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Preliminary communication

REACTION OF ACETYLENES WITH TRANSITION METALS

X*. A STABLE σ-BUTADIENYLPALLADIUM COMPLEX DERIVED FROM PHENYLMESITYLACETYLENE AND DICHLOROBIS(BENZONITRILE)-PALLADIUM

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Summary

Reaction of phenylmesitylacetylene with dichlorobis(benzonitrile)palladium (BNP) yields a σ-butadienylpalladium complex which on oxidation undergoes cyclisation to give a benzotropone.

As an extension of our study of steric control in the $PdCl_2$-induced oligomerization of diarylacetylenes substituted with bulky groups, the behaviour of phenylmesitylacetylene seemed of special interest. It was assumed that the greater size of the mesityl group compared with those of xylyl or t-butyl groups would furnish information about the intermediate steps of the oligomerization process.

A solution of BNP (0.60 g, 1.56 mmol) in benzene (30 ml) was treated with a solution of phenylmesitylacetylene (1.00 g, 4.55 mmol) in the same solvent (5 ml). After 48 h at room temperature, the solvent was removed in vacuo and the oily residue was triturated with petroleum ether. Chromatography of the crude product on Al_2O_2 with diethyl ether as eluent, afforded 0.40 g (41.5%) of I, as yellow crystals (m.p. 165°C, dec.).

On the basis of spectral data and chemical behaviour, the product was identified as the σ-butadienylpalladium complex I (di-μ-chlorodi-*S*-*cis*-1-chloro-1,4-dimesityl-2,3-diphenylbutadienyl-4-σ-dipalladium).

The UV spectrum [$\lambda_{max}^{(CHCl_3)}$ 238.2 nm (log ε 4.830), 274.6 (4.694)] is different from those of tetraarylcyclobutadiene- or tetraarylcyclobutenyl-palladium

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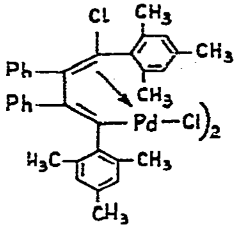
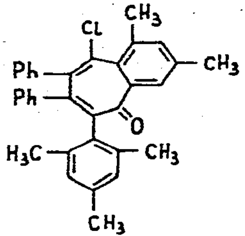
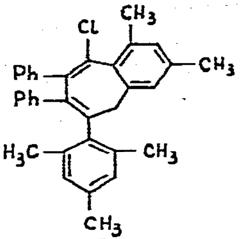
chloride complexes, previously reported [2]. The NMR spectrum ($CDCl_3$, δ, ppm) shows a shielded group of signals from the mesityl group near the PdCl bridge (1.06, s, 2 CH_3; 1.50, s, CH_3; 5.85; large s, 2 aromatic protons) and a less shielded group (2.15, s, 2 CH_3; 2.88, s, CH_3) from the other mesityl ring; the ring protons of the latter group are included in the multiplet of the aromatic protons (6.75—7.50, 12H).



I



II



III

The oxidative elimination of palladium by treatment of complex I with $CrO_3 \cdot py$ in methylene chloride, at room temperature, for 24 h gave a colourless ketone (II, m.p. 85°C, IR (CCl_4): $\nu(C{=}O)$ 1670, $\nu(C{=}C)$ 1640 cm^{-1}) in 75% yield*. The elemental analysis and spectral data indicate the disappearance of a methyl group from a mesityl ring.

The ascribed benzotropone structure II (1,3-dimethyl-6-mesityl-7,8-diphenyl-9-chloro-5*H*-benzocyclohepten-5-one) is consistent with the UV spectrum [$\lambda_{max}^{(EtOH)}$ 235.0 nm (log ϵ 4.689), 267.8 sh (4.297)] [3], and with the NMR spectrum (CCl_4, δ, ppm): 1.55, s, 6H, two *ortho*-CH_3 from the mesityl ring; 2.11, s, 6H, 2 CH_3 from the fused ring; 2.21, s, 3H, *para*-CH_3 from the mesityl ring; 6.20, large s, 2H from the mesityl ring; 6.60—7.20, large m, 12H from the aromatic rings). Using the europium shift technique, at the molar ratio $Eu(DPM)_3/II = 0.74$, the signals of the mesityl group are shifted (δ 6.20 at 16.90 ppm and δ 1.55 at 4.06 ppm); indicating that the mesityl ring is near the carbonyl group.

The formation of the ketone II from the complex I can be explained by intramolecular cyclisation, involving an *ortho*-methyl group from the mesityl ring which is close to the carbon atom bonded to the Pd—Cl bridge. The initially formed tropylidene III, undergoes subsequent oxidation at the CH_2 group to give the ketone II. Support for this hypothesis comes from the conversion of ketone II to the tropylidene III by reduction with AlH_3 and reoxidation of the latter with $CrO_3 \cdot py$ to ketone II.

The formation of the σ-butadienylpalladium complex I as the end-product of the oligomerization of phenylmesitylacetylene indicates that the size of the mesityl group hinders the formation of the cyclobutadiene—$PdCl_2$ complex.

There are strong arguments for the *cis* insertion rule in the oligomerization of acetylenes induced by $PdCl_2$ [4]. The intermediacy of σ-butadienylpalladium complexes with *cis*-stereochemistry at C(1) was detected in the oligomerization

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*Other isomeric structures which could undergo cyclisation would certainly lead to coloured naphthoquinone derivatives.

of t-butylacetylene [5]. *Trans*-chloropalladation can be ruled out as the source of the σ-butadienylpalladium complex I with *trans* stereochemistry at C(1), since in other reactions *cis*-chloropalladation of phenylmesitylacetylene was observed [6]. It is more probable that the *cis*-chloropalladation is initially formed and then undergoes inversion.

References

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