Reactivity of cyclopalladated compounds. 23. Formal carbon-carbon triple-bond splitting in an organopalladium compound

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Organometallics, **1990**, 9 (11), 3003-3005• DOI: 10.1021/om00161a034 • Publication Date (Web): 01 May 2002 localized on the germanium atom.[13] The shifts for ortho ($\Delta\delta = 0.6$ ppm) and meta carbons ($\Delta\delta = -2.3$ ppm) are weak. The shielding of the para carbon ($\Delta\delta = -5.9$ ppm) has been interpreted as an increase in π-electron density at this position corresponding to the resonance form **9** or to a polarization of the phenyl ring by the negatively charged germanium.[13]

Moreover, the deshielding of five-membered-ring carbons C_α ($\Delta\delta = 10.5$ ppm) and C_β ($\Delta\delta = 2.6$ ppm) do not correspond to a delocalization of the negative charge onto the ring. The increase of the π-electron density on the ethylenic carbons in the cyclopentadienide anion, with regard to those of cyclopentadiene, leads to an important shielding ($\Delta\delta \simeq -30$ ppm).[15] The high electronic cyclic delocalization within phospholyllithiums gives a double-bond character to the ring phosphorus–carbon bonds and a shielding of the C_β ring carbons ($\Delta\delta = -20$ ppm).[16]

Consequently, the field effect of the negatively charged germanium atom in **7** is clearly accentuated on the three neighboring carbons.

Our results demonstrate that the presence of phenyl groups on the ring carbons is not necessary to stabilize the germacyclopentadienide anion and that the negative charge is localized on the germanium atom.

Registry No. 2, 113111-20-9; 3, 127932-68-7; 4, 129466-89-3; 5, 129466-90-6; 6, 129466-91-7; 7, 129466-92-8; chlorotrimethylstannane, 1066-45-1.

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Formal C–C Triple-Bond Splitting in an Organopalladium Compound[1]

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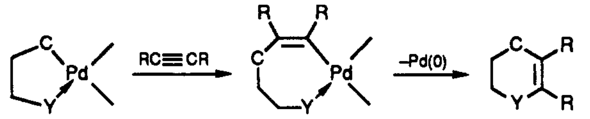
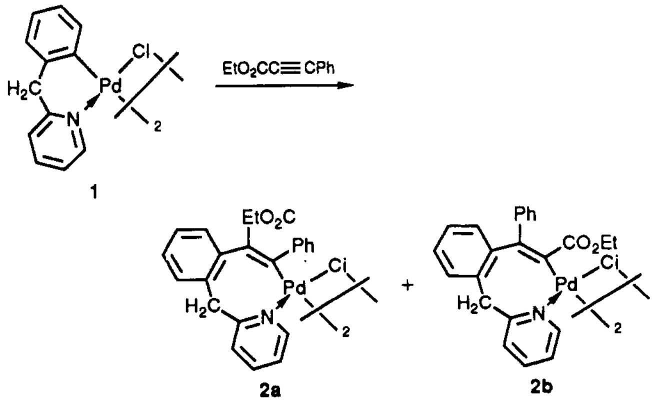
Summary: The cationic cyclopalladated compound derived from cyclometalated 2-benzylpyridine affords a heterocyclic compound containing a benzo[*b*]quinolizinium unit upon reaction with ethyl 3-phenylpropiolate through an overall C–C triple-bond cleavage of the alkyne.

It is known that the reaction between alkynes and cyclopalladated compounds can afford new synthetic pathways to heterocyclic compounds after depalladation of the organometallic intermediate.[2] This is indeed the case when one alkyne has been inserted into the Pd–C bond of the starting material, which then leads to six- or seven-membered heterocyclic rings, depending upon the size of the cyclopalladated ring. The following scheme summarizes this reaction sequence:



Herein we wish to report a reaction in which it is the vinyl carbon β to the palladium atom that is linked to the nitrogen, and hence, this result might shed some light on the depalladation process of the reaction described above.

We previously reported[3] that the cyclopalladated 2-benzylpyridine **1** leads to ring-expanded compounds when treated with internal alkynes. In contrast to related examples, the reaction with ethyl 3-phenylpropiolate afforded two isomers, **2a** and **2b**, in a 97/3 ratio:



The reaction between the iodide derivative of **1** and alkynes allowed isolation (in low yield, however) of seven-membered heterocyclic cations, this being the result of C–N bond formation between the palladated vinyl group and the nitrogen atom of intermediates analogous to **2a**.

