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Reactivity of cyclopalladated compounds

XXI *. Direct palladation of the prochiral CH_2 group of the α-trimethylsilyl-8-methylquinoline ligand by palladium(II), and reactions of the resulting Pd–C bond with alkynes

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Abstract

The reaction between α-trimethylsilyl-8-methylquinoline and palladium acetate, followed by metathesis of the acetato groups with lithium chloride, gave a mixture of chloride-bridged cyclopalladated dimers $[\{Pd\overline{CHRC_9H_6N}(\mu\text{-}Cl)\}]_2$ (**2**, R = H; **3**, R = $SiMe_3$) through cleavage of a C–Si and a C–H bond, respectively. In the presence of internal alkynes, compound **2** gave a stable chloride-bridged dimer by insertion of one molecule of dimethyl acetylenedicarboxylate (DMAD) into its Pd–C bond, and a monomeric compound by regioselective insertion of two molecules of ethyl-3-phenylpropiolate (EPP) into its Pd–C bond. In contrast, the reactions of **3** with both DMAD and EPP gave organometallic compounds containing η^3-allylic moieties; these were formed through insertion of the alkynes into the Pd–C bond of **3** followed by a 1,3-sigmatropic shift of the $SiMe_3$ group to the terminal carbon atom of the C(3) unit bridging the quinoline ring and the palladium atom.

Introduction

Cyclometallation is one of the most convenient methods for synthesizing organometallic compounds containing metal–carbon σ bonds. The scope of this reaction is now very well defined, and it has been shown that metallation can occur with almost any type of carbon atom [2]. Moreover it has been shown on many occasions that the cyclometallated compounds thus obtained, especially those in which the metal is palladium(II), can undergo several functionalization reactions of the metallated carbon atom that are relevant to organic synthesis [3]. We have thus

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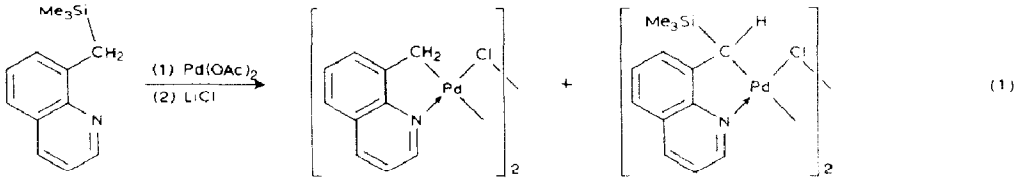
embarked on a study aimed at determining whether these latter reactions, involving complexes in which the palladated carbon atom is chiral [4], can afford functionalized ligands in which the chirality of the carbon atom is maintained. In previous studies we described the synthesis of such chiral cyclopalladated compounds containing the 2-(*N*,*N*-dimethylamino)-α-(trimethylsilyl)tolyl monoanion [5]. In these cases however, the complexes were obtained via the transmetallation of the lithiated ligand on a palladium(II) complex, since direct palladation of the prochiral CH_2 unit by Pd^{II} was not possible. We describe here the direct cyclopalladation of the prochiral α-(trimethylsilyl)-8-methylquinoline ligand (8mqSiH), which leads to the expected chiral cyclopalladated dimer, and also the reactions of this compound with internal alkynes.

Results and discussion

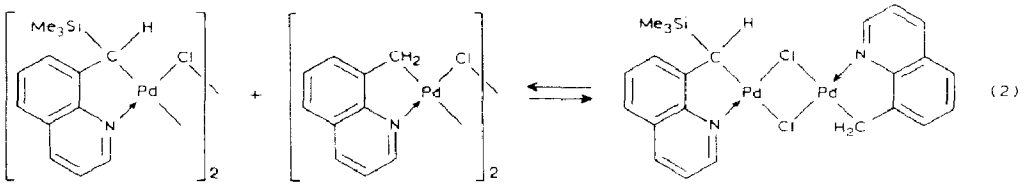
Synthesis of $[\{Pd\overline{CH(SiMe_3)C_9H_6N}(\mu\text{-}Cl)\}_2]$ *(3)*

Suggs and Lee have reported recently [6] that the reaction between $PdCl_2(PhCN)_2$ and 8mqSiH (**1**) in refluxing chloroform affords exclusively the cyclopalladated dimer **2** through cleavage of the C–Si bond of **1**. We have now found that with palladium acetate the reaction follows a different route. In the presence of one equivalent of **1** in toluene at 80 °C and after treatment of the product with lithium chloride, a mixture of the two chloride-bridged dimers **2** and **3** is obtained. Isolation



