

Control of the Reactivity of Cyclopalladated Complexes for the Synthesis of Heterocyclic Compounds

Fida Maassarani,^a Michel Pfeffer,^{a*} and Guy Le Borgne^b

^a Laboratoire de Chimie de Coordination, UA 416 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France

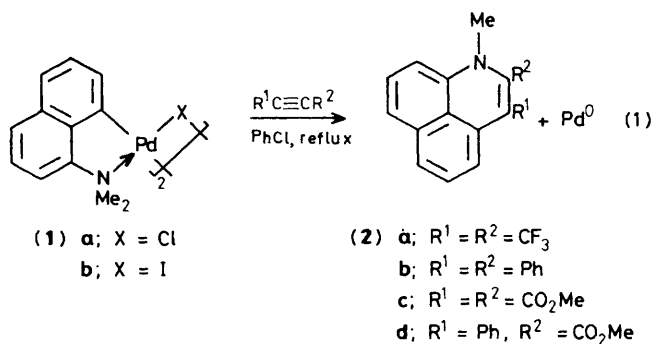
^b Laboratoire de Cristalochimie, UA 254, CNRS, Université de Rennes, 1 Avenue du Général Leclerc, F-35042 Rennes Cedex, France

Reactions between iodide or cationic derivatives of cyclopalladated complexes and alkynes lead to the synthesis of heterocyclic compounds through insertion of one or two alkynes into the Pd–C bonds, the new N–C bonds being formed *via* reductive elimination of palladium(0).

Our work on the reactivity of cyclopalladated complexes has focused mainly on the reactions of these organopalladium compounds towards alkynes.¹ In most cases we observed that new organometallic compounds are obtained through the insertion of the alkynes into the Pd–C bonds of the cyclopalladated compounds. We have now developed a strategy for easy depalladation of the compounds thus formed by activating the starting cyclopalladated complexes.² Recently, Heck and co-workers have reported some related results.³ In this communication we describe how depalladation can be achieved by simple changes in the ligands co-ordinated to the palladium atom.

We have previously shown^{1a} that the heterocyclic compound (**2a**) can be obtained in *ca.* 20% yield by the reaction of hexafluorobut-2-yne (Hfb) and bis(1-dimethyl-amino-8-naphthyl)dichloride dipalladium (**1a**). We have now found that the use of compound (**1b**), *i.e.* the iodine derivative of (**1a**), afforded compound (**2**) in more than 50% yield by reaction with Hfb.

Although no reaction was observed between (**1a**) and the other alkynes used in this study (even in refluxing chlorobenzene for several days), compound (**1b**) afforded the hetero-



cycles (**2b–d**)† by reaction with diphenylacetylene, dimethylacetylene dicarboxylate, or ethyl 3-phenylpropiolate respectively in good to excellent yields [(**2b**) and (**2d**) were obtained quantitatively, equation (1)].

The dramatic effect of the presence of the iodine atom in the starting cyclopalladated complexes upon the reaction course was also obvious in the case of compound (**3**) which led to compound (**5**) in *ca.* 30% yield by reaction with diphenylacetylene in refluxing chlorobenzene, equation (2).

The structure of the tetraphenylcyclobutene adduct of the 1*H*-benzo[*ij*]quinolizinium cation in (**5a**) was determined by X-ray crystallography.‡ The structure that was actually determined was that of a closely related compound (**5a'**) which contains the Pd₂Cl₆²⁻ unit as the counter anion. The cation moieties in (**5a**) and (**5a'**) are spectroscopically identical. Compound (**5a'**) is obtained in very small yields (*ca.* 1%) in independent experiments. That compound (**4**) (obtained previously as the chloride complex^{1a}) is an intermediate in the synthesis of (**5a**) was easily demonstrated since we could follow, by ¹H n.m.r. spectroscopy, the slow conversion over a 10 day period of (**4**) into (**5a**), together with some uncharacterized decomposition products. We have also found that the use of a cationic cyclopalladated derivative such as (**3b**)⁴ led to the quantitative formation of (**5b**), equation (3).

This general trend to form heterocyclic compounds from iodine containing cyclopalladated complexes, or from the

† All new heterocyclic compounds give satisfactory elemental analyses and mass spectra. Selected ¹H n.m.r. data (*J* in Hz) δ (CDCl₃), (**2b**): 3.87 (s, 3H, NCH₃); (**2c**): 3.93 (s, 3H, CO₂CH₃), 3.81 (s, 3H, CO₂CH₃), 3.09 (s, 3H, NCH₃); (**2d**): 3.86 (s, 3H, NCH₃), 3.80 (q, 2H, CO₂CH₂), 0.77 (t, 3H, CCH₃); (**5a**): 5.14 and 4.09 (2d, 2H, CH₂, ²*J*_{HH} 16.3); (**5b**): 4.62 and 4.06 (2d, 2H, CH₂, ²*J*_{HH} 16.4); (**7**) 10.45 (s, 1H, CH=N-), 4.50 (s, 3H, NCH₃), 4.16 (q, 2H, CO₂CH₂), 0.93 (t, 3H, CCH₃); (**8**): 9.35 (s, 1H, CH=N-), 4.22 (q, 2H, CO₂CH₂), 1.02 (t, 3H, CCH₃); (**10**): 5.06 (s, 2H, CH₂N), 3.99 (q, 2H, CO₂CH₂), 3.26 [s, 6H, N(CH₃)₂], 0.85 (t, 3H, CCH₃).