Table I. Selected Bond Lengths (Å) for Compound 4[a]

N–C1	1.454 (7)	C7–C8	1.424 (8)	B–F2	1.347 (7)
N–C5	1.446 (7)	C7–C12	1.385 (7)	B–F3	1.368 (7)
N–C13	1.429 (7)	C8–C9	1.322 (8)	B–F4	1.333 (7)
C1–C2	1.348 (7)	C9–C10	1.406 (8)	C14–C15	1.374 (7)
C2–C3	1.391 (8)	C10–C11	1.340 (7)	C14–C19	1.375 (6)
C3–C4	1.338 (9)	C11–C12	1.368 (7)	C15–C16	1.386 (7)
C4–C5	1.413 (8)	C12–C13	1.336 (6)	C16–C17	1.358 (8)
C5–C6	1.383 (8)	C13–C14	1.492 (7)	C17–C18	1.350 (8)
C6–C7	1.365 (7)	B–F1	1.346 (7)	C18–C19	1.364 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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0276-7333/90/2309-3003$02.50/0

Table II. Selected Bond Angles (deg) for Compound 4[a]

C1-N-C5	119.4 (6)	C8-C7-C12	119.2 (6)	F1-B-F4	109.3 (6)
C1-N-C13	122.9 (6)	C7-C8-C9	120.1 (7)	F2-B-F3	109.5 (6)
C5-N-C13	117.7 (6)	C8-C9-C10	120.4 (7)	F2-B-F4	111.2 (6)
N-C1-C2	118.7 (6)	C9-C10-C11	119.4 (7)	F3-B-F4	110.0 (5)
C1-C2-C3	121.3 (7)	C10-C11-C12	122.5 (6)	C13-C14-C15	120.4 (5)
C2-C3-C4	122.3 (7)	C7-C12-C11	118.4 (5)	C13-C14-C19	120.0 (5)
C3-C4-C5	121.1 (7)	C7-C12-C13	122.3 (6)	C15-C14-C19	119.6 (5)
N-C5-C4	117.2 (7)	C11-C12-C13	119.3 (5)	C14-C15-C16	118.7 (5)
N-C5-C6	118.7 (6)	N-C13-C12	120.1 (5)	C15-C16-C17	120.7 (6)
C4-C5-C6	124.1 (7)	N-C13-C14	119.1 (6)	C16-C17-C18	120.4 (6)
C5-C6-C7	121.5 (7)	C12-C13-C14	120.8 (5)	C17-C18-C19	120.0 (6)
C6-C7-C8	121.1 (7)	F1-B-F2	110.3 (6)	C14-C19-C18	120.6 (5)
C6-C7-C12	119.6 (6)	F1-B-F3	106.5 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
N	0.2063 (7)	0.0708 (3)	-0.1480 (3)	7.2 (2)
C1	0.3654 (8)	0.0671 (3)	-0.1798 (3)	5.6 (2)
C2	0.4330 (8)	0.0114 (3)	-0.1881 (4)	6.4 (2)
C3	0.353 (1)	-0.0420 (3)	-0.1679 (4)	7.6 (2)
C4	0.2060 (9)	-0.0410 (3)	-0.1387 (4)	6.5 (2)
C5	0.1244 (8)	0.0149 (2)	-0.1272 (3)	4.9 (1)
C6	-0.0269 (8)	0.0192 (3)	-0.0969 (3)	5.7 (2)
C7	-0.0989 (7)	0.0746 (3)	-0.0859 (3)	5.0 (2)
C8	-0.2534 (8)	0.0786 (3)	-0.0534 (4)	6.4 (2)
C9	-0.3192 (8)	0.1328 (3)	-0.0412 (4)	7.0 (2)
C10	-0.2385 (8)	0.1869 (3)	-0.0614 (4)	6.0 (2)
C11	-0.0938 (7)	0.1830 (3)	-0.0926 (3)	5.0 (2)
C12	-0.0201 (6)	0.1281 (2)	-0.1057 (3)	2.2 (1)
C13	0.1250 (7)	0.1276 (2)	-0.1365 (3)	4.0 (1)
B	-0.2774 (8)	-0.1211 (3)	-0.0799 (4)	4.5 (2)
F1	-0.1376 (5)	-0.1386 (2)	-0.0498 (3)	10.8 (1)
F2	-0.3792 (5)	-0.1688 (2)	-0.0819 (2)	8.2 (1)
F3	-0.3369 (5)	-0.0763 (2)	-0.0337 (2)	8.5 (1)
F4	-0.2523 (6)	-0.0985 (2)	-0.1489 (2)	9.8 (1)
C14	0.2044 (7)	0.1860 (2)	-0.1592 (3)	3.8 (1)
C15	0.3025 (7)	0.2163 (3)	-0.1096 (3)	4.9 (2)
C16	0.3689 (8)	0.2717 (3)	-0.1318 (4)	6.2 (2)
C17	0.3414 (8)	0.2947 (2)	-0.2019 (4)	5.8 (2)
C18	0.2450 (9)	0.2647 (2)	-0.2504 (4)	6.0 (2)
C19	0.1786 (7)	0.2100 (2)	-0.2300 (3)	5.1 (2)
H1	0.4215	0.1050	-0.1940	
H2	0.5428	0.0069	-0.2093	
H3	0.3957	-0.0820	-0.1757	
H4	0.1569	-0.0788	-0.1200	
H6	-0.0803	-0.0192	-0.0842	
H8	-0.3100	0.0406	-0.0406	
H9	-0.4265	0.1358	-0.0205	
H10	-0.2898	0.2268	-0.0534	
H11	-0.0363	0.2215	-0.1050	
H15	0.3246	0.1983	-0.0602	
H16	0.4416	0.2924	-0.0965	
H17	0.3907	0.3344	-0.2163	
H18	0.2247	0.2842	-0.3002	
H19	0.1085	0.1877	-0.2648	

