Journal of Organometallic Chemistry, 286 (1985) C13—C16
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PALLADIUM-CATALYZED SYNTHESIS OF 1,2,3,4,4*a*,12*b*-HEXAHYDRO-1,4-METHANOTRIPHENYLENES

MARTA CATELLANI and GIAN PAOLO CHIUSOLI
Istituto di Chimica Organica, Universita', Via D'Azeglio 85, 43100 Parma (Italy)

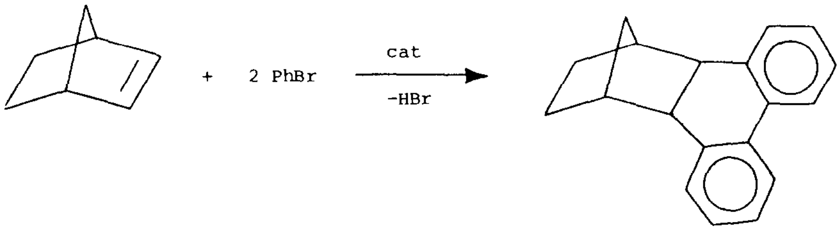
(Received January 14th, 1985)

Summary

A catalytic synthesis of hexahydromethanotriphenylenes from bicyclo[2.2.1]hept-2-ene and aryl bromides is reported. Palladacycles are shown to be intermediates. Two modes of reaction of the latter with aryl bromides are observed.

The involvement of metallacycles in organometallic synthesis is attracting increasing attention [1]. We previously postulated the intermediacy of palladacycles in some catalytic syntheses [2], and we now report a new stereoselective synthesis of hitherto unknown hexahydromethanotriphenylenes which provides further indirect evidence for a palladacycle intermediate which reacts with aryl bromides in two ways.

If bromobenzene is treated with bicyclo[2.2.1]hept-2-ene in anisole in the presence of potassium t-butoxyde at 80—105°C reaction takes place readily to give *cis,exo*-1,2,3,4,4*a*,12*b*-hexahydro-1,4-methanotriphenylene in a 65% yield (eq. 1).

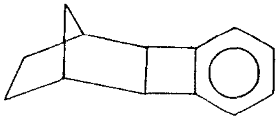


(1)

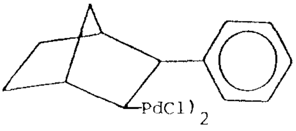
(I)

Biphenyl is the major by-product. Small amounts of II and of other compounds resulting from addition of one molecule of bromobenzene to two molecules of bicycloheptene [2,3] are also present.

0022-328X/85/$03.30



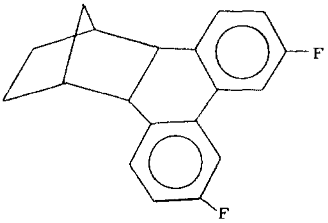
(II)



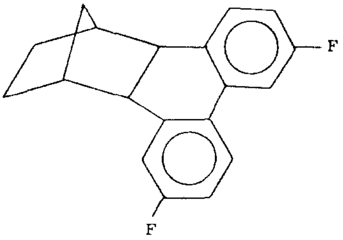
(III)

The reaction was also carried out stoichiometrically with complex III [4], bromobenzene, and added triphenylphosphine (2 mol). In this case compounds I and II were formed in a 1/2 ratio. Slight variations in reaction conditions appear to lead to large differences in product distribution.

The reaction might conceivably have involved formation of a 2,3-diphenylbicycloheptene, followed by its reaction with a Pd^{II} species to give I. However, if this were true, with a substituted aryl bromide we should obtain a symmetrically substituted I. We observed, on the contrary, that when substituents such as F, Cl, OMe are present in the aromatic nucleus, two products are formed; for example IV and V (ca. 1/3 by NMR) from *p*-fluorobromobenzene.



