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Preliminary communication

Novel carbon–carbon bond formation induced by depalladation of organometallic compounds

Michel Pfeffer, Marc A. Rotteveel, Jean-Pascal Sutter,
Laboratoire de chimie de coordination. UA 416, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex (France)

André De Cian and Jean Fischer
Laboratoire de cristallochimie, UA 424, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex (France)

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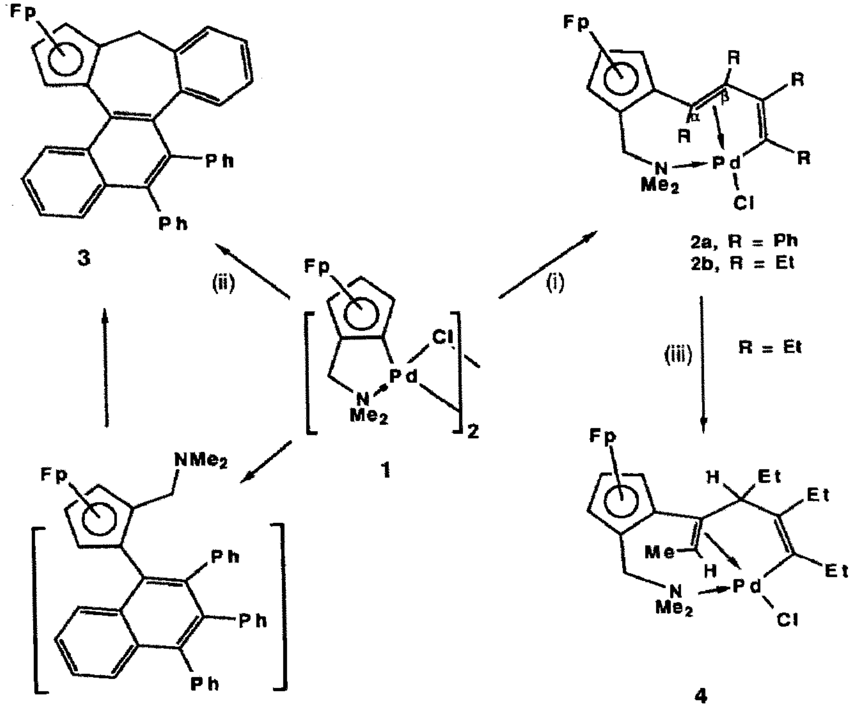
Abstract

Two internal alkynes undergo insertion at 20 °C into the Pd–C bond of the cyclopalladated derivative of dimethylaminomethylferrocene to give new organometallic compounds. When the reaction with diphenylacetylene is performed at higher temperatures, depalladation occurs readily to give six- and seven-membered *ortho*-fused rings through new annulation reactions of phenyl groups, formation of one of these involving also the cleavage of a C–N bond.

Insertion of alkynes into the Pd–C bond of cyclometallated compounds has attracted much interest recently [1,2], since it has been shown that it provides a new selective route to heterocyclic compounds [1a–c,e,f], and because of the possibility that unprecedented annulation of aryl units might be discovered [1d,2]. Most of the reactions studied so far have been observed with compounds in which an aromatic carbon atom has been metallated; in view of the large variety of reactions that have already been observed, it appeared to us worthwhile to investigate the insertion of alkynes in greater detail with various starting materials in order to define the scope and limitations of the reactions. Among the various cyclopalladated compounds known, those in which a cyclopentadienyl ring has been palladated are excellent candidates for such a study; it has been shown that the Pd–C bonds in these compounds display a reactivity towards either CO or alkenes similar to that of analogous compounds containing a metallated aryl ring [3].

It appeared at first sight that the reactions of **1** [4] with internal alkynes are similar to those observed earlier with the compound containing the *ortho* palladated *N,N*-dimethylbenzylamine (DMBA) ligand [1a,b]. Thus when **1** was treated with



Scheme 1. Reaction conditions for the reactions of compound 1 with alkynes. (i) RC≡CR, r.t., CH_2Cl_2, 3 h, yield 93% (R = Ph), 72% (R = Et); (ii) diphenylacetylene, PhCl, reflux 3 h (yield 15%), (iii) toluene, maleic anhydride, reflux 0.5 h.

two equivalents of either diphenylacetylene or hex-3-yne in CH_2Cl_2 at room temperature, compounds **2a** * and **2b** * were obtained in high yields (Scheme 1).

