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Preliminary Communication

Ambivalence of nucleophilic attack on central and terminal allyl carbon atoms of $[(\eta^3\text{-allyl})ML_2]^+$ (M = Pd or Pt) complexes

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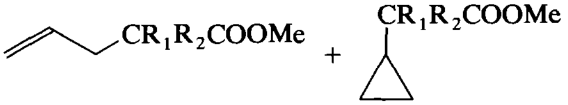
Abstract

The coordinated allyl group of complexes $[(\eta^3\text{-allyl})ML_2]^+$ (M = Pd or Pt) is shown experimentally to undergo nucleophilic attack on either central (C_c) or terminal (C_t) allyl carbon atoms. A new theoretical discussion is presented, showing that the feasibility of attack at the C_c atom is not as low as previously thought.

A recent paper by Hoffmann *et al.* [1] on the stoichiometric formation of cyclopropanes from $[\{(\eta^3\text{-allyl})PdCl\}_2]$ and lithium ester enolates in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) prompts us to disclose further data on the reaction of η^3-allyl complexes of Pd and Pt with ketene silyl acetals. Some of us have recently shown that ketene silyl acetals attack the allyl group of $[(\eta^3\text{-allyl})PdL_2]OAc$ (L = phosphorus ligand) either on the central or on the terminal carbon atom of the allyl group (eqn. (1)) [2].

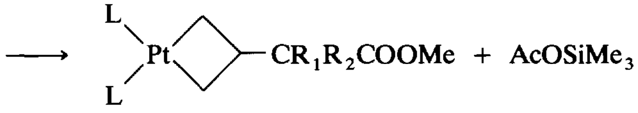
$$[(\eta^3\text{-allyl})PdL_2]OAc + R_1R_2C{=}C(OMe)(OSiMe_3) \longrightarrow$$



$$+\ PdL_2 + AcOSiMe_3 \qquad (1)$$

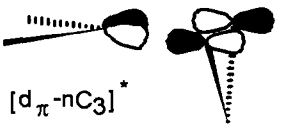
The regioselectivity of the reaction is low, as cyclopropane is at best 50% of the reaction products. A catalytic cycle occurs with allyl acetates as the allyl source. Hegedus, in his pioneering work [3] on the formation of cyclopropanes from the reaction of $[(\eta^3\text{-allyl})PdCl]_2$ with lithium ester enolates in the presence of hexamethylphosphoric triamide, proposed that cyclopropanes are formed through reductive elimination from a labile palladacyclobutane intermediate. Indeed, some of us found recently that $[(\eta^3\text{-allyl})PtL_2]OAc$ reacts regioselectively with ketene silyl acetals to yield thermally stable platinacyclobutane complexes in good yields (eqn. (2)) [4].

$$[(\eta^3\text{-allyl})PtL_2]OAc + R_1R_2C{=}C(OMe)(OSiMe_3)$$

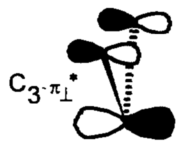


(2)

The above results deviate from the known chemistry of η^3-allyl complexes of palladium and platinum, which usually react with nucleophiles at the terminal allyl carbon atoms (C_t) [5]. According to the theoretical results from Curtis and Eisenstein [6], who assumed an ideal planar geometry for the coordinated allyl group, the LUMO of $(\eta^3\text{-allyl})Pd$ complexes is metal–allyl antibonding and largely centred on C_t atoms (I, $[d_\pi\text{–}n(C_3)]^*$). They would thus be the sites of nucleophilic attack. A second LUMO (II, $C_3\text{-}\pi_\perp{}^*$), more centred on the central carbon atom (C_c), appears energetically less accessible. Attack on the C_c atom would be possible only in a charge-controlled reaction.



I



II

Since the observed nucleophilic attack of silyl enolates on C_c of allyl-palladium and -platinum complexes deviates from the expected regiochemistry, a theoretical reinvestigation of this class of compound appears necessary. Our preliminary results [7*] show the importance of the model used for the coordinated allyl

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

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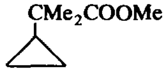
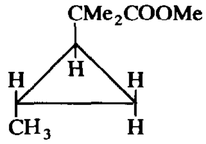
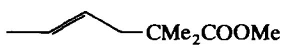
TABLE 1. Nucleophilic attack of $Me_2C{=}C(OMe)(OSiMe_3)$ (**1**) on palladium and platinum allyl complexes [a]

	Allyl complex	Ligand	Reaction time (h)	Products formed (yield [c])	
H	[(η^3-allyl)PdCl]	TMEDA [b]	3	 **4a** (97)	**6** (3)
H	[(η^3-allyl)PdCl]	bipy [d]	1	**4a** (19)	**6** (traces)
H	$(allylPtCl)_4$	TMEDA	6	 **6** (72)	**4a** (8)
CH_3	[(η^3-allyl)PdCl]	TMEDA	1	 **4b** (58)	 **7** (13)
CH_3	[(η^3-allyl)PdCl]	bipy	1	**4b** (15)	**7** (13)

