine was used. ^1H NMR: δ 7.33−7.40 (m, 6H), 7.23−7.31 (m, 24H), 4.25 (m, 2H), 3.83 (broad s, 2H). ^{13}C NMR: δ 133.66 (t, J_P = 6.8 HZ), 131.29 (t, C_c, J_P = 6.1 Hz), 131.05, 130.58 (t, J_P = 22.3 Hz),128.84 (t, J_P = 5.7 Hz), 78.56 (t, C_t, J_P = 16.6 Hz).

Bis(triphenyl phosphite)(η^3-2-chloropropenyl)palladium tetrafluoroborate (1h) was prepared as **1b**, but the reaction was done at 0 °C and only 2 equiv of triphenyl phosphite was used. ^1H NMR: δ 7.40 (app t, 12H, J_{av} = 7.55 Hz), 7.28 (broad t, 6H, J = 7.15 Hz), 7.05 (broad d, 12H, J = 8.0 Hz), 4.13−4.19 (m, 2H), 3.45−3.55 (m, 2H). ^{13}C NMR: δ 149.65 (t, J_P = 2.8 Hz), 133.32 (t, C_c, J_P = 12.2 Hz), 130.6, 126.41, 120.51 (t, J_P = 2.5 Hz), 74.11 (t, C_t, J_P = 23.3 Hz).

(5,8-Dithiadodecane)(η^3-2-chloropropenyl)palladium tetrafluoroborate (1p) was prepared as **1b**, but 2 equiv of 5,8-dithiadodecane was used. ^1H NMR: δ 4.68 (broad s, 2H), 3.96 (broad s, 2H), 3.03−3.22 (m, 8H), 1.64−1.73 (m, 4H), 1.45−1.55 (m, 4H), 0.96 (t, 6H, J = 7.3 Hz). ^{13}C NMR: δ 129.96 (C_c), 69.02 (C_t), 36.46, 35.13, 30.80, 21.64, 13.54.

(1,5-Cyclooctadiene)(η^3-2-chloropropenyl)palladium tetrafluoroborate (1n) was prepared as **1b**, but 1 equiv of 1,5-cyclooctadiene was used. ^1H NMR: δ 6.38 (broad s, 2H), 6.33 (broad s, 2H), 4.96 (s, 2H), 4.25 (s, 2H), 2.76−2.87 (m, 2H), 2.63−2.74 (m, 4H), 2.26−2.39 (m, 2H). ^{13}C NMR: δ 133.06 (C_t), 115.26, 111.17, 76.43 (C_c), 29.43.

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