When this latter reaction with diphenylacetylene was carried out in refluxing chlorobenzene, the palladium-free compound **3** * was obtained in ca. 15% yield. Its elemental analysis and ^1H NMR spectrum indicated that two diphenylacetylene units had been incorporated into the ferrocenyl moiety and that the NMe_2 group had been lost. The geometry of **2a** and **3** were unambiguously confirmed by single-crystal X-ray diffraction studies **. The palladium environment in **2a** is very similar to that found earlier for the related complex obtained from the DMBA-containing complex and methyl phenylprop-2-yne [1a].

The important feature of the structure of **2a** is that the phenyl groups are *trans* to

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* Selected ^1H NMR Data (200 MHz, $CDCl_3$, 293K) δ in ppm, J in Hz: **2a**: 7.24–6.53 (m, 20H, Ar); 4.35 and 3.95 (2m, 3H, C_5H_3); 3.95 (s, 5H, Cp); 3.08 and 2.50 (2s, 6H, NMe_2); 2.25 and 1.67 (2d, 2H, CH_2, $^2J(HH)$ 14). **2b**: 4.19 (s, 5H, Cp); 4.17, 4.13 and 4.03 (3m, 3H, C_5H_3); 2.63 and 1.88 (2s, 6H, NMe_2); 2.54, 2.27, 2.05 and 1.52 (4m, 10H, $5CH_2$); 1.70, 1.24, 1.15 and 0.94 (4t, 12H, $4CH_3$, $^3J(HH)$ 7). **3**: 9.98 and 7.70–6.51 (m, 18H, Ar); 4.73, 4.23 and 4.19 (m, 3H, C_5H_3); 4.19 (s, 5H, Cp); 3.90 and 3.51 (dd, 2H, CH_2, $^2J(HH)$ 12.7). **4**: 5.82 (q, 1H, C*H*Me, $^3J(HH)$ 7); 4.60, 4.22 and 4.11 (3m, 3H, C_5H_3); 4.06 (s, 5H, Cp); 4.41 and 3.15 (2d, 2H, CH_2N, $^2J(HH)$ 13); 3.56 (dd, 1H, C*H*Et, $^3J(HH)$ 5.6 and 5.9); 2.60 and 2.52 (2s, 6H, NMe_2); 2.45, 2.07 and 1.70 (3m, 6H, $3CH_2$); 1.40 (d, 3H, $CHCH_3$), $^3J(HH)$ 7); 1.39, 1.31 and 1.09 (3t, 9H, $3CH_3$, $^3J(HH)$ 7.5). **6**: 7.67–6.74 (m, 23H, Ar); 3.14 and 3.03 (2d, 2H, CH_2N, $^2J(HH)$ 14.5); 2.06 (s, 6H, NMe_2). **7**: 7.75–6.72 (m, 23H, Ar); 3.94 and 3.77 (2d, 2H, CH_2N, $^2J(HH)$ 13.5); 2.84 and 1.68 (2s, 6H, NMe_2).