(IV)



(V)

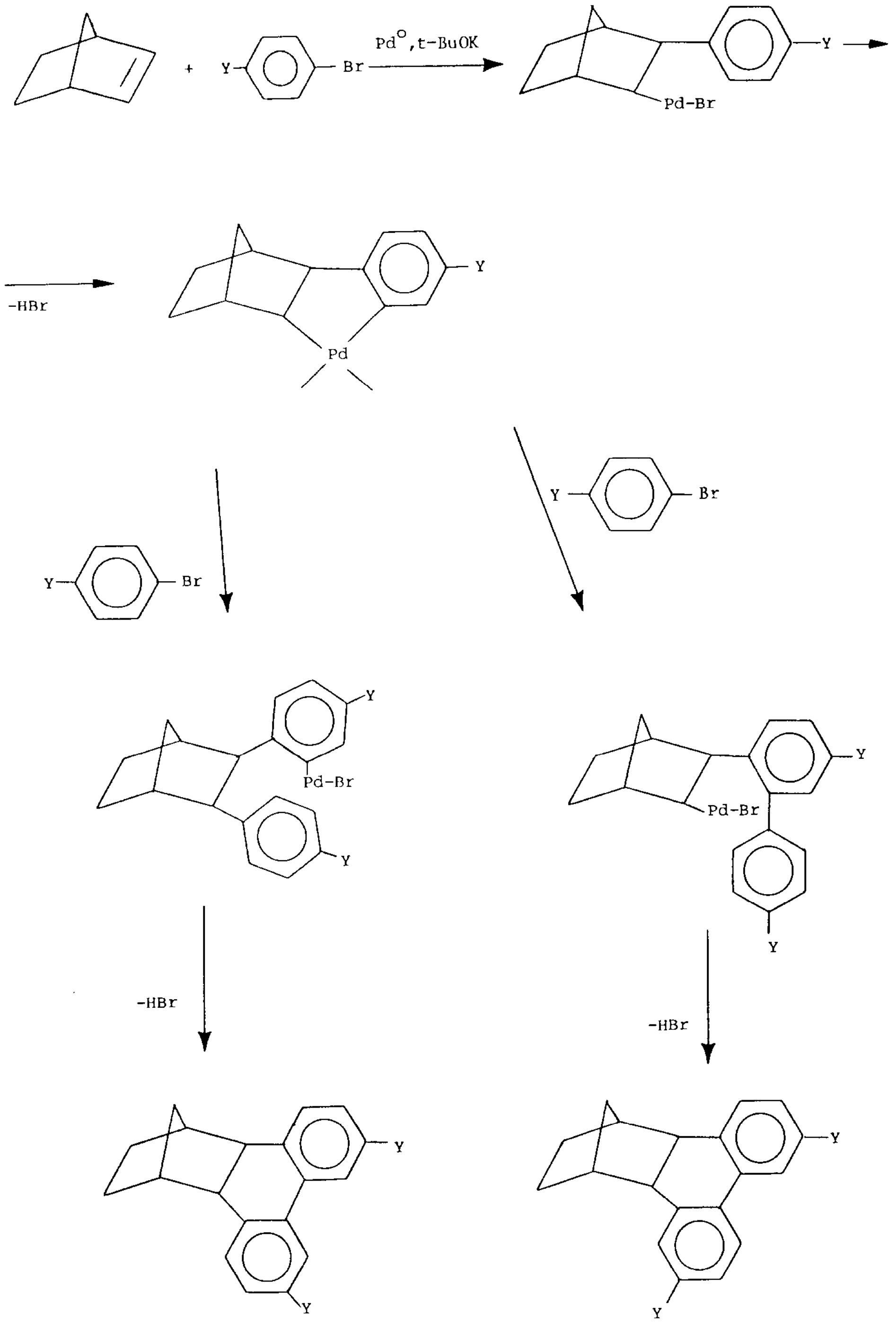
This is consistent with the formation of a palladacycle, which undergoes reaction with the aryl bromide at both of the two Pd-bonded carbons, as in the Scheme 1.

The metallacycle reaction with bromobenzene must involve an intermediate complex, possibly containing Pd^{IV}, but this has not been isolated so far. The products obtained, however, show unequivocally that the catalysis involves two different reactions between the palladacycle and the aryl halides.

General procedure

The general procedure is illustrated by the synthesis of I. $Pd(PPh_3)_4$ (114 mg, 0.098 mmol) and t-BuOK (238 mg, 2.12 mmol) are placed under N_2 in a Schlenk-type flask containing a magnetic stirring bar. Bicycloheptene (130 mg, 1.38 mmol) and bromobenzene (334 mg, 2.12 mmol) dissolved in dry anisole (4 ml) are immediately added. The mixture is stirred at 105°C for 10 h. After conventional work-up the product is separated by chromatography on a SiO_2 column, with hexane as eluent. A 65% yield of I, determined by GLC, is obtained, along with ca. 6% of biphenyl and 2—4% of compound II and of other compounds corresponding to addition of one molecule of bromobenzene to two molecules of bicycloheptene [2,3]. Approximately 10% of unchanged bromobenzene is also detected.

