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COMMUNICATION

CHLOROPALLADATION OF PROPARGYL THIOETHERS: A FACILE SYNTHESIS OF CYCLOPALLADATED COMPOUNDS

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Abstract—The reaction of the propargyl thioethers Ph—C≡C—CH(R_1)SR (R = Me, Pr^i, Ph and R_1 = H, Me) with Li_2PdCl_4 in methanol at room temperature produced in very good yields (70–90%) five-membered palladocycles [Pd(C(Ph)=C(Cl)CH(R_1)SR)(μ-Cl)]$_2$. Under the same reaction conditions the homopropargylthioether Ph—C≡C—$(CH_2)_2$SPh yielded unexpectedly the complex {Pd[S(Ph)$(CH_2)_3$C=O(Ph)](Cl)(μ-Cl)}$_2$ resulting from the hydrolysis of the C≡C bond.

It is well known that group 8 and 10 metal complexes catalyse many remarkable oligomerization reactions of acetylenes.[1] For example, palladium chloride complexes catalyse the trimerization of diphenylacetylene and mono-*tert*-butylacetylene, producing selectively hexaphenylbenzene and 1,3,5-tri-*tert*-butylbenzene, respectively.[2] The mechanism of these palladium chloride-catalysed oligomerizations of acetylenes is characterized by a series of acetylene insertion steps.[3,4] It is assumed that in the first step an acetylene complex of $PdCl_2$ is formed that rapidly rearranges to a chlorovinyl derivative by insertion of the C≡C bond into the Pd—Cl bond. This is followed by successive insertion of acetylenes into the Pd—C vinyl bond.[2–4] However, the presence of potential coordinating groups attached to the alkyne apparently inhibit these multiple insertion reactions and allow the isolation of chloropalladated complexes.[5] In this respect, we have recently shown that in the case of Pt chloride complexes, the chlorination reaction is strongly dependent on the nature of the coordinating group attached to the C≡C bond.[6] In this work, we present the chemical behaviour of a series of homo- and propargyl thioethers towards palladium chloride compounds.

RESULTS AND DISCUSSION

The homo- and propargyl thioethers **1–3** were easily prepared in 70–95% yield by substitution of the corresponding mesylated hydroxyl groups of the homo- and propargyl alcohols with NaSR.[7] The phenyl derivatives **4–6** were prepared from **1–3** and phenyliodide in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$/CuI (Scheme 1).[8]

The reaction of the terminal alkynes **1–3** with Li_2PdCl_4 in methanol or with $PdCl_2(PhCN)_2$ in dichloromethane, under various reaction conditions, afforded a complex mixture of products, probably resulting from the oligomerization of these alkynes. However, the addition of equimolar amounts of the alkyne **4** to a methanolic solution of Li_2PdCl_4 resulted almost instantaneously in the air stable compound **7** as a yellow solid in 85% yield (Scheme 2). The presence of an AB spin system centred at 3.98 ppm for the methylene protons in the ^{1}H NMR spectrum and the C=C bond resonances at 148.0 and 120.4 ppm in the ^{13}C NMR spectrum of compound **7** are good evidence for the formation of the five-membered palladocyclic ring.

Under the same reaction conditions used above

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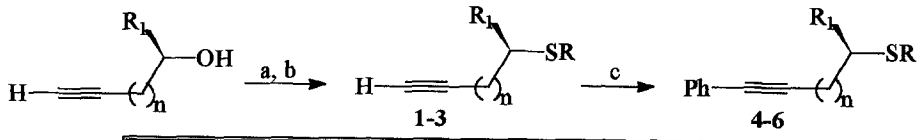


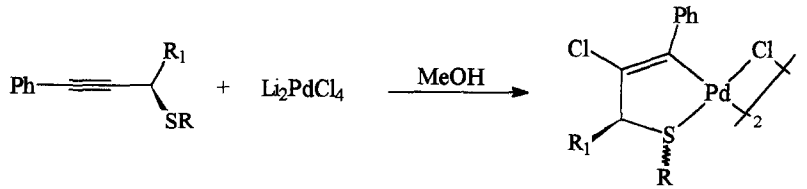
Alkyne	R	R_1	n	Alkyne	R	R_1	n
1	Ph	H	0	4	Ph	H	0
2a	Me	Me	0	5a	Me	Me	0
2b	^{i}Pr	Me	0	5b	^{i}Pr	Me	0
2c	Ph	Me	0	5c	Ph	Me	0
3	Ph	H	1	6	Ph	H	1

Scheme 1. (a) $ClSO_2Me$, CH_2Cl_2, NEt_3; (b) NaSR, EtOH; (c) PhI, $PdCl_2(PPh_3)_2$/CuI.