** See page C23.

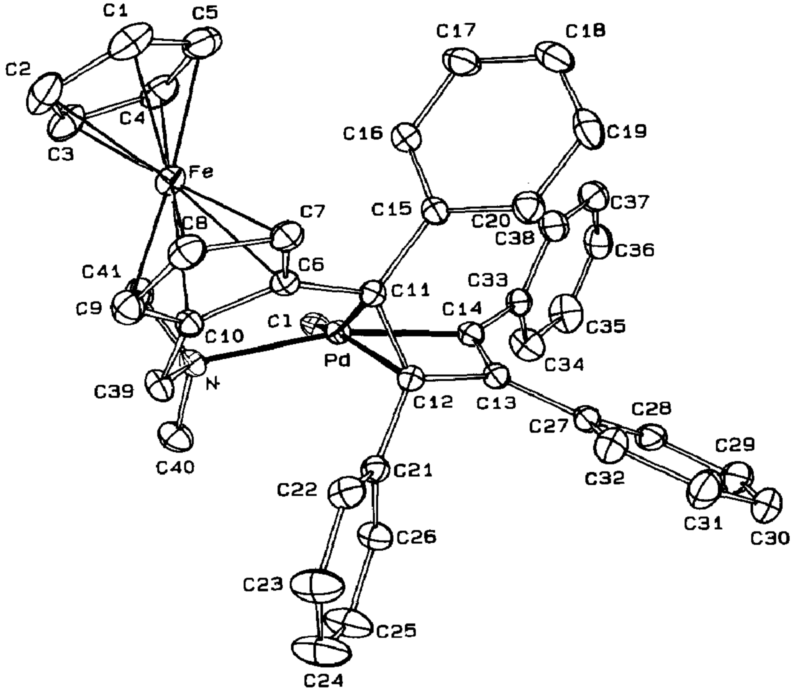

Fig. 1. ORTEP view of compound **2a**. Selected bond distances (Å): Pd–Cl, 2.329(1); Pd–C11, 2.225(4); Pd–C12, 2.148(4); Pd–C14, 2.002(4); Pd–N, 2.233(3); C11–C12, 1.415(5); C13–C14, 1.320(5).

the olefinic unit η^2-bonded to Pd. The structure of **3** is much more surprising since it shows the presence of seven- and six-membered *ortho*-fused rings.

The six-membered ring is produced through formation of a C–C bond between the palladated carbon atom C14 in **2a** and one of the *ortho*-carbon atoms of the phenyl group on the carbon α to the substituted Cp unit, which leads to a tetrasubstituted naphthyl group. The seven-membered ring is formed by linkage of

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** Crystal data: $C_{87}H_{82}Cl_2Fe_2N_2Pd_2$ (**2a**+cyclopentane in a 2/1 ratio). M = 1551.04, orthorhombic, space group *Pccn* (No. 56), a 14.740(4), b 24.281(7), c 20.342(6) Å, V 7280.4 Å^3, $Z = 4$, ρ(calc) 1.415 gcm^{-3}, $F(000) = 3184$, μ 9.898 cm^{-1}, λ 0.71069 Å. 7038 independent h,k,l reflections were measured ($2° < \theta < 25°$) for which 4297 reflections with $I > 3\sigma(I)$ were treated as observed. $R(F) = 0.034$, $R_W(F) = 0.058$, GOF = 1.29. $C_{39}H_{28}Fe$ (**3**), M = 552.51, monoclinic, space group $P2_1/c$ (No. 14), a 13.672(3), b 16.518(7), c 13.722(2) Å, β 118.24(2)°, V 2730.1 Å^3, $Z = 4$, ρ(calc) = 1.344 g cm^{-3}, $F(000) = 1152$, μ 5.763 cm^{-1}, λ 0.71069 Å. 6737 independent $\pm h,k,l$ reflections were measured ($22° < \theta < 27.5°$) for which 2217 with $I > 3\sigma(I)$ were treated as observed. $R(F) = 0.034$, $R_W(F) = 0.042$, GOF = 1.04.

The data were collected on an Enraf–Nonius CAD-4 diffractometer (graphite monochromated Mo-K_α radiation) with the $\theta/2\theta$ scan mode. The structures were solved by the heavy atom method. All non-hydrogen atoms were found by difference-Fourier syntheses. Hydrogen atoms were placed at calculated positions (C–H = 0.95Å, B(H) = 1.3 B_{eq}(C) Å^2) and not refined. Scattering factors and anomalous dispersion coefficients were from ref 5. Further details of the structural investigations are available from the authors. Tables of atomic coordinates and lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. They may be obtained on request from the director by citing the full literature reference for this communication.

