Palladium-Promoted Amination of Olefins. Direct Proof for the Trans Stereochemistry

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Abstract: The palladium-promoted amination of (*E*)- and (*Z*)-2-butene at low temperature each yields a cyclic σ complex. The stereochemistry of the two σ complexes, which are stereoisomers, has been determined by ^{13}C NMR at about −50 °C, a temperature where the complexes are stable. The result shows unequivocally that the amination is a trans process.

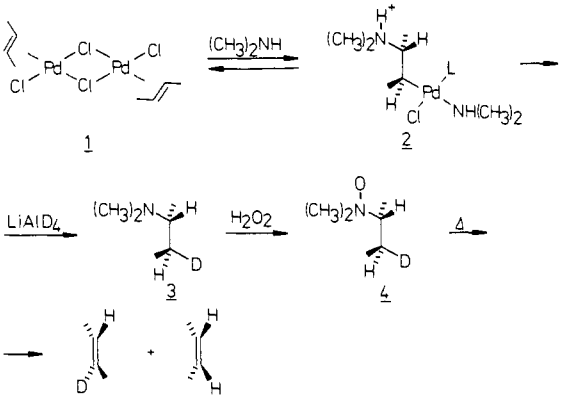
By complexing to palladium(II), simple olefins, generally accepted as electron rich and thus weakly nucleophilic reagents, are transformed into electrophiles that react with ordinary nucleophiles under mild conditions. The reaction, which is regio- and stereoselective, has been extensively applied to organic synthesis.[1] When the nucleophile is a secondary amine, it has been shown by an indirect route that the nucleophile attacks from the face of the olefin opposite to palladium (trans addition) (Scheme I).[2]

In the related platinum-promoted reaction, the intermediate σ complex is stable and trans addition has been established by X-ray crystallography.[3] However, until now no direct examination of the corresponding, very labile σ-palladium complexes has been possible. We would therefore like to report on the preparation of σ complexes of the type **2** from (*E*)- and (*Z*)-2-butene (Scheme II) and the determination of the stereochemistry of these complexes by ^{13}C NMR at low temperatures (ca. −50 °C).

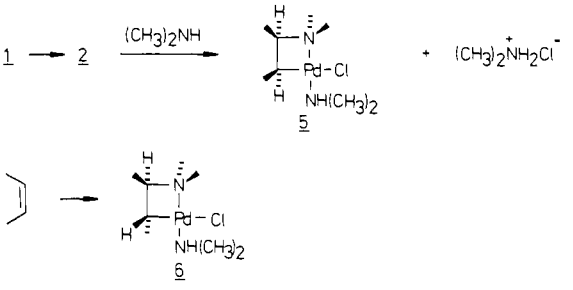
In a representative experiment, the (*E*)-2-butene complex **1** was first prepared from (*E*)-2-butene and bis(benzonitrile)palladium chloride in THF-d_8 solution in an NMR tube. The mixture was cooled to −78 °C, and ca. 5 equiv of dimethylamine was added from a syringe. The "linear" σ complex **2** was first formed in a very rapid reaction and then cyclized to **5** in a distinctly slower but still rapid reaction (Scheme II). Similarly, (*Z*)-2-butene yielded the cyclic σ complex **6**, although the yield was lower.[4]

The two σ complexes **5** and **6** are readily characterized by their NMR spectra, and **5** has even recently been isolated in pure state.[5] Somewhat surprisingly the coupling constants for the ring protons of **5** and **6** are very close, 8.9 and 9.4 Hz, repsectively, but the stereochemistry of the two complexes may be determined by ^{13}C NMR. This is based on the earlier observation that due to a mutual sheilding effect, *cis*-methyl groups absorb at higher fields than the corresponding *trans*-methyl groups.[6] More specifically, for 1,2-dimethylcyclopentane,[7] dimethylcyclopropane[8] and 2-butene,[9] the ^{13}C signals for the cis compounds appears at 4–6 ppm higher field than in the corresponding trans compounds. Since the methyl signals of **5** appear at 11.95 and 15.94 ppm and those of **6** at 14.44 and 18.71 ppm, **5** must be the cis compound and

Scheme I



Scheme II



6 the trans compound. The palladium-promoted amination is thus a trans process, in accordance with the earlier, indirect assignment.[2]

The result of this earlier assignment (Scheme I) rests on the assumption that hydride cleavage of a carbon–palladium bond proceeds with retention at carbon, as proved experimentally for some systems related to norbornadiene.[10] There is a tendency to refute the generality of stereochemical results from such systems. However, the present results, in combination with the reactions described in Scheme I, show that the simple system **2** (or **5**) reacts with hydride exactly as that obtained from norboradiene and similar structures.

Finally, the stereochemistry of a number of other palladium-promoted reactions, e.g., diamination,[11] oxyamination,[12] and aminocarbonylation,[13] is based on the assumption that aminopalladation proceeds trans. These assignments are now secured.

Experimental Section

The NMR spectra were recorded at 200 MHz for ^1H and 50.29 MHz for ^{13}C on a Bruker Model WP 200 spectrometer equipped with a Bruker

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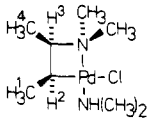
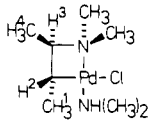
Table I. ^1H and ^{13}C NMR Shifts for the Amination Products[a]



5



6

	^1H NMR	
H^1	0.83 (d, J_{1-2} = 7.3 Hz)	0.70 (d, J_{1-2} = 6.4 Hz)
H^2	1.11 (m, J_{2-3} = 8.9 Hz)	0.52 (m, J_{2-3} = 9.4 Hz)
H^3	4.16 (m)	3.62 (m)
H^4	0.99 (d, J_{3-4} = 7.1 Hz)	0.93 (d, J_{3-4} = 6.7 Hz)
H_3C–N	2.3–2.6	2.3–2.5
	^{13}C NMR	
C^1	11.95	14.44
C^2	–3.12	0.90
C^3	76.64	81.38
C^4	15.94	18.71
H_3C–N	42.2–50.0	41.6–49.5

[a] Expressed as δ relative to Me_4Si.

