Remarkable, Sterically Induced Rate Enhancement in the Insertion of Allenes into Palladium−Methyl Bonds

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Received December 21, 1999

Summary: The rate of insertion of methyl-substituted allenes into the Pd−Me bond in chelate pyridine−thioether complexes [PdCl(Me)(R′N-SR)] (R′N-SR = 6-R′-C_5H_3N-2-CH_2SR) to give 2-methylallyl derivatives is remarkably enhanced by the presence of a methyl group in position 6 of the pyridine ring, which induces distortion on the main coordination plane, resulting in a metal substrate more prone to allene insertion. The flexibility of the sulfur-donor chelate ligand appears to be a paramount requisite.

The insertion reactions of unsaturated molecules into the metal−carbon bond of transition metal−alkyl and −aryl chelate complexes is a subject of great current interest.[1] Particularly important appear to be the interactions of organopalladium species with allenic compounds under catalytic conditions involving the polymolecular assembly of allenes, carbon monoxide, and a wide range of nucleophiles. The ensuing reaction products may be allylamines, methacrylate derivatives, or etherocycles and carbocycles.[1c−e] Despite the wealth of preparative and mechanistic studies, the factors affecting the course and rates of these reactions have yet to be rationalized. In particular, steric, structural, and electronic properties of the chelating ligand may lead to different results. Thus, insertion is made easier by flexible diphosphine ligands with a large bite angle,[2] while rigid diimine ligands with a small bite angle will enhance the rate of insertion.[3] Also, hemilability of the polydentate ligand plays an important role.[4]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1a and 1b

	1a	1b		1a	1b
Pd−Cl	2.347(1)	2.336(2)	Pd−N	2.162(5)	2.229(4)
Pd−S	2.259(1)	2.268(2)	P−C(11)	2.035(7)	2.048(5)
Cl−Pd−S	178.8(1)	168.4(1)	S−Pd−N	84.8(1)	82.8(1)
Cl−Pd−N	95.3(1)	99.4(1)	S−Pd−C(11)	90.7(2)	89.9(2)
Cl−Pd−C(11)	89.3(2)	87.6(2)	N−Pd−C(11)	174.9(2)	172.7(2)

In the course of our systematic studies on the synthesis and reactivity of palladium(II) chelate complexes with hemilabile, mixed donor polydentate ligands,[5] we conceived that the rate of insertion of allenes into the palladium−methyl bond in pyridine−thioether complexes [PdCl(Me)(R′N−SR)] (R′N−SR = 6-R′-C_5H_3N-2-CH_2SR) could be enhanced by the presence of the substituent in position 6 of the pyridine ring. This was expected to induce distortion of the main coordination plane, resulting in a metal center more prone to prior coordination of allene, the latter being considered a requisite preliminary step in these insertion reactions.[1b,3d,e]

To this purpose we have prepared the complexes **1a**,**b** and **2a**,**b**.[6−8] The crystal structures of substrates **1a** and **1b** are shown in Figure 1,[9] and selected bond lengths and angles are given in Table 1. A superimposition of