[a] Allylic bromide, 1 mmol; TlOAc, 1 mmol; **1**, 2 mmol; allylMCl, 0.05 mmol; ligand, 0.055 mmol; CH_2Cl_2, 6 ml; room temperature. Reaction products have been characterized by comparison (GLC, FTIR–GLC, NMR) with authentic samples [2]. [b] *N,N,N′,N′*-tetramethylethylenediamine. [c] Yield based on the allylic bromide and GLC estimated. [d] 2,2′-Bipyridine.

group. A neutron diffraction study by Krüger *et al.* [8] has shown a significant displacement of all of the allyl hydrogen atoms out of the plane formed by the three carbon atoms (C_3 plane) in *trans*-(η^3-allyl)$_2$Ni. This deformation can be parametrized and the Walsh diagram for the conversion of an ideal model (planar allyl) into a more realistic one can be constructed (see Fig. 1). The reaction coordinate is defined by appropriate combinations of the angles α, β, γ (θ is fixed at 110°). Both the α and β rotations (carried out consecutively) reorient the C_tH_2 planes with respect to the C_3 plane: α pivots on an axis in the C_3 plane, through the atom C_t and perpendicular to the C_c–C_t bond, while β rotates about the C_c–C_t bond itself. The total energy gain is calculated to be *ca.* 1 eV.

As shown by the three-dimensional drawings, the loss of parallelism between the C_3-p_π atomic orbitals affects the energies of important frontier MOs, in particular of the two LUMOs. Whereas the $[d_\pi$–$n(C_3)]^*$ combination is destabilized because the antibonding character between metal and C_t atoms increases, the overall C_3-$\pi_\perp^*$ character of the second LUMO is diminished by loss of planarity. In addition, the stabilization of the latter MO is somewhat influenced by improved overlap with the metal p_z orbital, usually considered uninvolved in square planar coordination. There appears to be a clear-cut trend to reduce the gap and even to invert the order of the two LUMOs. The new major implication is that there should be an almost equal facility of nucleophilic attack at either the C_t or the C_c atoms. The factors governing the point of attack in the presence of a typical transition metal fragment (*e.g.* ML_2; M = Pd or Pt and L = phosphine, amine) are very subtle, and perhaps unpredictable, as the following experimental results seem to indicate.