the alkynes **5** afforded in very good yields (70–90%) the corresponding cyclopalladated complexes **8**. The presence of two sets of signals in the ^{1}H NMR spectrum of the monomeric compound derived from **8a** (prepared *in situ* by the addition of pyridine-d_5 to a $CDCl_3$ solution of **8a** in the NMR tube) indicates the presence of two diastereoisomers in a 4:1 ratio. On the other hand, a single diastereoisomer has been observed for compounds **8b** and **c**, as indicated by the analysis of their ^{1}H and ^{13}C NMR spectra at room temperature. It is reasonable to assume for steric reasons an *anti* relationship between C-Me and S-R groups in **8b** and in the major diastereoisomer of **8a**. Interestingly, the ^{1}H NMR spectrum of **8c** is temperature dependent. At low temperatures (below 0°C) the CH group appears as a quartet centred at 4.05 ppm. The signal of this proton broadens at higher temperatures and coalesce at *ca* 20°C. This fluxional behaviour can be explained by the pyramidal inversion of the configuration of the sulfur atom in **8c**. In this compound the CMe and SPh groups probably possess an *anti* relationship at temperatures below 0°C. Indeed, a similar behaviour was already observed for related sulfur-containing palladocyclic compounds.[9]

The observed *trans* stereochemistry of the C=C bond in compounds **7** and **8** (with respect to the Cl atom and the Pd centre) suggests that this reaction proceeds via the coordination of the C≡C bond to the metal centre followed by external nucleophilic addition of a chloride anion to this activated triple bond yielding the more stable five-membered palladocycle.[6] However, it should be mentioned that a mechanism involving the isomerization (*via* a carbene-palladium transient species) of a *cis*-chlorovinylpalladium derivative resulting from the insertion of the alkyne into the Pd—Cl bond (Scheme 3), or even a more directly concerted reaction path cannot be discarded at this stage of our studies.[10]

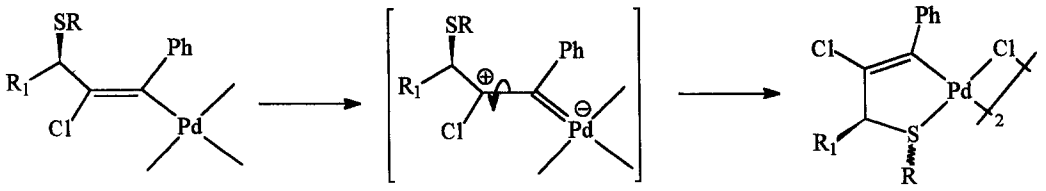
The reaction of the homopropargyl thioether **6** with Li_2PdCl_4 in wet methanol, at room temperature produced compound **9** in 45% yield (Scheme 4). The assignment of the structure of **9** was deduced from its IR and ^{1}H NMR spectrum and elemental analysis. Moreover, treatment of **9** with 2 equiv. of pyridine affords quantitatively *trans*-$PdCl_2Py_2$ and the palladium free ligand **10**.



	R	R_1
4	Ph	H
5a	Me	Me
5b	^{i}Pr	Me
5c	Ph	Me

	R	R_1
7	Ph	H
8a	Me	Me
8b	^{i}Pr	Me
8c	Ph	Me

Scheme 2. Chloropalladation of propargyl thioethers **4** and **5**.



Scheme 3.

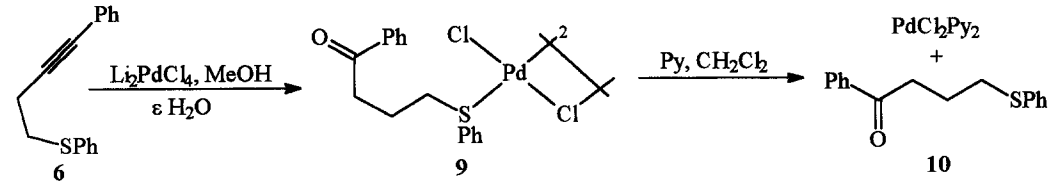
The unexpected formation of **9** can be understood in terms of a nucleophilic addition of water to the palladium-activated C≡C bond of **6**. This might give an enol that produces the observed ketone **10** by isomerization. This oxidation of the C≡C bond is somehow analogous to the monohydration of homopropargyl alcohols catalysed by Pd^{II}.[11]

In summary, we have shown that the chloropalladation of propargyl thioether occurs readily yielding five-membered palladocycles and that in the case of homopropargyl thioether a hydrolysis reaction of the C≡C bond sets in preferentially. The chloropalladation and oxidation reactions of a series of other homo- and propargyl thioethers and amines are underway in our laboratory.