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(6) Complexes **1** and **2** were obtained by reacting the appropriate pyridine−thioether ligand with a stoichiometric amount of [PdCl(Me)(COD)][7] (COD = 1,5-cyclooctadiene) in anhydrous, freshly distilled toluene under an inert atmosphere (N_2). The reaction mixture was stirred at room temperature for several hours. The resulting yellowish solution was dried under vacuum, dissolved in anhydrous CH_2Cl_2, and treated with charcoal. Filtration on a Celite filter, reduction to small volume, and addition of diethyl ether yields the required complex. In any case only one isomer was detected, which was identified with the species containing the thioetheric sulfur *trans* to the chlorine atom on the basis of structural data and of the mutual *trans* influence.[3b,8] **1a**: yield 89%. Anal. Found: C, 39.28; H, 5.61; N, 4.21. Calcd for $C_{11}H_{18}ClNPdS$: C, 39.07; H, 5.36; N, 4.14%. ^{1}H NMR (298 K, $CDCl_3$, ppm): δ 0.92 (3H, s, Pd−CH_3), 1.34 (9H, s, S−C (CH_3)$_3$), 4.27 (2H, bs, CH_2−S), 7.34 (1H, dd, J = 7.8, 5.1 Hz, H^5_{pyr}), 7.45 (1H, d, J = 7.8 Hz, H^3_{pyr}), 7.69 (1H, td, J = 7.8, 1.7 Hz, H^4_{pyr}), 9.21 (1H, d, J = 5.1 Hz, H^6_{pyr}). **1b**: yield 80%. Anal. Found: C, 41.01; H, 5.81; N, 4.02. Calcd for $C_{12}H_{20}ClNPdS$: C, 40.92; H, 5.72; N. 3.98. ^{1}H NMR (298 K, $CDCl_3$, ppm): δ 1.12 (3H, s, Pd−CH_3), 1.25 (9H, s, S−C(CH_3)$_3$), 3.08 (3H, s, C_5H_3N-6−CH_3, 4.05, 4.51 (2H, AB $_{sys}$, J = 17.18 Hz, CH_2−S), 7.14 (1H, d, J = 7.7 Hz, H^5_{pyr}), 7.19 (1H, d, J = 7.7 Hz, H^3_{pyr}), 7.61 (1H, t, J = 7.7 Hz, H^4_{pyr}). **2a**: yield 93%. Anal. Found: C, 43.81; H, 3.66; N, 3.82. Calcd for $C_{13}H_{14}ClNPdS$: C, 43.59; H, 3.94; N, 3.91. ^{1}H NMR (298 K, $CDCl_3$, ppm): δ 0.91 (3H, s, Pd−CH_3), 4.52 (2H, bs, CH_2−S); H^5_{pyr}), 7.58 (8H, m, H^3_{pyr}, H^5_{pyr}, H^4_{pyr}, H_{phen}), 9.29 (1H, d, J = 5.0 Hz, H^6_{pyr}). **2b**: yield 94%. Anal. Found: C, 45.11; H, 4.51; N, 3.74. Calcd for $C_{14}H_{16}ClNPdS$: C, 45.17; H, 4.33; N, 3.76. ^{1}H NMR (298 K, $CDCl_3$, ppm): δ 1.14 (3H, s, Pd−CH_3), 3.10 (3H, s, C_5H_3N-6-CH_3), 4.61 (2H, bAB$_{sys}$, CH_2−S), 7.02 (1H, d, J = 7.7 Hz, H^5_{pyr}), 7.12 (1H, d, J = 7.7 Hz, H^3_{pyr}), 7.52 (1H, t, J = 7.7 Hz, H^4_{pyr}), 7.33 (3H, m, H_{phen}), 7.63 (2H, m, H_{phen}).

10.1021/om991018p CCC: $19.00
Publication on Web 03/21/2000

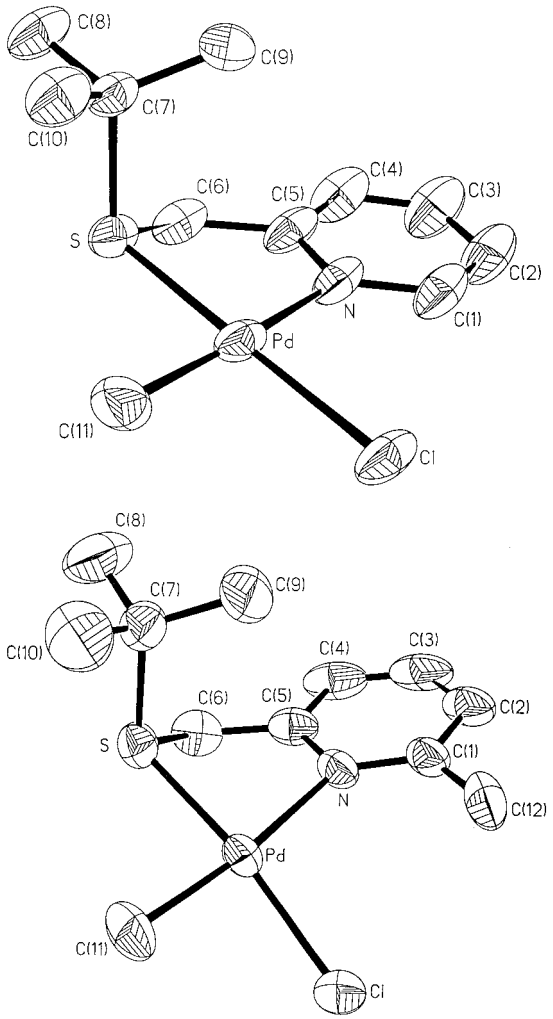
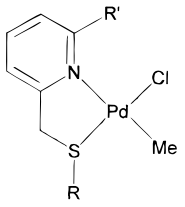