(1)

of **3** in a pure state was not easy (the yield of this chiral dimer was never higher than 8%) because during its separation from the reaction mixture it is difficult to eliminate completely **2** (see below) despite its known very low solubility in CH_2Cl_2 or $CHCl_3$ [7]. The ^1H NMR spectrum of **3** shows two singlets for the benzylic proton as well as two singlets for the $SiMe_3$ group. In the presence of pyridine-d_5, which is known to cleave the chloride bridges of these dimers, each of these signals gave rise to one singlet. These features are strong indications that **3** is a mixture of two diastereoisomers, with the configuration of the chiral carbon atoms being either *SS,RR*, or *SR,RS*, and the geometry of the dimer is probably *trans* with respect to the Pd_2Cl_2 central unit. As stated above it was difficult to separate **2** and **3** since in the presence of **3**, the dimer **2** dissolves in CH_2Cl_2. The ^1H NMR spectrum of a mixture of **2** and **3**, obtained by dissolving the maximum amount of **2** in a solution



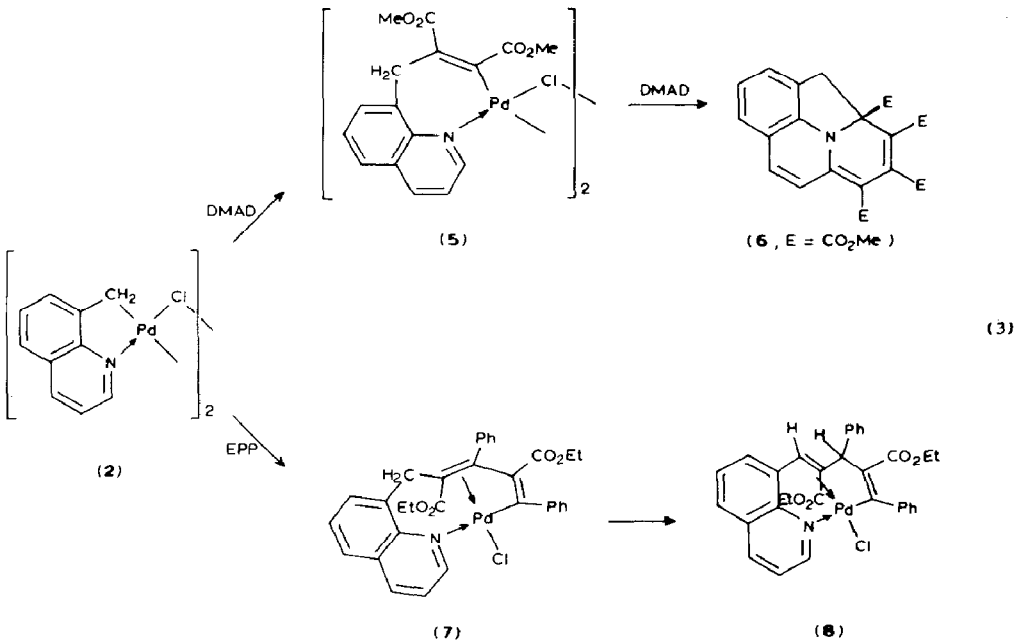
(2)

of **3** in $CDCl_3$ shows, inter alia, two new broad resonances for the benzylic proton at 4.06 and 3.86 ppm, whose integrals are in the ratio 1/2. (It has so far been impossible to get a good ^1H NMR spectrum of **2** in $CDCl_3$ or CD_2Cl_2.) These signals are assigned to a new dimer **4**, which could be formed in the reaction shown in eq. 2. In addition to the signals of **4**, we detected those of **3**, the ratio between **3** and **4** being ca. 1/2.

Reaction with alkynes

We showed previously that the reaction between **2** and an alkyne bearing electron-withdrawing groups, such as hexafluorobut-2-yne (HFB), affords a dimeric compound in which one HFB molecule has been inserted into the Pd–C bond of **2** [8]. We have now shown that upon treatment of **2** with one equivalent of dimethylacetylene dicarboxylate (DMAD) a similar reaction occurs, to give **5** in high yields. When **2** was treated with an excess of DMAD, the palladium-free compound **6** was obtained quantitatively. The elemental analyses and ^1H NMR data suggested that **6** has the structure depicted in eq. 3, i.e. that of a cycl[3.3.2]azine [9]. The features providing the strongest indication of this geometry were the disappearance of the proton *ortho* to N (H^o) on the quinoline ring and the fact that the protons *meta* (H^m) and *para* (H^p) to N now give rise to an AB pattern. The structure of **6** was further unambiguously characterized by an X-ray diffraction study. Full details of the synthesis and properties of **6** and related compounds will be presented elsewhere [10].