EXPERIMENTAL

All preparative processes were carried out under dry argon using standard Schlenk techniques. The solvents were distilled from appropriate drying agents under argon. ^1H and ^{13}C NMR were recorded on a Varian Gemini 200 MHz spectrometer. The chemical shifts were measured in ppm relative to TMS as external standard. IR spectra were recorded on a Mattson 3020 FTIR spectrophotometer. Elemental analyses were carried out by the "Central Analítica-UFRGS", Brazil.

All the new compounds gave satisfactory CH analyses. Selected spectroscopic data are as follows: **(7)** IR (KBr pellets): 1607 (w), ν(C=C); 693 (m) cm^{-1}, ν(C—S). ^1H NMR ($CDCl_3$): 7.91, 7.52, 7.20 and 7.03 (4m, 10H, aromatic H); 4.27 and 3.70 [2d, 2H, AB system, J(AB) = 16.5 Hz, CH_2]. ^{13}C $\{^1H\}$ NMR ($CDCl_3$): 148.0 and 120.4 (C=C); 143.8 and 132.0 (C_{ipso}); 131.9, 130.9, 130.2, 128.1, 127.9 and 126.6 (aromatic CH); 50.7 (CH_2). **(8a)** IR (KBr pellets): 1602 (w), ν(C=C); 697 (m) cm^{-1}, ν(C—S). ^1H NMR ($CDCl_3+\varepsilon$Py-d_5): Major isomer: 7.02–6.83 (m, 5H, aromatic H); 3.80 [q, 1H, ^3J(HH) = 6.9 Hz, CH]; 2.87 (s, 3H, SMe); 1.72 (d, 3H, Me). Minor isomer: 7.02–6.83 (m, 5H, aromatic H), 4.13 (br s, 1H, CH); 2.65 (s, 3H, SMe); 1.70 [d, 3H, ^3J(HH) = 7.2 Hz, Me]. ^{13}C $\{^1H\}$ NMR ($CDCl_3+\varepsilon$Py-d_5): Major isomer: 148.3, 144.4 and 126.8 (C=C and C_{ipso}); 128.5, 127.8 and 125.1 (aromatic CH); 57.8 (SMe); 23.6 (CH); 21.1 (Me). Minor isomer: 52.9 (SMe); 20.1 (CH); 18.2 (Me). **(8b)** IR (KBr pellets): 1606 (w), ν(C=C); 695 (m) cm^{-1}, ν(C—S). ^1H NMR ($CDCl_3$): 6.94 and 6.71 (2m, 5H, aromatic H); 3.60 (m, 2H, 2CH); 1.65 (m, 9H, Me). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): 145.9, 144.0 and 126.9 (C=C and C_{ipso}); 128.1, 128.0 and 126.5 (aromatic CH); 52.9 and 45.4 (CH); 24.7; 23.4 and 21.3 (Me). **(8c)** IR (KBr pellets): 1608 (w), ν(C=C); 690 (m) cm^{-1}, ν(C—S). ^1H NMR ($CDCl_3$): 7.94–6.86 (m, 10H, aromatic H); 3.87 (br s, 1H, CH); 1.75 (br s, 3H, Me); $CDCl_3$, −20°C): 8.32, 8.05, 7.50 and 6.80 (4m, 10H, aromatic H); 4.05 [q, 1H, ^3J(HH) = 7.7 Hz, CH]; 1.82 (d, 3H, Me). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): 146.0, 143.5, 131.8 and 128.8 (C=C and C_{ipso}); 132.2, 130.9 and 128.8, 128.1, 127.9 and 126.4 (aromatic CH); 61.2 (CH); 20.5 (Me). **(9)** IR (KBr pellets): 1680 (s) cm^{-1}, ν(C=O). ^1H NMR ($CDCl_3$): 7.81–7.43 (m, 10H, aromatic H); 3.35 [t, 2H, ^3J(HH) = 7.0 Hz, CH_2]; 3.15 [t, 2H, ^3J(HH) = 6.9 Hz, CH_2]; 2.12 (m, 2H, CH_2). **(10)** IR (film): 1682 (s) cm^{-1}, ν(C=O). ^1H NMR ($CDCl_3$): 7.59–7.15 (m, 10H, aromatic H); 3.18 [t, 2H, ^3J(HH) = 7.0 Hz, CH_2]; 3.08 [t, 2H, ^3J(HH) = 6.9 Hz, CH_2]; 2.13 (m, 2H, CH_2). ^{13}C



Scheme 4. Reaction of the homopropargyl thioether **6** with Li_2PdCl_4.

{^{1}H} NMR ($CDCl_3$): 199.8 (CO); 137.5 and 136.4 (C_{ipso}); 133.3, 129.4, 129.1, 128.8, 128.2 and 126.2 (aromatic CH); 37.2, 33.4 and 23.7 (CH_2).

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