Figure 1. Perspective views of the complexes **1a** (top) and **1b** (bottom), showing the numbering scheme and the thermal ellipsoids at the 40% probability level.

the two structures is shown in Figure 2. It appears that complex **1b** is significantly distorted as compared to **1a**



R' = H R = *t*-Bu **1a**
R' = H R = Ph **2a**
R' = Me R = *t*-Bu **1b**
R' = Me R = Ph **2b**

as far as the C(7)−S−C(6)−C(5)−N−C(1) backbone is concerned. In fact the *trans* donors S and Cl lie below the average coordination plane by 0.03 Å in **1a** and by 0.10 Å in **1b**, with the other two donors N and C(11) lying above the plane by 0.03 Å in **1a** and 0.10 Å in **1b**. The central metal lies in the plane in **1a**, whereas it is above it by 0.13 Å in **1b**. The average coordination plane

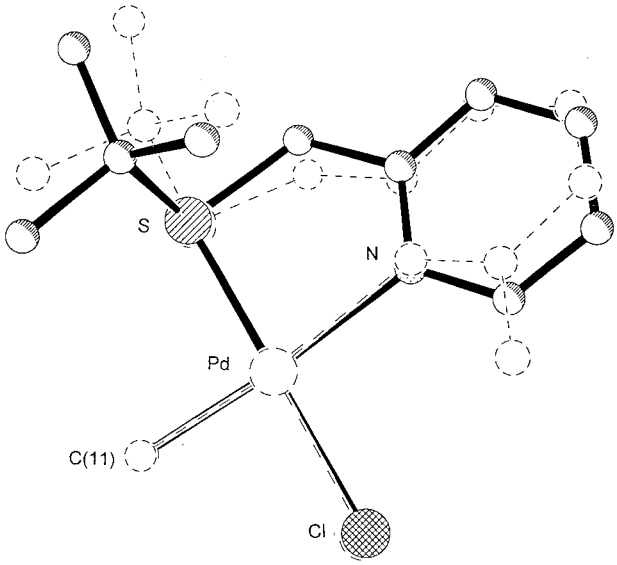


Figure 2. Superimposition of complexes **1a** (bold line) and **1b** (dotted line).

makes a dihedral angle of 10.5° in **1a** and 34.4° in **1b** with the pyridine ring plane, whereas the dihedral angle between the planes N−Pd−S and Cl−Pd−C(11) is 2.6° in **1a** and 11.4° in **1b**. The five-membered ring Pd−S−C(6)−C(5)−N adopts an envelope conformation (C_s) with Pd, N, C(5), and C(6) coplanar, whereas S lies off by 0.49 Å in **1a** and by as much as 0.93 Å in **1b**. Torsion angles range from −25.5 to +21.5° in **1a** and from −44.2° to +33.5° in **1b**. The five-membered ring forms dihedral angles with the pyridine ring and with the plane Cl−Pd−C(11) of 9.9 and 9.0°, respectively, in **1a** and of 17.6 and 28.4°, respectively, in **1b**. The Pd−N distances and the Cl−Pd−S and Pd−N−C(5) bond angles are 2.162(5) Å and 178(1) and 118.2(4)°, respectively, in **1a**, whereas they are 2.229(4) Å and 168.4(1) and 112.3(3)°, respectively, in **1b**. The bite angles and other relevant structural features of the two compounds are comparable.