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2b_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Our earlier attempts to perform similar reactions with the cationic compound 3 derived from 1 by chloride abstraction were not successful. We have now found that 3 leads to the isolation of a new cation, 4, in ca. 20% yield upon reaction with ethyl 3-phenylpropiolate in chlorobenzene at reflux temperature. the ^{1}H NMR spectrum of 4 indicates that only aromatic protons are present. The CH_2 and the carboethoxy groups are notably absent. An X-ray structure analysis of 4 showed that it consists of a 1-phenylbenzo[*b*]quinolizinium cation (see Figure 1), which is actually formed by linking the palladated carbon atom in 3 to the nitrogen atom with a "phenyl-carbyne" unit.

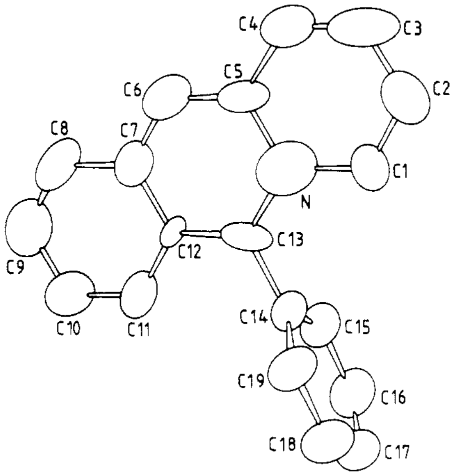
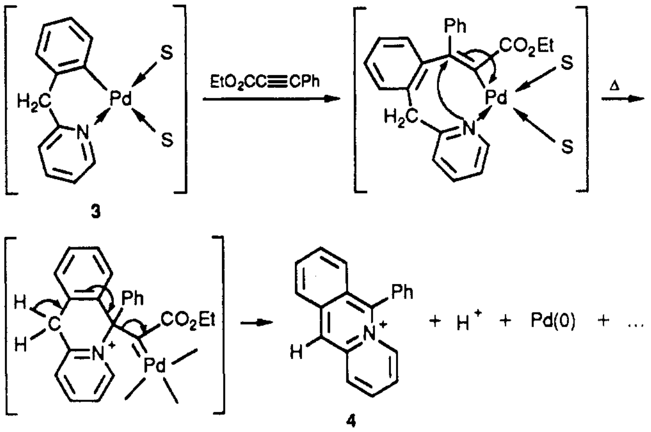


Figure 1. ORTEP view of the cationic part of compound 4.

Scheme I



3

4

Thus, this reaction is formally the result of a palladium-induced C-C triple-bond cleavage. We have also shown that when heating a mixture of compounds **2a** and **2b**, which was first treated with $AgBF_4$ so that **2a** and **2b** were converted into their cationic derivatives, in refluxing chlorobenzene, compound 4 could also be obtained in yields that are directly related to the abundance of **2b** in the reaction mixture. A likely reaction path is depicted in Scheme I. It involves at an early stage a nucleophilic attack of the nitrogen atom on the palladated vinyl group at the carbon β to Pd, akin to a classical Michael-type addition of a tertiary amine[4] on an alkene activated by an ester group.