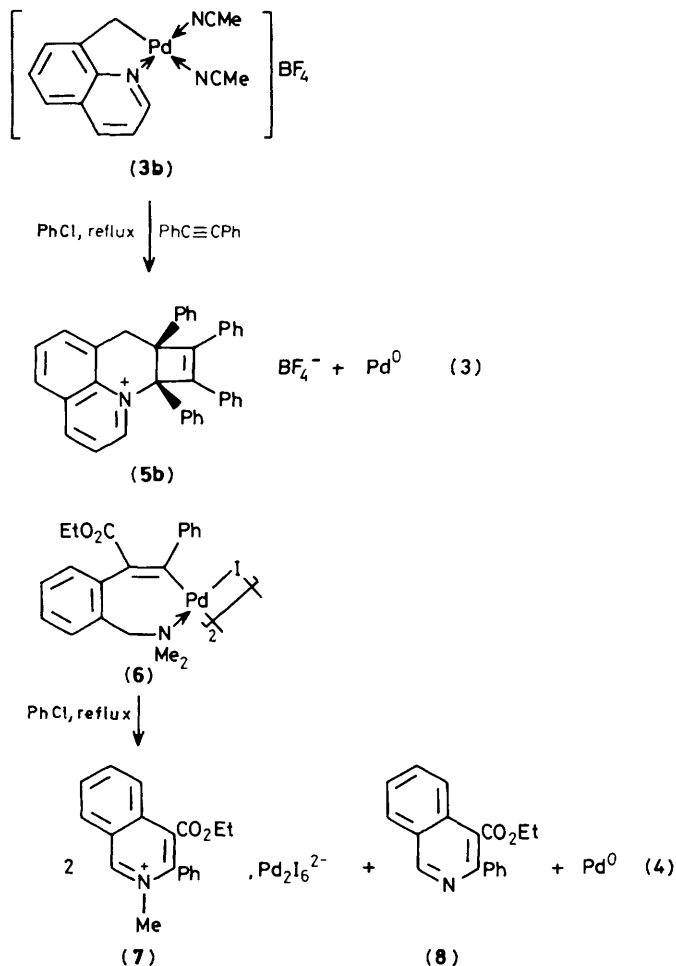
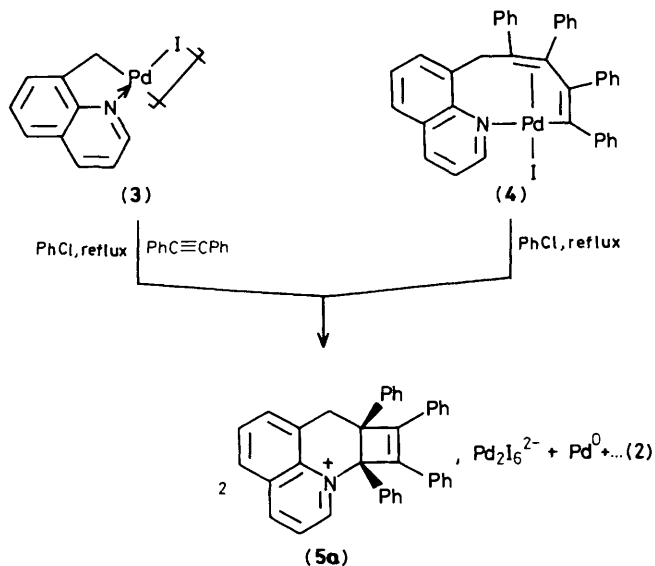
‡ Crystal data for (**5a'**): C₃₈H₂₈Cl₃NPd, *M* = 711, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 10.407(4), *b* = 16.354(3), *c* = 9.992(5) Å, α = 92.09(2), β = 109.23(5), γ = 80.50(2)°, *U* = 1583.3 g cm⁻³, *Z* = 2, λ(Mo-K_α) = 0.71073 Å, μ = 8.60 cm⁻¹, *F*(000) = 720, 1° < θ < 25°. Of 5906 observed reflections, 3734 with *I* > σ(*I*) were used to solve the structure to give *R* = 3.5%, *R*_w = 4.7%.

(**7**): C₁₉H₁₈I₃NO₂Pd, *M* = 779, monoclinic, space group *P*2₁/*n*, *a* = 13.364(8), *b* = 12.316(4), *c* = 14.645(9) Å, β = 105.45(3)° *U* = 2323.2 g cm⁻³, *Z* = 4, λ(Mo-K_α) = 0.71073 Å, μ = 47.5 cm⁻¹, *F*(000) = 1440, 1° < θ < 25°. Of 4473 observed reflections, 2700 with *I* > 3σ(*I*) were used to solve the structure to give *R* = 6.4%, *R*_w = 8.4%.

