Journal of Organometallic Chemistry, 71 (1974) C41—C42
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Preliminary communication

THE REACTION BETWEEN ORGANOMERCURIALS AND PLATINUM(0) PHOSPHINE COMPLEXES: A NEW VERSATILE SYNTHESIS OF σ-BONDED ORGANOPLATINUM(II) COMPOUNDS

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(Received March 27th, 1974)

Summary

A novel reaction between both kinds of organomercurials and triphenylphosphine Pt^0 complexes is described, giving a useful route to σ-bonded organoplatinum(II) derivatives. Pd^0 complexes seem to follow a similar reaction pattern.

The oxidative addition of organic halides to platinum(0) and palladium(0) complexes is well-known [1]. The electron transfer from L_nM^0 to RX (X = halogen) seems to be the first step in the process. Then any different stronger electron-acceptor than alkyl halide can be expected to take part in a similar reaction. Therefore it could be predicted that not only organomercuric salts like halides but also symmetrical organomercurials R_2Hg will react with L_nM^0 to give σ derivatives of L_2M^{II} *. In fact, this is the case. Triphenylphosphine complexes of zerovalent platinum L_nPt^0 (n = 3 or 4, L = Ph_3P) react readily with organomercurials in benzene solution under argon at room temperature according to the following equation:

$$L_nPt^0 + R{-}Hg{-}R' \rightarrow L_2Pt^{II}(HgR)R' + (n-2)L \rightarrow L_2PtRR' + Hg^0 + (n-2)L$$

The resulting products were purified by silicagel column or thick-layer chromatography followed by crystallization. The organoplatinum derivatives prepared so far by this organomercurial route are summarized in Table 1.

This procedure can be used to obtain alkyl, aryl, and vinyl derivatives, mono- and di-substituted, as well as those containing the functional groups otherwise accessible only with difficulty. The method is free of the limitations encountered in the use of very active organolithiums or organomagnesiums required by the Chatt—Shaw method [3].

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[*] RHgX can be formally considered as a special kind of "organic halides". The participation of R_2Hg can be explained using the electron transfer concept. The electron-accepting properties change in the sequence [2]: $RHgX > R_2Hg \geqslant RX$, when X = Cl or Br for the same R.

TABLE 1

SOME $(Ph_3P)_2PtRR'$ COMPOUNDS [a] PREPARED BY THE ORGANOMERCURIAL ROUTE

R	R'	yield [b] (%)	M.p. (corr.) (°C)
p-$CH_3C_6H_4$	Br	84	270—271
(p-$CH_3OC_6H_4)_2C$=CH	Cl	66	239—242
CH_3OCOCH_2	Cl	36	198—202
CH_3	Br	43	253
C_6H_5	C_6H_5	54.5	157—158 [c]
$C_5H_5FeC_5H_4$	Cl	50	190 (dec.)

[a] All compounds were analysed satisfactorily. [b] Calculated on a purified product. [c] *cis*-$(Ph_3P)_2Pt(C_6H_5)_2$ prepared through Grignard reagent [3] had m.p. 144—160° (dec.)

In some experiments, there was a delay of minutes or even hours between the time the colour of L_nPt^0 faded and the time metallic mercury separated. Sometimes the heating of a reaction mixture was necessary to complete the mercury separation. We believe that generally the intermediates having a Pt—Hg σ-bond occur, in all cases stability depends very much on their structure. With appropriate R and R′ these compounds can probably be isolated.

Similarly, L_nPd^0 reacts to give σ-organopalladium(II) as shown for R = p-$CH_3C_6H_4$, R = Cl. Mechanistic and preparative aspects of this reaction are under active investigation. It can possibly be extended for others transition metals in low-valency state like rhodium(I) or iridium(I).

References

1 R. Ugo, Coordin. Chem. Rev., 3 (1968) 319.
2 (a) K.P. Butin, I.P. Beletzkaya, A.N. Kashin and O.A. Reutov, J. Organometal. Chem., 10 (1967) 197.
(b) K.P. Butin, N.A. Belokoneva, A.A. Zenkin, I.P. Beletzkaya, and O.A. Reutov, Doklady Akad. Nauk SSSR, 211 (1973) 878.
3 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 4020.