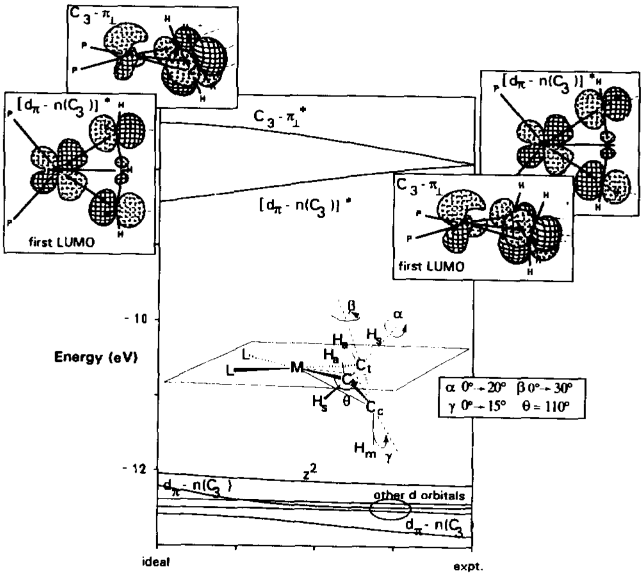


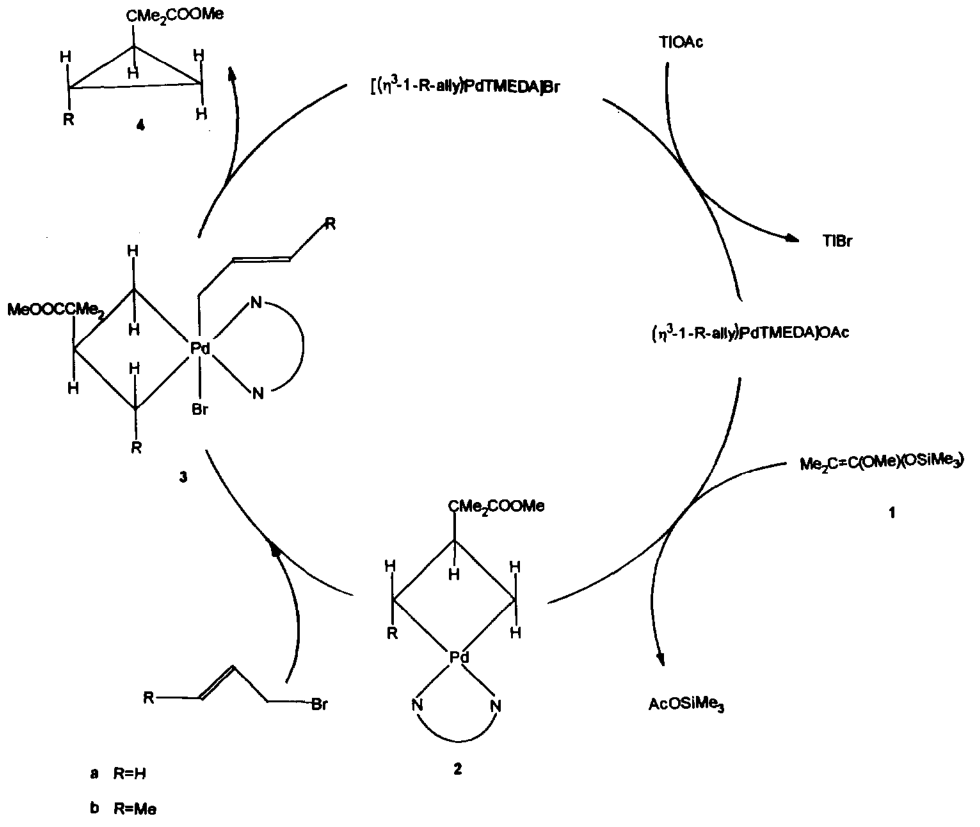
Fig. 1. Walsh diagram for the interconversion of an ideal $[(\eta^3$-allyl)$Pt(PH_3)_2]^+$ model (C_3H_5, planar) into a more realistic one (conforming to the experimental structure of bis-(allyl)nickel [8]). The geometric parameters defining the deformation coordinates are shown. The drawings illustrate the reorientation of the C_3-p_π atomic orbitals of the two LUMOs, and hence the reduced energy gap, or even inverted order.

Whereas allylplatinum complexes yield platinacyclobutanes with ketene silyl acetals as the nucleophiles in presence of tertiary phosphines (eqn. (2), the analogous Pd complexes have a much lower regioselectivity (eqn. (1)). Surprisingly, coordination of a nitrogen ligand to either palladium or to platinum removes the regiochemistry previously observed.

We have found that allyl bromide (0.120 g, 1.0 mmol) and 1-methyl-2-methoxy-2-trimethylsiloxypropene (**1**) (0.35 g, 2.0 mmol) in CH_2Cl_2 (6 ml) at room temperature in the presence of $[(\eta^3\text{-allyl})PdCl_2]$ (0.010 g, 0.025 mmol), TlOAc (0.26 g, 1.0 mmol) and TMEDA (0.0063 g, 0.054 mmol) give cyclopropane **4a** (Table 1) quantitatively with respect to the allyl bromide. Lower yields are obtained in presence of 2,2′-bipyridine. We propose the catalytic cycle shown in Scheme 1. Allyl bromide adds to the palladacyclobutane **2** to yield a Pd^{IV} [9] intermediate **3** which reductively eliminates cyclopropane **4a** to yield $[(\eta^3\text{-allyl})Pd(TMEDA)]Br$ which sustains the catalytic cycle. As previously observed, the AcO^- anion is essential for activating the Si–O bond of the silyl enolate [2] and no reaction is observed in the absence of TlOAc. Upon replacing allyl bromide by allyl acetate and using $[(\eta^3\text{-allyl})PdOAc]_2$ as the Pd source cyclopropane **4a** is obtained in trace amounts, and an immediate precipitation of metallic Pd occurs. We conclude that the fast addition of allyl bromide to **2** keeps the palladium in solution, allowing a catalytic cycle to develop. Table 1 summarizes the results of a few catalytic runs performed in the same reaction conditions as above. Crotyl bromide behaves similarly to allyl bromide in the coupling reaction with ketene silyl acetal **1** as good conversion to cyclopropane **4b** is observed.

Formation of the allylation product methyl 2-dimethyl-4-pentenoate (**6**) from allyl bromide and silyl enolate **1** in the presence of allylplatinum complexes is surprising in view of eqn. (2).

In contrast to earlier and accepted ideas, nucleophilic attack at the C_c atom of $[(\eta^3\text{-allyl})ML_2]^+$ complexes does not appear impossible. Experimental data confirm that by adopting various combinations of metal, ancillary ligands and attacking nucleophile, regioselectivity can be switched. In addition, our results open a new synthetic route to the catalytic and regioselective preparation of cyclopropanes from allyl electrophiles and ester enolates in very mild conditions. Finally, the theoretical discussion presented above is consistent with the experimental facts. Orbital control of the regioselectivity of nucleophilic attack offers, at least



Scheme 1. Catalytic cycle for cyclopropane formation.

initially, almost equal reactivity at either the C_t or the C_c atoms. A more detailed study of the MO evolution and the barriers encountered along the alternative pathways is in progress, and will be presented later.

Acknowledgments

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