

**Preliminary communication**

---

**ONE-POT SYNTHESIS OF HETEROCYCLIC COMPOUNDS THROUGH  
INSERTION OF ALKYNES INTO THE Pd-C BOND OF ACTIVATED  
CYCLOPALLADATED BENZYL METHYL SULPHIDE**

JAIRTON DUPONT and MICHEL PFEFFER \*

*Laboratoire de Chimie de Coordination, UA 416 du CNRS, Université Louis Pasteur, 4 rue Blaise Pascal,  
F-67070 Strasbourg Cédex (France)*

(Received October 16th, 1986)

**Summary**

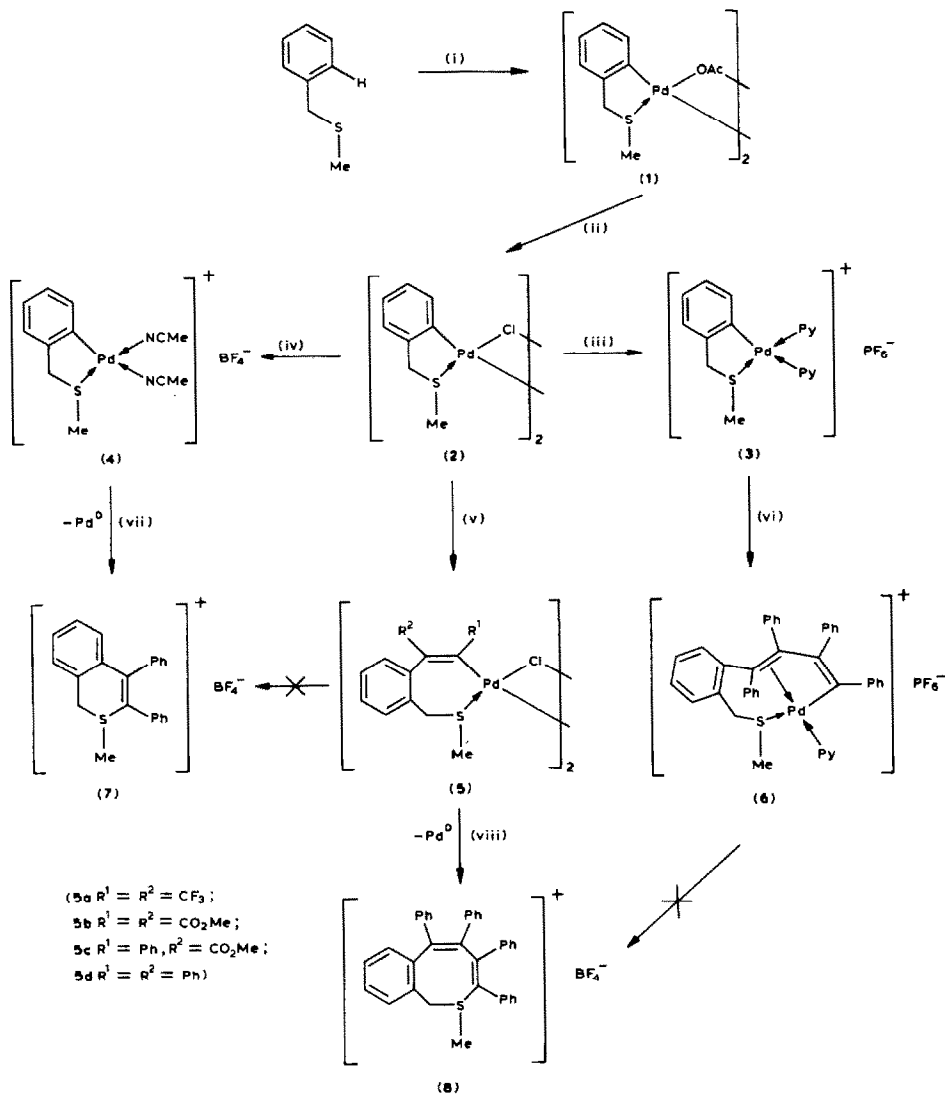
Benzyl methyl sulphide is readily cyclopalladated by palladium acetate. Compared with the chloride bridged-derivative, the cationic cyclopalladated compounds are more reactive towards the insertion of alkyne into their Pd-C  $\sigma$  bonds, which leads in some cases to cationic organic heterocycles containing either a six- or an eight-membered ring, arising from insertion of one or two alkyne molecules, the C-S bond being formed via reductive elimination of palladium(0).

