Journal of Organometallic Chemistry, 112 (1976) C25—C26

Preliminary communication

THE SYNTHESIS OF TRIS(METHYL-*o*-CARBORANYL)PHOSPHINE

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(Received March 20th, 1976)

Summary

The possibility of the substitution of the three chlorine atoms in PCl_3 by methyl-*o*-carboranyl groups is shown.

It has been shown previously that the reaction of phenyl-*o*-carboranyllithium with PCl_3 leads to the substitution of only two of the chlorine atoms [1]. At the same time the analogous reactions with $AsCl_3$ and with $SbCl_3$ give tris(carboranyl) derivatives [1].

Such a difference in the reaction courses was explained by the steric hindrance of the carboranyl groups at the phosphorus atom. In order to examine the possibility of the existence of phosphine with three carboranyl substituents, we attempted the synthesis of tris(carboranyl)phosphine. We obtained such a compound by the reaction of methyl-*o*-carboranyllithium with bis(methyl-*o*-carboranyl)chlorophosphine:

$$2\,CH_3\text{-}o\text{-}CB_{10}H_{10}CLi + PCl_3 \rightarrow \underset{(I)}{(CH_3\text{-}o\text{-}CB_{10}H_{10}C)_2PCl} + 2LiCl$$

$$I + CH_3\text{-}o\text{-}CB_{10}H_{10}CLi \rightarrow (CH_3\text{-}o\text{-}CB_{10}H_{10}C)_3P + LiCl$$

In the mass spectrum a molecular ion peak is found at m/e 503 representing $(CH_3CB_{10}H_{10}C)_3P^+$. In the ^{31}P NMR spectrum, $\delta(^{31}P)$ is — 23.36 ppm. Thus the possibility of the existence of phosphine with three carboranyl substituents is shown.

Tris(methyl-*o*-carboranyl)phosphine is a microcrystallinic colourless powder which is insoluble in water, slightly soluble in ethanol, ether, carbon tetrachloride and hydrocarbons, and more soluble in benzene.

Experimental

Bis(methyl-o-carboranyl)chlorophosphine (I)

An ether/hexane solution (50 ml) of methyl-*o*-carboranyllithium prepared from 6.35 g (0.04 mol) of methyl-*o*-carborane was added with stirring and cooling (—60 to —70°C) to a solution of 2.75 g (0.02 mol) of phosphorus trichloride in 25 ml of dry ether in an inert atmosphere. The mixture was allowed to reach room temperature during 3 h, then it was boiled for 1 h and cooled. The mixture was treated with 30 ml of dilute (1:4) HCl. The organic layer was separated and dried. After the solvent had been removed under vacuum the residue was recrystallized from cyclohexane to yield 5.63 g (70%) of I, m.p. 176—177°C (lit. [2] m.p. 174°C), $\delta(^{31}P)$ (C_6H_6/85% H_3PO_4) — 97.57 ppm. (Found: C, 19.2; H, 7.0; B, 56.7; Cl, 9.1. $C_6H_{26}B_{20}PCl$ calcd.: C, 18.9; H, 6.9; B, 56.8; Cl, 9.3%).

Tris(methyl-o-carboranyl)phosphine (II)

An ether/hexane solution (20 ml) of methyl-*o*-carboranyllithium prepared from 1.7 g (0.011 mol) methyl-*o*-carborane was added with stirring and cooling (—60°C) to a suspension of 3.55 g (0.009 mol) of I in 50 ml of dry ether in an inert atmosphere. The mixture was allowed to reach room temperature and was then boiled for 4 h. After treatment as I, the residue was purified on a silica gel column. The residue remaining after removing the solvent was recrystallized from cyclohexane to yield 1.6 g (32%) of II, m.p. 326—327°C. (Found: C, 21.4; H, 7.7; B, 64.6; P, 6.4. $C_9H_{39}B_{30}P$ calcd.: C, 21.5; H, 7.8; B, 64.5; P, 6.2%), $\delta(^{31}P)$ — 23.36 ppm.

References

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