Compound I: white crystals, m.p. (n-hexane, 0°C) 139—141°C. MS (70 eV):



SCHEME 1

M^+ = 246, *m/e* 217, 205, 203, 202, 180, 179, 178, 177, 176, 152, 151, 108, 101, 94, 67, 53; ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 7.89—7.78 (m, 2H), 7.28—7.10 (m, 6H), 3.19 (d, *J* 1.4 Hz, 2H, HC(4a), HC(12b)), 2.36 (br s, 2H, HC(1), HC(4)), 1.76—1.53 (m, 4H, $H_2C(2)$, $H_2C(3)$), 1.40 (d quintets, *J* 10 Hz, *J* 1.7 Hz, 1H, HC(methano) *syn*), 1.02 (d further split, *J* 10 Hz, *J* 1.7 Hz, *J* 1.4 Hz, 1H, HC (methano) *anti*) ppm; ^{13}C NMR (25.2 MHz, $CDCl_3$ TMS): δ 137.4, 131.0, 129.9, 127.3, 125.9, 121.7 (aromatic carbons), 49.4 (d, C(4a), C(12b)), 45.8 (d, C(1), C(4)), 33.1 (t, C(methano)), 30.2 (t, C(2), C(3)) ppm.

Starting from *p*-fluorobromobenzene compounds IV and V were obtained in 45% yield (ca. 1/3 molar ratio) together with 10% of *p,p'*-difluorobiphenyl.

Compound IV: MS (70 eV): M^+ = 282. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 7.37 (dd, *J* 11 Hz, *J* 2.6 Hz, 2H, HC(8), HC(9)), 7.18 (dd, *J* 8.5 Hz, *J* 6.0 Hz, 2H, HC(5), HC(12)), 6.92 (ddd, *J* 10.6 Hz, *J* 8.5 Hz, *J* 2.6 Hz, 2H, HC(6), HC(11)), 3.19 (br s, 2H, HC(4a), HC(12b)), 2.32 (br s, 2H, HC(1), HC(4)), 1.75—1.56 (m, 4H, $H_2C(2)$, $H_2C(3)$), 1.35 (d quintets, *J* 10 Hz, *J* 1.7 Hz, 1H, HC(methano) *syn*), 1.05 (d further split, *J* 10 Hz, *J* 1.6 Hz, *J* 1.4 Hz, 1H, HC(methano) *anti*) ppm.

Compound V: white crystals, m.p. (n-hexane, 0°C) 107°C. MS (70 eV): M^+ = 282, *m/e* 253, 241, 216, 215, 214, 67; ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 7.66 (dd, *J* 8.5 Hz, *J* 5.5 Hz, 1H, HC(8)), 7.40 (dd, *J* 11 Hz, *J* 2.6 Hz, 1H, HC(9)), 7.17 (dd, *J* 8.5 Hz, *J* 6 Hz, 1H, HC (12)), 6.95—6.82 (m, 3H, HC(5), HC(7), HC(11)), 3.19 (br s, 2H, HC(4a), HC(12b)), 2.36 (br s, 1H, HC(4) or HC(1)), 2.32 (br s, 1H, HC(1) or HC(4)), 1.74—1.54 (m, 4H, $H_2C(2)$, $H_2C(3)$), 1.35 (d quintets, *J* 10 Hz, *J* 1.6 Hz, 1H, HC(methano) *syn*), 1.05 (d further split, *J* 10 Hz, *J* 1.5 Hz, *J* 1.4 Hz, 1H, HC(methano) *anti*) ppm.

Acknowledgement. We thank the Italian Ministero della Pubblica Istruzione and Consiglio Nazionale delle Ricerche for financial support.

References

1 R.H. Grubbs and A. Miyashita, in M. Tsutsui (Ed.), Fundamental Research in Homogeneous Catalysis, Vol. 3, 151 and lit. cited therein, Plenum Press, London, 1979.

2 M. Catellani and G.P. Chiusoli, Abs. 4th Int. Symposium on Homogeneous Catalysis, Leningrad, Sept. 1984, Vol. I, p. 225; J. Organomet. Chem., 265 (1984) C9; G. Bocelli, M. Catellani and G.P. Chiusoli, ibid., 279 (1985) 225.

3 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 239 (1982) C35.

4 H. Horino, M. Arai and N. Inoue, Tetrahedron Lett., (1974) 647.