This can, however, only occur via dissociation of the nitrogen from the palladium to form a transient Pd(II)

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(4) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 3rd ed.; Wiley: New York, 1985; p 689.

complex that is coordinatively unsaturated. Such a 14e species has never been structurally characterized; nevertheless, it has been postulated to be the intermediate to reductive-elimination processes for Pd(II) compounds on the basis of theoretical calculations.[5] Moreover, the fourth coordination site on the metal might be occupied by a solvent (chlorobenzene), since it was shown recently that chlorinated solvents such as CH_2Cl_2 can indeed coordinate to Pd(II).[6] It is well-known that the Michael-type addition of pyridine to activated alkenes is catalyzed by acids. However, it was proposed that the role of the acid is to protonate the carbanion formed after the C–N bond between the alkene and pyridine has been completed.[7] In the present case the palladium atom could trap this carbanion to form a palladacarbene moiety (although we have no evidence for it), which should be rather unstable and rearrange to afford **4**, metallic palladium, and other decomposition products.[8] The depalladation of the major isomer **2a** should accordingly afford a seven-membered heterocycle by nucleophilic attack of the nitrogen atom at the carbon α to the palladium center; however, this compound was never characterized, most probably due to extensive decomposition under the reaction conditions.

It appears therefore from this study that the intramolecular formation of the C–N bond in the heterocyclic compounds obtained through the depalladation of organopalladium compounds cannot be simply rationalized by a reductive-elimination process. A reaction path involving a nucleophilic attack of the nitrogen on the palladated carbon atom is more likely to take into account the results described here.

Experimental Section

General procedures and spectroscopic measurements were performed as described previously. Compound **3** was prepared by published methods.[2a]

Synthesis of 4. Ethyl 3-phenylpropiolate (0.26 g; 1.5 mmol) was added to a solution of compound **3** in chlorobenzene (40 mL). The solution was heated at reflux temperature for 45 min. The metallic palladium formed was removed by filtering the solution on a Celite column (5 cm). The solvent was then removed under vacuum, and the residue was washed with *n*-pentane (2 × 10 mL). The red residue was dissolved in CH_2Cl_2 (10 mL), and a layer of pentane was added to this solution (25 mL). After several days at room temperature this afforded compound **4** as colorless needles (0.030 g, 17%). Anal. Calcd for $C_{19}H_{14}BF_4N$: C, 66.51; H, 4.11; N, 4.08. Found: C, 66.10; H, 4.16; N, 3.92. ^1H NMR (CD_3CN, δ): 9.08 (s, 1 H, H^6), 8.58–7.47 (4 m, 13 H, aromatic protons). ^{13}C NMR (CD_3CN, δ): 148.14, 138.24, 135.68, 129.0, 126.9 (5 s, quaternary aromatic carbons); 131.44, 130.33, 130.03, 127.83, 122.79 (5 m, tertiary aromatic carbons).

Crystal Structure of 4: orthorhombic; space group *Pbca*; a = 8.410 (8) Å, b = 21.79 (1) Å, c = 17.705 (5) Å; V = 3244.1 Å^3, Z = 8; ρ_{calcd} = 1.41 g·cm^{-3}; F_{000} = 1408; λ = 0.71073 Å; 3246 independent reflections were measured (Enraf-Nonius CAD-4 diffractometer, $\theta/2\theta$ flying step scan, $1° < \theta < 25°$), for which corrections for Lorentz and polarization effects were applied, but not for absorption, owing to the low value of the linear coefficient. The structure was solved on a PDP 11/60 computer with the SDP package.[9] The atomic positions of the independent atoms of the molecular unit were found with the program Multan and subsequent Fourier difference syntheses. A total of 969 data with $I > \sigma(I)$ were available for the refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of the 25 independent non-hydrogen atoms, leading to R and R_w values of 0.097 and 0.090, respectively. At this stage, introduction of the 14 hydrogen atoms in calculated positions, held fixed with isotropic thermal parameters of 5 Å^2, was very significant, leading to final R and R_w values of 0.071 and 0.062 after two last cycles of refinement of the non-hydrogen atoms.

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Registry No. 3, 129620-57-1; 4, 129620-56-0; ethyl 3-phenylpropiolate, 2216-94-6.

Supplementary Material Available: A table of thermal parameters for 4 (2 pages); a listing of observed and calculated structure factors for 4 (6 pages). Ordering information is given on any current masthead page.

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(8) A reviewer has suggested an alternate mechanism in which proton transfer from the CH_2 group occurs initially to give a palladacarbene stabilized by intramolecular coordination of the pyridine to Pd, the C–N bond formation then being induced by an electrocyclic reaction from which compound 4 is formed by loss of the Pd carbene moiety.

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