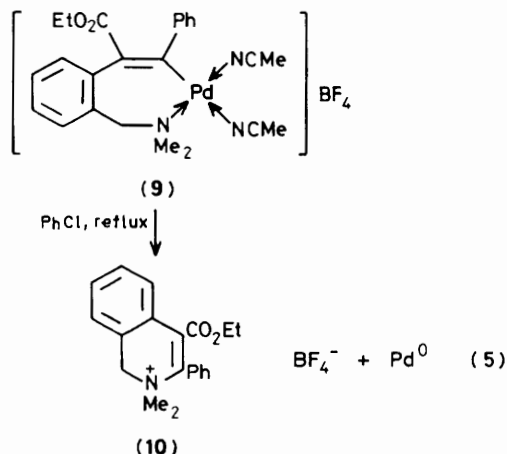
For both structure determinations intensities were measured on an Enraf-Nonius CAD-4 diffractometer. No intensity decay was observed during the data collection period. No absorption corrections were applied.

The structures were solved using the Enraf-Nonius SDP package on a PDP 11-60 computer. The atomic positions of the independent non-hydrogen atoms were found with the program MULTAN and subsequent Fourier difference syntheses. Refinement of their co-ordinates and thermal parameters first isotropically, then anisotropically, led to the final *R* values reported. For the compound (**5a'**), the co-ordinates of the hydrogen atoms were computed and their contributions introduced in the refinement with thermal parameters equal to those of the atoms to which they were bonded (the crystals, in which no solvent were present, were obtained from a toluene-pentane solution). For the compound (**7**), the hydrogen atoms were not introduced into the refinement because of the large *R* and *R*_w values; in this case, the last Fourier difference synthesis did not show any residual electronic density except for peaks at 1.5 e Å⁻³ close to the Pd or I atoms.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



corresponding cationic compounds, was also found to occur in the case of the cyclopalladated *N,N*-dimethylbenzylamine (dmba) complexes, equation (4). Compound (**6**) {obtained by a 1:2 reaction between [Pd(dmba)I]₂ and Ph-C≡C-CO₂Et} after heating in refluxing chlorobenzene for 3 h, afforded compounds (**7**) and (**8**) in 14% and 60% yields, respectively.



The structure of the isoquinolium cation in (7) was determined by an X-ray diffraction study,[‡] whereas that of (8) was deduced from the structure of (7) and from its ¹H n.m.r. and mass spectra. A different heterocycle (10) was obtained through similar thermal depalladation of the cationic compound (9), obtained by treating (6) with AgBF₄ in the presence of acetonitrile, equation (5).

These results contradict the recent report by Heck stating that a N–C bond cannot be formed using cyclopalladated dmba compounds for steric reasons. The course of the reaction is very dependent on the nature of the alkyne used, since Heck observed his result with different alkynes.

These few examples emphasize the crucial role that the ligand attached to the palladium centre plays upon the course

of the reaction as well as upon the thermal stability of the organopalladium compounds. Thus, the substitution of the more commonly used chloride anion by iodide or weakly co-ordinated solvents in these cyclopalladated complexes increases markedly the reductibility of the palladium centre. Indeed the formation of the carbon–nitrogen bond must obviously occur *via* reductive elimination of palladium. In the case of compounds (5a) and (7) the presence of Pd₂I₆²⁻ as a counter anion might be due to some decomposition process: the iodide ion does not seem able to stabilize the new cations formed and it is thus evolved as methyl iodide [in the case of the synthesis of compounds (2)] or it may react with Pd^{II} species still present in the reaction mixture to form the Pd₂I₆ dianion which then stabilizes the heterocyclic cation in (5a) and (7).

We thank the Commission of the European Communities for financial support of this work [contract no. ST2J-0090-1-F(CD)].

Received, 20th October 1986; Com. 1491

References

- (a) A. Bahsoun, J. Dehand, M. Pfeffer, M. Zinsius, S. E. Bouaoud, and G. Le Borgne, *J. Chem. Soc., Dalton Trans.*, 1979, 547; (b) C. Arlen, M. Pfeffer, O. Bars, and D. Grandjean, *ibid.*, 1983, 1535; (c) F. Maassarani, G. Le Borgne, and M. Pfeffer, *J. Chem. Soc., Chem. Commun.*, 1986, 489.
- F. Maassarani, G. Le Borgne, and M. Pfeffer, *Organometallics*, submitted for publication.
- G. Wu, A. L. Rheingold, and R. F. Heck, *Organometallics*, 1986, 5, 1922.
- P. Braunstein, J. Fischer, D. Matt, and M. Pfeffer, *J. Am. Chem. Soc.*, 1984, 106, 410.