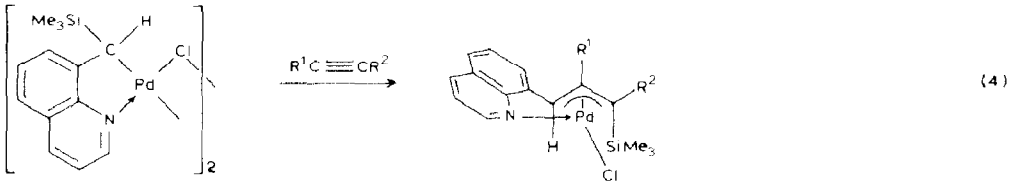
In reaction with an excess of ethyl 3-phenylpropiolate (EPP) at room temperature, compound **2** gave quantitatively the monomeric compound **7** through insertion of two alkynes into its Pd–C bond; it was not possible to observe insertion of only one EPP molecule by varying the stoichiometry or the reaction conditions. The ^1H



(3)

NMR spectrum of **7** showed the presence of a single isomer, so that both insertions of EPP must be regioselective. We believe that the positions of the phenyl and the carboethoxy substituents on the butadienyl chain shown in eq. 3 are correct; we have found on several occasions that this is invariably the orientation of the insertion of this unsymmetrical alkyne into Pd–C bonds [11,12]. When **7** was heated in refluxing chlorobenzene for 2 h, a mixture of products was obtained, and a new compound, **8**, which no longer contained a CH_2 group, was isolated in low yield. The ^{1}H NMR spectrum of **8** showed two singlets at 6.37 and 5.94 ppm. We suggest that the formation of **8** occurs via a 1,3 shift of one of the methylene protons of **7**, behaviour analogous to that observed previously for a related compound from **2** and diphenylacetylene [11].

In marked contrast to the behaviour of **2** with alkynes, compound **3** in the presence of both DMAD and EPP affords the mono inserted products **9a** and **9b**, respectively (see eq. 4). These compounds were found to be monomeric, as indicated



(4)

(3)

(**9a**: $R^1 = R^2 = CO_2Me$; **9b**: $R^1 = CO_2Et$, $R^2 = Ph$)

by their ^{1}H NMR spectra, which did not change in the presence of pyridine-d_5 (in contrast to **5** which gave a monomer in presence of pyridine-d_5, as noted in the Experimental section). In the ^{1}H NMR spectrum the allylic unit η^3-bonded to Pd shows characteristic resonances at 5.86 (**9a**) and 5.67 (**9b**) ppm that are attributable to the allylic proton.

A NOE experiment on **9b** confirmed this attribution. Thus irradiation at the $SiMe_3$ resonance led to significant enhancement of the signal of the allylic proton (59.4%) and of the phenyl group (9.0%), whereas irradiation at the allylic H induced enhancement of the $SiMe_3$ signal (3.5%) and of the proton of the quinoline ring which is in *ortho* position with respect to the allylic fragment. Thus, the $SiMe_3$ and the allylic proton cannot be on the same carbon atom; this was further supported by the absence of a significant NOE effect on the signal of the CO_2Et unit, during irradiation at the latter signals. It can be concluded that the carboethoxy group must thus be in the *anti*-position, whereas $SiMe_3$ and H must be in the *syn*-position with respect to the η^3-allylic moiety.

The formation of **9a** and **9b** is probably due to steric hindrance at the benzylic carbon atom after insertion of one alkyne into the Pd–C bond of **3** to form an hypothetical seven-membered ring analogous to **6**. This steric congestion should promote a 1,3 sigmatropic shift of the $SiMe_3$ unit, a feature in line with that observed recently for the related compound containing the 2-(*N*,*N*-dimethylamino)-α-(trimethylsilyl)tolyl monoanion [13].

Experimental

General procedures and spectroscopic measurements were as described previously [13]. Commercially available DMAD, EPP, and 8mqH were used without

further purification. α-Trimethylsilyl-8-methylquinoline (**1**) [6], and compound **2** [7], were prepared by published methods. Unless otherwise stated, ^{1}H NMR spectra were recorded in $CDCl_3$ at 20 °C; δ values are in ppm and J values in Hz.