We have carried out a kinetic study of the reaction of insertion of 1,1′-dimethylpropadiene (DMA) and 1,1′,3,3′-tetramethylpropadiene (TMA) across the Pd−Me bond in these complexes in CH_2Cl_2 at room temperature, to

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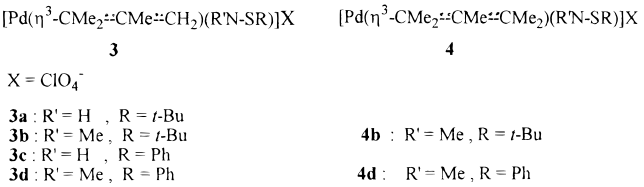
(9) Crystal data are as follows. **1a**: $C_{11}H_{18}ClNPdS$, fw = 338.2, triclinic, space group $I\bar{1}$, a = 8.626(5) Å, b = 10.610(6) Å, c = 15.051(6) Å, V = 1374(1) Å^3, Z = 4, ρ = 1.635 g/cm^3, μ = 1.67 mm^{-1}. **1b**: $C_{12}H_{20}ClNPdS$, fw = 352.2, monoclinic, space group $P2_1/n$, a = 11.792(5) Å, b = 10.013(5) Å, c = 13.301(6) Å, V = 1513(1) Å^3, Z = 4, ρ = 1.546 g/cm^3, μ = 1.517 mm^{-1}. Suitable crystals (obtained by slow diffusion of hexane in CH_2Cl_2 solutions) of complexes **1a** and **1b** were mounted on a glass fiber at room temperature (20 °C). Data collection for both crystals was performed on a Nicolet Siemens R3m/V diffractometer (oriented graphite monochromator; Mo Kα radiation, λ = 0.710 73 Å at 293(2) K). No sign of crystal deterioration was revealed by monitoring 3 standard reflections after every 200 measurements for **1a** (2 standards every 150 reflections for **1b**). The stuctures were solved by heavy-atom methods and completed by a combination of least-squares techniques (on F^2) and Fourier syntheses with the SHELXTL program library. Totals of 2890 and 2151 unique reflections with $I > 2\sigma(I)$ were observed for **1a** and **1b**, respectively. All hydrogen atoms, apart from those at C(11), were included in the idealized positions with C−H distances and isotropic temperature factors fixed at 1.2 times the U_{eq} value of the preceding carbon atom. All non-hydrogen atoms were refined anisotropically. Selected bond distances and angles are summarized in Table 1. Final agreement factors were R = 0.045, R_w = 0.105, and GOF = 1.187 for **1a** and R = 0.037, R_w = 0.105, and GOF = 1.110 for **1b**. Additional crystallographic data (atomic coordinates, full listings of bond lengths and angles, anisotropic thermal parameters) are provided as Supporting Information.

Table 2. Second-Order Rate Constants, k_2 (mol^{-1} dm^3 s^{-1}), for the Reactions of DMA and TMA with 1 and 2 at 25 °C

[PdCl(Me)(R′N−SR)]	DMA	TMA
1a: R′ = H, R = *t*-Bu	2.3×10^{-4} [a]	*b*
1b: R′ = Me, R = *t*-Bu	$(3.3 \pm 0.1) \times 10^{-1}$ [c]	$(1.07 \pm 0.05) \times 10^{-2}$ [c]
2a: R′ = H, R = Ph	$(4.0 \pm 0.3) \times 10^{-2}$ [c]	*b*
2b: R′ = Me, R = Ph	23 ± 1 [c]	$(4.6 \pm 0.1) \times 10^{-1}$ [c]

[a] Computed from $t_{1/2}$ values in CD_2Cl_2 by ^1H NMR. [b] Too slow to measure. [c] In CH_2Cl_2 by UV/vis.

give the allyl complexes **3** and **4** upon addition of $NaClO_4$.[10] The pyridine−thioether ligands chosen impart sufficient stability to both the reacting metal substrates and the η^3-allyl derivatives to warrant a smooth reaction course which can be easily monitored by ^1H NMR or UV/vis techniques.