---

Use of cyclopalladated compounds as reactive intermediates for the synthesis of new carbon-carbon and carbon-heteroatom bonds is of considerable potential interest [1], and our efforts have for several years concentrated on the reactivity of these organometallic compounds towards various reagents [2]. Our main interest has been in the reactions of the cyclopalladated complexes with alkynes, which generally lead to new organopalladium complexes arising from insertion of the alkynes into the Pd-C bonds [3]. In one case [3a] we observed a spontaneous depalladation of the formed organometallic compound, leading to a heterocyclic compound via the formation of a C-N bond. This prompted us to study this type of reaction in more detail, and we have therefore embarked on investigations aimed at increasing the reactivity of the cyclopalladated compounds to give easier depalladation reactions. We have already shown how this aim can be achieved in the case of such complexes containing tertiary amines [4], and similar preliminary results were reported recently by Heck et al. [5]. We present here some of our results on the reactivity of cyclopalladated sulphide complexes which, providing that cationic species are used, can be readily converted into sulphur containing heterocycles.

It has long been thought that benzyl methyl sulphide could not be metallated by palladium(II) complexes. Several unsuccessful attempts have been made involving lithium or sodium tetrachloropalladate as the metallating agent in the presence of various bases [6], but only the stable bis-adduct  $(C_6H_5CH_2SCH_3)_2PdCl_2$  was

obtained. We have now found that in refluxing acetic acid palladium acetate readily metallates the benzyl methyl sulphide ligand to give compound **1** in high yields (> 80%). This result clearly demonstrates that the presence of a bulky substituent, such as a *t*- or *i*-butyl group on the sulphur atom is not necessary for this reaction,



SCHEME 1. Reaction sequences for the synthesis of the cyclopalladated compounds and their reactions with alkynes. (i) [Pd(OAc)<sub>2</sub>]<sub>3</sub>, CH<sub>3</sub>COOH, 118 °C, 30 min; (ii) LiCl, 20 °C, acetone; (iii) pyridine, 20 °C, H<sub>2</sub>O, NH<sub>4</sub>PF<sub>6</sub>; (iv) AgBF<sub>4</sub>, 20 °C, CH<sub>2</sub>Cl<sub>2</sub>/MeCN; (v) R<sup>1</sup>C≡CR<sup>2</sup>, 20 °C, CH<sub>2</sub>Cl<sub>2</sub>, 2 h (R<sup>1</sup> = R<sup>2</sup> = CF<sub>3</sub> or CO<sub>2</sub>Me; R<sup>1</sup> = Ph, R<sup>2</sup> = CO<sub>2</sub>Me), PhC≡CPh, 110 °C, PhCl, 30 min; (vi) PhC≡CPh, 110 °C, PhCl, 30 min; (vii) PhC≡CPh, 110 °C, PhCl, 45 min; (viii) R<sup>1</sup> = R<sup>2</sup> = Ph. (1) AgBF<sub>4</sub>, 20 °C, CH<sub>2</sub>Cl<sub>2</sub>/MeCN, (2) PhC≡CPh, 110 °C, PhCl, 1 h. Satisfactory elemental analyses were obtained for all compounds. For compounds **7** and **8** the molecular peaks were observed in the mass spectra.

as was recently suggested [7]. Compound 1 was converted into compounds 2–4 by established procedures [6–8].

The reactions between 2 and alkynes containing at least one electron-withdrawing group occurred at room temperature to afford quantitative yields of compounds 5a–5c (see Scheme 1). In the case of methyl phenyl-3-propiolate the insertion was regio- and stereo-specific, since only one isomer could be detected in the  $^1\text{H}$  NMR spectrum of 5c. (Note: These spectra were in fact obtained in the presence of pyridine- $d_5$ , and so actually refer to the monomeric pyridine adducts derived from the dimers 5). Reaction between 2 and diphenylacetylene took place only in refluxing chlorobenzene and gave compound 5d, in which, only one alkyne has inserted per palladium atom, and no reaction was observed in the case of 1-phenylpropyne and but-2-yne at any temperature. This behaviour is in marked contrast to that of analogous compounds containing the closely related *N,N*-dimethylamino methyl phenyl-2-chelate (dmba), which reacted readily with the last three alkynes at room temperature, and moreover, two alkyne molecules were found to have inserted into the Pd–C bond of this cyclopalladated tertiary amine [3a].