Synthesis of [{Pd CH(SiMe$_3$)C$_9$H$_6$N (μ-Cl)}$_2$] (3)

Complex **1** (0.494 g, 2.29 mmol) was added to a solution of palladium acetate (0.529 g, 2.35 mmol) in toluene (30 ml). This solution was kept at 80 °C for 20 minutes, and the solvent then removed in vacuo. The residue was washed with pentane (3 × 5 ml) and extracted with 30 ml acetone. An excess of LiCl was added to the extract, and after 5 min stirring the solution was filtered through a Celite plug, and the solvent removed in vacuo. Column chromatography of the residue on a short (6 cm) column of alumina, with elution initially with CH_2Cl_2 (50 ml) and then with a mixture of CH_2Cl_2/MeOH (200/1) afforded a yellow solution. Removal of the solvent in vacuo afforded a yellow residue, from which **3** was extracted with CH_2Cl_2 (15 ml). Addition of hexane to this solution, gave pure **3** as a yellow powder; yield 0.075 g, 8.5%. Anal. Found: C, 44.0; H, 4.5; N, 3.9. $C_{13}H_{16}ClNPdSi$ calc.: C,43.82; H, 4.49; N, 3.93%. ^{1}H NMR: 8.75 (m, 1H, H^o); 8.17 (m, 1H, H^p); 7.45–7.26 (m, 4H, Ar); 4.01 and 3.98 (2s, 1H, CHSi); 0.05 and −0.01 (2s, 9H, $SiMe_3$).

[{Pd (MeO$_2$C)C=C(CO$_2$Me)CH$_2$C$_9$H$_6$N (μ-Cl)}$_2$], (5)

A solution of DMAD (1.0 g, 7.04 mmol) in 60 ml of CH_2Cl_2 was added dropwise to a suspension of **2** (2.01 g, 3.52 mmol) in CH_2Cl_2 (400 ml) during 1.5 h. The mixture was refluxed for 1.5 h, during which time an orange solution was formed. The solution was concentrated in vacuo to 50 ml and the bright yellow **5** which separated out was filtered off and washed several times with diethyl ether. The filtrate from the washings was evaporated to dryness, and the orange residue washed with CH_2Cl_2/hexane (1/1) (3 × 25 ml) to give a further sample of **5**. The combined fractions were dried in vacuo to give 2.51g (83%) of **5**. Anal. Found: C, 45.1; H, 3.2; N, 3.0. $C_{16}H_{14}ClNO_4Pd$ calc: C, 45.08; H, 3.29; N, 3.29. ^{1}H NMR ($CDCl_3$ + ε py d^5): 9.81–7.39 (m, 6H, Ar); 6.56 and 4.45 (2d, 2H, CH_2, ^2J(HH) 13.4); 3.54 and 3.43 (2s, 6H, $2CH_3$)

2H-2a,3,4,5-Tetramethoxycarbonyl-benzo[i,j]cycl[3.3.2]azine (6)

To a suspension of **2** (2 g, 3.51 mmol) in 100 ml of PhCl was added DMAD (2.1 g, 14.8 mmol). The mixture was stirred at 100 °C for 20 min and the solvent then removed in vacuo. The residue was extracted with 2 × 50 ml CH_2Cl_2, and the extract was filtered through a Celite plug to remove the metallic palladium formed. The orange filtrate was concentrated to ca 20 ml and chromatographed on an alumina column (6 cm). Elution with CH_2Cl_2 removed the excess of alkyne and impurities, and the product was eluted with acetone to give an orange solution, which was evaporated in vacuo to give 1.36 g (91%) of **6**. Crystals were obtained from a CH_2Cl_2/hexane mixture; m.p. 225–226 °C. Anal. Found: C, 61.6; H, 4.4; N, 3.15. $C_{22}H_{18}NO_8$ calc.: C, 61.95; H, 4.59; N, 3.29%. ^{1}H NMR: 8.40 and 7.78 (2d, 2H, H^m and H^p, ^3J(HH) 9.6); 4.14 and 3.91 (2d, 2H, CH_2, ^2J(HH) 17.5); 3.88, 3.79, 3.77 and 3.62 (4s, 12H, $4CH_3$).