The course of the reactions was followed by either ^1H NMR or UV/vis techniques,[11] depending on reaction rates. Slower reactions were followed only by ^1H NMR to prevent partial decomposition occurring under UV/vis concentration conditions (disappearance of Pd−CH_3 protons at ∼1 ppm was monitored). Faster reactions were studied by UV/vis techniques and confirmed, when possible, by ^1H NMR. The results are summarized in Table 2. Strictly speaking, the reactivity of **1a** could not be directly compared with other data reported in Table 2 owing to the larger error affecting NMR rate measurements. However, the reactivities are so markedly dissimilar that the accelerating effect of the methyl group in position 6 of pyridine ring is borne out clearly when **1a** is compared with **1b**. Complexes **2a** and **2b** display the same reactivity trend, **2b** being more reactive than **2a** by almost 3 orders of magnitude. To the best of our knowledge, complex **2b** displays the highest reactivity toward insertion of allene observed so far. This fact, in our opinion, can be traced back to the peculiar electronic characteristics of the phenyl substituent to sulfur, which render the metal more efficient as an electrophilic center compared with the bulky and electron donating *tert*-butyl group, compounded with the severe distortion induced by the methyl moiety on the pyridine ring. Moreover, the high flexibility of the S-donor chelate ligand allows for distortion of the coordinating environment while providing for sufficient stability of the metal−polydentate ring.

The resulting enhanced reactivity and the subsequent facile insertion of the hindered TMA yields the corresponding pentamethyl-substituted allyl derivative **4d**, which can be easily converted to various different allylic species owing to the lability of the MeN−SPh ancillary ligand toward substitution by nucleophiles.[5b]

A 6-methyl-substituted pyridyl group in a pyridyl−phosphine ligand bound to palladium(II) has been shown earlier to play a marked role in enhancing the rate and selectivity of formation of methyl methacrylate by methoxycarbonylation of propyne catalyzed by such palladium(II) complexes.[13]