B-VT-1000 temperature-control unit. The shifts are expressed as δ relative to Me_4Si. Tetrahydrofuran (THF) was distilled from potassium–benzophenone prior to use. THF-d_8 and methanol-d_4 (Stohler Isotope Chemicals) were taken from freshly opened ampules and used as received.

^{13}C NMR Procedure. Bis(benzonitrile)palladium dichloride (192 mg, 0.50 mmol) was dissolved in 2 mL of THF in a 10-mm NMR tube. The NMR tube was cooled by immersion into a tube containing finely crushed dry ice, and (*E*)-2-butene (34 mL, ca 1.5 mmol) was added from a syringe under stirring with a vortex stirrer. The NMR tube was allowed to warm to ca. –10 °C and then cooled to about -78 °C, and gaseous dimethylamine (56 mL, ca. 2.5 mmol) was slowly added from a syringe. With stirring the temperature was increased and held at ca. –35 °C for a few minutes to ensure complete formation of cyclic chloro(dimethylamino)[*erythro*-3-(*N*,*N*-dimethylamino)but-2-yl-*C*,*N*]palladium(II) (**5**). After addition of 0.5 mL of methanol-d_4 that was used to achieve internal lock, the NMR spectrum was recorded at 223 K. With use of the same procedure, (*Z*)-2 butene was converted to chloro(dimethylamine)[*threo*-3-(*N*,*N*-dimethylamino)but-2-yl-*C*,*N*]palldium(II) (**6**). The ^{13}C NMR data are presented in Table I.

^1H NMR Procedure. The cyclic complexes were prepared in the same way as described for the ^{13}C NMR except that the scale was decreased to one-tenth, that is 19.2 mg (0.05 mmol) of bis(benzonitrile)palladium dichloride was used, that was dissolved in 0.7 mL of THF-d_8 in a 5-mm NMR tube. The ^1H NMR data are presented in Table I.

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Registry No. 5, 91409-21-1; **6**, 91464-43-6; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; bis(benzonitrile)palladium chloride, 14220-64-5; dimethylamine, 124-40-3.

Chromium, Molybdenum, and Tungsten Chlorophosphazenes: Molecular Structures of $N_3P_3Cl_5[Cr(CO)_3(\eta\text{-}C_5H_5)]$ and $N_3P_3Cl_4(C_5H_5)[Mo(CO)_3(\eta\text{-}C_5H_5)]$[1,2]

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Abstract: Cyclopentadienylchromium tricarbonyl anion reacts with hexachlorocyclotriphosphazene, $(NPCl_2)_3$, to form a metallophosphazene of formula $N_3P_3Cl_5[Cr(CO)_3(\eta\text{-}C_5H_5)]$ (**5**). The reactions of the analogous molybdenum and tungsten anions with $(NPCl_2)_3$ are more complex and lead to the formation of metallophosphazenes of formula $N_3P_3Cl_4(C_5H_5)[M(CO)_3(\eta\text{-}C_5H_5)]$ (**6a**, M = Mo; **6b**, M = W) in which the chlorine atom geminal to the metal has been replaced by a cyclopentadiene group. A key requirement for the success of these reactions is the use of a tetra-*n*-butylammonium counterion. The products are among the first *chloro*phosphazenes to contain metal–phosphorus side-group bonds. The structures of **5** and **6a** were examined in detail by spectroscopic and X-ray diffraction techniques. In both compounds the N–P–N bond angle at the metal-bearing phosphorus is unusually narrow, being 112.3 (3)° in **5** and 111.0 (3)° in **6a**. Moreover, an alternation of longer and shorter bond lengths is found for the P–N bonds located at increasing distances from the metal. For **5**, the phosphazene ring was found to be significantly nonplanar. These features are compatible with appreciable interaction between the metal and the phosphorus–nitrogen ring. Crystal data: crystals of **5** are monoclinic with the space group $P2_1/m$ and with a = 8.334 (3) Å, b = 12.897 (8) Å, c = 8.783 (4) Å, β = 105.44 (3)°, V = 909.9 (15) Å^3, and Z = 2; crystals of **6a** are orthorhombic with the space group $Pca2_1$ and with a = 16.075 (3) Å, b = 8.832 (3) Å, c = 14.780 (3) Å, V = 2098 (1) Å^3, and Z = 4.

An expanding interest exists in transition-metal derivatives of the main group inorganic rings, cages, and high-polymeric chains. Part of this interest reflects a search for new catalytic or electroactive materials. One of the largest classes of inorganic rings and chains is the phosphazene system,[3] which has been investigated broadly with respect to organic-type substitution processes. By contrast, few transition-metal derivatives of phosphazenes are known although, in theory, this interfacial area offers much promise for pioneering synthesis, understanding of structural problems, and the discovery of new phenomena.

Recent attempts have been made to link transition metals to phosphazene rings or high polymers by the use of the electron-donor coordination properties of the skeletal nitrogen atoms (**1**)[4-9]

(1) This work was presented at the 186th National Meeting of the American Chemical Society, Washington, D.C., August 30, 1983.
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