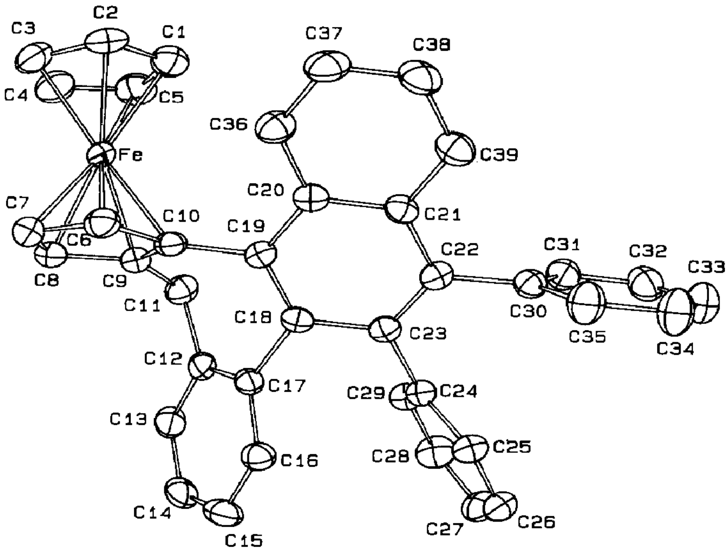


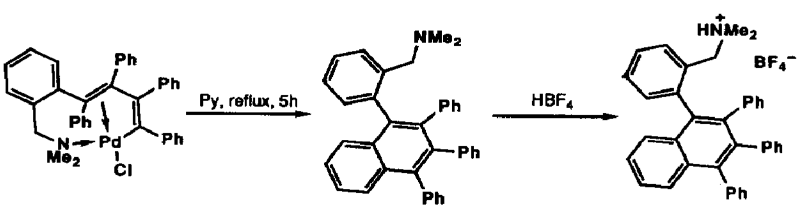
Fig. 2. ORTEP view of compound 3.

an *ortho* carbon atom of the second phenyl (i.e. on the carbon β to Cp on the butadienyl chain) to the CH_2 group, with displacement of the NMe_2 unit.

The formation of the bond between C21 and C22 in **3** is akin to the annulation reactions of palladated aryl rings with internal alkynes [1d,2]. A probable intermediate in the formation of **3** is thus that depicted in Scheme 1 in which the seven-membered ring has not been formed. ^1H NMR spectroscopy showed the presence of such an intermediate, but it has not yet been fully characterised. The formation of the bond between C11 and C12 in **3** is less straightforward, since it involves cleavage of the CH_2–NMe_2 bond in addition to the activation of one of the C–H bonds in an *ortho* position of a phenyl ring. Whether the palladium atom plays a crucial role in this rearrangement is not yet fully established, and this question is currently under detailed study.

Compound **2b** undergoes a completely different rearrangement, giving compound **4**. Elemental analysis and ^1H NMR data indicate that **4** is an isomer of **2b**; we suggest that **4** is formed by a 1,3-hydrogen shift from the CH_2 of one ethyl group to the carbon β of the butadienyl chain in **2b**. A similar reaction was previously observed with a related compound which contained a methylene group in a similar position [1b]. However, this reaction occurs in the presence of maleic anhydride, the role of which is not yet understood.

The formation of compound **3** led us to wonder whether analogous results could be observed when the cyclopalladated ligands is DMBA, for which, as we have seen, the behaviour of the Pd–C bond towards alkyne insertion is quite close to that of **1**.



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When compound **5** [1a] was kept in refluxing pyridine for several hours a new organic product **6** *, which is highly soluble in all common organic solvents, was obtained in moderate yields (10–20%) as an off-white crystalline solid. Its elemental analysis and mass spectrum suggest that it is a 1/2 adduct between DMBA and diphenylacetylene. The ^1H NMR spectrum * indicates that the molecule must be chiral since the methylene group is diastereotopic whereas the NMe_2 unit gives one singlet even at $-80\,^\circ C$. The chirality of **6** may arise from hindered rotation around the C–C bond between the DMBA and the naphthyl moieties. Protonation of the nitrogen atom with HBF_4 led to compound **7** *, whose ^1H NMR spectrum is consistent with the proposed assignment. Moreover this spectrum is very similar, though not identical (as far as the signals of the aromatic protons are concerned), to that of the compound obtained previously upon treatment of a cationic cyclopalladated derivative of DMBA with diphenylacetylene in refluxing chlorobenzene [1b]. The formulation of this latter compound as an organic heterocycle is therefore likely to be erronous in the light of the results described above.

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