Supporting Information Available: Tables giving atomic coordinates, bond distances and angles, and anisotropic displacement parameters for **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Complexes **3** and **4** were obtained from the CD_2Cl_2 (or $CDCl_3$) ^1H NMR reaction mixtures. The solutions were dried under vacuum, dissolved in a small volume of CH_2Cl_2, and treated with a methanolic solution of $NaClO_4$. Alternatively, complexes **3** and **4** were obtained by reacting the appropriate allene with [PdCl(Me)(COD)] in freshly distilled CH_2Cl_2. The resulting dimeric [PdCl(η^3-allyl)]$_2$ complexes were converted into the corresponding complexes **3** and **4** by addition of the required R′N−SR ligand and of stoichiometric $NaClO_4$ dissolved in MeOH (CH_2Cl_2/MeOH 3/1 v/v). Reduction to small volume and addition of diethyl ether yield the required complex. The analysis and ^1H NMR spectra of the complexes obtained by the two alternative routes turn out to be coincident. The isomers arising from the stereogenic character of the sulfur atom and the pseudo-*cis* or pseudo-*trans* species (dimethyl-substituted allylic carbon *cis* to sulfur and vice versa) were not detected owing to the general fluxionality affecting these systems at room temperature: i.e., sulfur inversion and allyl apparent rotation. However, a detailed analysis of this behavior for analogous complexes by variable-temperature ^1H NMR spectrometry has been carried out and described in a previous paper.[5b] **3a**: yield 80%. Anal. Found: C, 40.98; H, 5.61; N, 2.93. Calcd for $C_{16}H_{26}O_4ClNPdS$: C, 40.86; H, 5.57; *N*, 2.98. ^1H NMR (323 K, $CDCl_3$, ppm): δ 1.40 (9H, s, C(CH_3)$_3$), 1.53 (3H, s, Me_{anti}), 1.81 (3H, s, Me_{syn}), 2.18 (3H, s, $Me_{central}$), 4.11 (2H, bs, H_{anti}, H_{syn}), 4.55 (2H, bs, CH_2−S), 7.51 (1H, bs, H^5_{pyr}), 7.95 (2H, m, H^3_{pyr}, H^4_{pyr}), 8.65 (1H, bs, H^6_{pyr}). **3b**: yield 92%. Anal. Found: C, 41.98; H, 5.67; N, 2.83. Calcd for $C_{17}H_{28}O_4ClNPdS$: C, 42.16; H, 5.82; N, 2.89. ^1H NMR (298 K, $CDCl_3$, ppm): δ 1.26 (9H, s, C(CH_3)$_3$), 1.50 (3H, s, Me_{anti}), 1.75 (3H, s, Me_{syn}), 2.16 (3H, s, $Me_{central}$), 2.75 (3H, s, C_5H_3N-6-CH_3), 3.76 (1H, s, H_{anti}), 4.45 (1H, s, H_{syn}), 4.51 (2H, bs, CH_2−S), 7.36 (1H, d, J = 7.7 Hz, H^5_{pyr}), 7.65 (1H, d, J = 7.7 Hz, H^3_{pyr}), 7.84 (1H, t, J = 7.7 Hz, H^4_{pyr}). **3c**: yield 93%. Anal. Found: C, 44.15; H, 4.67; N, 2.81. Calcd for $C_{18}H_{22}O_4ClNPdS$: C, 44.09; H, 4.52; N, 2.86. ^1H NMR (298 K, $CDCl_3$, ppm): δ 1.33 (3H, bs, Me_{anti}), 1.61 (3H, bs, Me_{syn}), 2.18 (3H, s, $Me_{central}$), 4.02 (1H, bs, H_{anti}), 4.35 (1H, bs, H_{syn}), 4.76 (2H, bs, CH_2−S), 7.47 (5H, m, H^5_{pyr}, H_{phen}), 7.66 (1H, d, J = 7.7 Hz, H^3_{pyr}), 7.92 (1H, td, J = 7.7, 1.6 Hz, H^4_{pyr}), 8.88 (1H, bs, H^6_{pyr}). **3d**: yield 97%. Anal. Found: C, 45.31; H, 4.87; N, 2.80. Calcd for $C_{19}H_{24}O_4ClNPdS$: C, 45.25; H, 4.80; N, 2.78. ^1H NMR (298 K, $CDCl_3$, ppm): δ 1.42 (3H, s, Me_{anti}), 1.65 (3H, s, Me_{syn}), 2.21 (3H, s, $Me_{central}$), 2.81 (3H, s, C_5H_3N-6-CH_3), 3.94 (1H, s, H_{anti}), 4.57 (1H, s, H_{syn}), 4.82 (2H, bs, CH_2−S), 7.42 (7H, m, H^3_{pyr}, H^5_{pyr}, H_{phen}), 7.73 (1H, t, J = 7.7 Hz, H^4_{pyr}). **4b**: yield 85%. Anal. Found: C, 44.61, H, 5.98, N, 2.81. Calcd for $C_{19}H_{32}O_4ClNPdS$: C, 44.54, H, 6.29; N, 2.73. ^1H NMR (298 K, $CDCl_3$, ppm): δ 1.21 (9H, s, C(CH_3)$_3$), 1.75 (6H, s, Me_{anti}), 1.82 (6H, s, Me_{syn}), 2.10 (3H, s, $Me_{central}$), 2.83 (3H, s, C_5H_3N-6-CH_3), 4.48 (2H, bs, CH_2−S), 7.43 (1H, d, J = 7.7 Hz, H^5_{pyr}), 7.64 (1H, d, J = 7.7 Hz, H^3_{pyr}), 7.83 (1H, t, J = 7.7 Hz, H^4_{pyr}). **4d**: yield 82%. Anal. Found: C, 47.41; H, 5.28; N, 2.71. Calcd for $C_{21}H_{28}O_4ClNPdS$: C, 47.38; H, 5.30; N, 2.63. ^1H NMR (298 K, $CDCl_3$, ppm): δ 1.79 (6H, s, Me_{anti}), 1.86 (6H, s, Me_{syn}), 2.17 (3H, s, $Me_{central}$), 2.84 (3H, s, C_5H_3N-6-CH_3), 4.78 (2H, bs, CH_2−S), 7.35 (7H, m, H^3_{pyr}, H^5_{pyr}, H_{phen}), 7.67 (1H, t, J = 7.7 Hz, H^4_{pyr}).

(11) The kinetics were followed under pseudo-first-order conditions ([allene] ≥ 10[Pd]$_0$) by mixing known aliquots of prethermostated CH_2Cl_2 solutions of reactants in the cell compartment of a Perkin-Elmer Lambda 40 spectrophotometer. The reactions followed a monoexponential rate law with the pseudo-first-order constant k_{obsd} equal to k_2[allene]. No statistically significant allene-independent k_1 path was observed, at variance with earlier related systems.[3d,e] For the reaction of **1a** with TMA in CD_2Cl_2 monitored under second-order conditions by ^1H NMR techniques, the rate constant k_2 was computed from half-life values ([allene] ≈ 5[Pd]$_0$ = 0.05 mol dm^{-3}).

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