The use of the cationic compound 3 as the starting material improved the reactivity of the cyclopalladated moiety to such an extent that two diphenylacetylene molecules could be inserted into its Pd–C bond to give 6. The probable structure of this latter complex is depicted in Scheme 1, this being the geometry found for the nine-membered ring in related compounds containing the dmba chelate [3a]. When the pyridine ligands in 3 were replaced by weaker nucleophiles, such as acetonitrile in 4, the reactivity of the metallocyclic unit was markedly increased. When 4 was heated in chlorobenzene in the presence of excess of diphenylacetylene the organic cation 7 was obtained in good yield (> 80%), along with the metallic palladium in quantitative amount.

Treatment of 5d with silver tetrafluoroborate in the presence of acetonitrile gave a yellow oil. After removal of the silver chloride and the solvent, the oil resisted all attempts to crystallize it to permit identification, but it is very likely to be a cationic derivative of compound 5d. On treatment with diphenylacetylene it gave the new heterocyclic compound 8 as pale yellow crystals in ca. 70% yield. The structures of 7 and 8 were based on their  $^1\text{H}$  NMR spectra. As expected, the spectrum of 7 showed the presence of a diastereotopic methylene unit centered at 5.10 ppm ( $^2J(\text{HH})$  16.1 Hz). Compound 8 was shown to be a fluxional species, since at  $-70^\circ\text{C}$  the  $\text{CH}_2$  protons were diastereotopic ( $^2J(\text{HH})$  16.4 Hz) whereas at room temperature only one singlet at 5.07 ppm was observed for these protons. Similar behaviour was found for a benzazocine derivative containing a related eight-membered heterocyclic ring [9].

The scope of this procedure for making various heterocyclic compounds is currently being investigated for a series of cyclopalladated complexes.

**Acknowledgements.** Thanks are due to the CNPq (Brazil) for a fellowship (to J.D.), the Commission of the European Communities for financial support of this work, and Dr. M. Luke for help in proof-reading of the manuscript.

## References

- 1 A.D. Ryabov, *Synthesis*, (1985) 233.
- 2 M. Pfeffer, J. Fischer and A. Mitschler, *Organometallics*, 3 (1984) 1531; H. Ossor and M. Pfeffer, *J. Chem. Soc. Chem. Commun.*, (1985) 1540; F. Maassarani, M. Pfeffer, G. Le Borgne and D. Grandjean, *Organometallics*, 5 (1986) 1511.

- 3 (a) A. Bahsoun, J. Dehand, M. Pfeffer, M. Zinsius, S.E. Bouaoud and G. Le Borgne, *J. Chem. Soc. Dalton Trans.*, (1979) 547; (b) J. Dehand, C. Mutet and M. Pfeffer, *J. Organomet. Chem.*, 209 (1981) 255; (c) C. Arlen, M. Pfeffer, O. Bars and D. Grandjean, *J. Chem. Soc. Dalton Trans.*, (1983) 1535; (d) F. Maassarani, M. Pfeffer and G. Le Borgne, *J. Chem. Soc. Chem. Commun.*, (1986) 488; (e) F. Maassarani, M. Pfeffer, G. Le Borgne, E. Wehman and G. van Koten, *J. Am. Chem. Soc.*, 106 (1984) 8002.
- 4 F. Maassarani, G. Le Borgne and M. Pfeffer, submitted for publication.
- 5 G. Wu, A.L. Rheingold and R.F. Heck, *Organometallics*, 5 (1986) 1922.
- 6 S. Trofimenko, *Inorg. Chem.*, 12 (1973) 1215; R.L. Bennett, M.I. Bruce and T. Matsuda, *Aust. J. Chem.*, 28 (1975) 2307.
- 7 Y. Fushita, K. Hiraki, T. Yamaguchi and T. Maruta, *J. Chem. Soc. Dalton Trans.*, (1981) 2405.
- 8 P. Braunstein, J. Fischer, D. Matt and M. Pfeffer, *J. Am. Chem. Soc.*, 106 (1984) 410.
- 9 P.G. Lehman, *Tetrahedron Lett.*, 48 (1972) 4864.