[Pd(Ph)C=C(CO$_2$Et)C(Ph)=C(CO$_2$Et)CH$_2$C$_9$H$_6$N Cl] (7)

To a suspension of **2** (0.628 g, 1.11 mmol) in 50 ml of PhCl was added EPP (0.73 ml, 4.42 mmol). The mixture was stirred for 4 days at room temperature, and unchanged **2** was filtered off and the orange filtrate evaporated to dryness in vacuo. The residue was washed with pentane (2 × 15 ml) to remove traces of alkyne, and dried in vacuo to give 0.875 g (64%) of beige-yellow **7** as a single regioisomer. Anal. Found: C, 61.5; H, 4.5; N, 2.1 $C_{32}H_{28}ClNO_4Pd$ calc.: C, 60.77; H, 4.46; N, 2.22%. ^{1}H NMR: 9.82 (dd,1H, H^o, ^4J(HH) 1.7, ^3J(HH) 5.1); 8.17 (dd, 1H, H^p, ^3J(HH) 8.2); 8.03–7.24 (m, 14H, Ar); 4.18 (dq(ABX$_3$), 2H, CH_2CH$_3$); 3.88 (q, 2H, CH_2CH$_3$); 3.97 and 3.76 (2d, 2H, CH$_2$, ^2J(HH) 15); 1.06 and 0.91 (2t, 6H, 2CH$_3$, ^3J(HH) 7.1).

[Pd(Ph)C=C(CO$_2$Et)CH(Ph)C(CO$_2$Et)=CHC$_9$H$_6$N Cl] (8)

A solution of 7 (0.6 g, 0.95 mmol) in 20 ml of PhCl was refluxed for 2 h. After evaporation of the solvent in vacuo the residue was extracted with 50 ml CH_2Cl_2 and chromatographed on a silica column. Elution with CH_2Cl_2/acetone (1/1) afforded several dark bands, the second one of which gave compound **8** in low yield. This product was crystallised from CH_2Cl_2/hexane to give deep yellow crystals (10 mg, 2%). Anal. Found: C, 61.6; H, 4.6; N, 2.0 $C_{32}H_{28}ClNO_4Pd$ calc.: C, 60.77; H, 4.46; N, 2.22%. ^{1}H NMR: 9.23 (dd, 1H, H^o, ^4J(HH) 1.4, ^3J(HH) 4.7); 8.20 (dd, 1H, H^p, ^3J(HH) 8.3), 7.85–7.08 (m, 14H, Ar); 6.37 (s, 1H, *H*CPh); 5.94 (s, 1H, *H*C=C); 3.87 (q, 2H, CH_2CH$_3$); 3.60 (dq(ABX$_3$), 2H, CH_2CH$_3$); 0.80 and 0.51 (2t, 6H, 2CH$_3$, ^3J(HH) 7.1).

[Pd{η^3-C(CO$_2$Me)SiMe$_3$=C(CO$_2$Me)=CH}C$_9$H$_6$N Cl] (9a)

To a solution of **3** (66 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was added DMAD (50 μl, 0.4 mmol). The solution was stirred overnight at room temperature and the solvent then removed in vacuo. The light yellow residue was washed with pentane (3 × 5 ml) to remove unchanged alkyne, and the solid was dried in vacuo to afford 79 mg (84%) of **9a**. Anal. Found: C, 46.3; H, 4.35; N, 2.75. $C_{19}H_{22}Cl\ NO_4PdSi$ calc.: C, 45.79; H, 4.45; N, 2.81%. ^{1}H NMR: 9.20–7.40 (3 m, 6H, Ar); 5.86 (s, 1H, H(allyl)); 3.76 and 3.42 (2s, 6H, 2CH$_3$); 0.41 (s, 9H, SiMe$_3$).

[Pd{η^3-C(Ph)SiMe$_3$=C(CO$_2$Et)=CH}C$_9$H$_6$N Cl] (9b)

To a solution of **3** (40 mg, 0.06 mmol) in CH_2Cl_2 (10 ml) was added EPP (41 μl, 0.25 mmol). The mixture was stirred at room temperature for 48 h. (After 0.5 h a light yellow precipitate was formed; its ^{1}H NMR spectrum showed the presence of unchanged **3** together with an equal amount of EPP) The solvent was removed in vacuo, and the pale yellow residue was washed with pentane (3 × 5 ml) to remove unchanged alkyne and the remaining solid was dried in vacuo to afford 60 mg (94%) of **9b**. Anal. Found: C, 53.4; H, 4.7; N, 2.6. $C_{24}H_{26}ClNO_2PdSi$ calc.: C, 54.34; H, 4.94; N, 2.64%. ^{1}H NMR: 9.22 (dd, 1H, H^o, ^4J(HH) 1.5, ^3J(HH) 4.7 Hz); 8.31 (dd, 1H, H^p, ^3J(HH) 8.4); 7.86–7.11 (m, 9H, Ar); 5.76 (s,1H, H(allyl)); 3.51 (dq (ABX$_3$), 2H, CH_2CH$_3$); 0.36 (t, 3H, CH$_3$); 0.29 (s, 9H, SiMe$_3$).

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