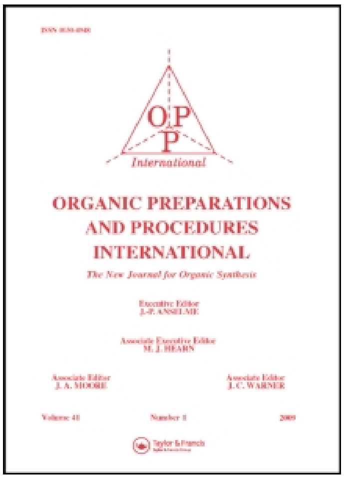

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THE SYNTHESIS OF TRICHLOROTRIS(4-BIPHENYLYL-1-NAPHTHYLPHENYL PHOSPHINE)RHODIUM(III). A NEW OCTAHEDRAL COMPLEX.

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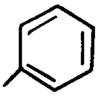
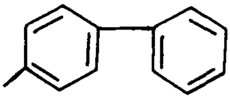
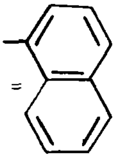
In this paper we wish to describe the synthesis of trichlorotris(4-biphenylyl-1-naphthylphenylphosphine)rhodium(III), (7), a new octahedral complex. The synthesis of 7 was accomplished by the reaction of 4-biphenylyl-1-naphthylphenylphosphine (4) with rhodium trichloride trihydrate. Only the physical properties of the ligand 4 have, so far, been reported in the literature.[1] Because of the significance of 4 in the preparation of the complex 7 a brief description about the synthesis of 4 is deemed necessary. The compound 4 was prepared by the reaction of dichlorophenylphosphine (1) with 4-biphenylyl magnesium bromide (2) and naphthyl magnesium bromide (3). This reaction afforded a crude mixture of all the three possible triaryl

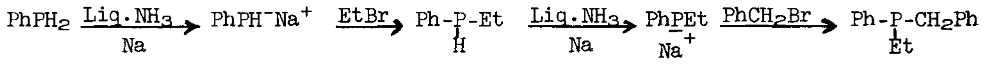
$$\underset{\underline{1}}{ArPCl_2} + \underset{\underline{2}}{Ar_1MgBr} + \underset{\underline{3}}{Ar_2MgBr} \longrightarrow \underset{\underline{4}}{ArAr_1Ar_2P} + \underset{\underline{5}}{Ar(Ar_1)_2P} + \underset{\underline{6}}{Ar(Ar_2)_2P}$$

$$\underset{\underline{4}}{3ArAr_1Ar_2P} + RhCl_3 3H_2O \longrightarrow \underset{\underline{7}}{Rh(ArAr_1Ar_2P)_3Cl_3}$$

where Ar =

; Ar_1 =

; Ar_2 =


phosphines 4, 5, and 6. However, the major component of the reaction mixture was the desired 4-biphenylyl-1-naphthylphenylphosphine (4) which was obtained in 15% yield by fractional crystallization. Treatment of the phosphine 4 (3 moles) with rhodium trichloride trihydrate (1 mole) led to the formation of a new rhodium (III) complex, namely, trichlorotris(4-biphenylyl-1-naphthylphenyl phosphine)rhodium (III) (7). The elemental analysis of 7 indicated it to be an octahedral complex.

The synthetic utility of unsymmetrical dialkylarylphosphines in the preparation of homogenous hydrogenation catalysts and optically active phosphine oxides was recently illustrated by Knowles *et al.*[2] and McEwen *et al.*[3] The preparation of benzylethylphenylphosphine (8) by the reaction of dichlorophenylphosphine with benzylmagnesiumbromide and ethylmagnesiumbromide[3] gave a complex mixture of all the three possible trisubstituted phosphines from which 8 was isolated in 41% yield by fractional distillation. We have improved the synthesis of 8 (74% yield) as shown in the following equations. This procedure can be conveniently used to prepare aryl-alkyltrisubstituted unsymmetrical phosphines, in general.



$$PhPH_2 \xrightarrow[Na]{Liq.NH_3} PhPH^-Na^+ \xrightarrow{EtBr} Ph\text{-}\underset{H}{P}\text{-}Et \xrightarrow[Na]{Liq.NH_3} Ph\underset{Na^+}{\bar{P}}Et \xrightarrow{PhCH_2Br} Ph\text{-}\underset{Et}{P}\text{-}CH_2Ph$$

8

EXPERIMENTAL

The melting points were taken on a Thomas Hoover unimelt apparatus and are corrected. A Beckman IR-8 spectrophotometer was used to determine the infrared spectra. The nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer. All the transfers were made under a nitrogen gas atmosphere.

4-Biphenylyl-1-Naphthylphenylphosphine (4).--Dichlorophenylphosphine (1) was distilled in vacuo (0.1 mm) before use. 4-Biphenylylmagnesium bromide (2) and 2-naphthylmagnesium bromide (3) were prepared by Grignard reactions from the corresponding aromatic bromides and magnesium turnings. The compounds 2 (89.9 g, 0.35 mole) and 3 (80.9 g, 0.35 mole) were dissolved in anhydrous tetrahydrofuran (1.2 l) in a three neck flask equipped with a mechanical stirrer, a 500 ml dropping funnel, and a gas dispersion tube. The solution was cooled to 0° and flushed with nitrogen gas during the course of the reaction. A solution of 1 (62.6 g, 0.35 mole) in anhydrous ether (300 ml) was added dropwise to the mixed Grignard reagents with vigorous stirring. After the addition was over (Ca. 2 hr.), the reaction mixture was stirred at room temperature for 30 min. After distilling off one l of the solvent, 300 ml of water was added to the reaction mixture with stirring. The mixture was extracted twice with ethyl ether (1200 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated to yield an oily residue. This crude material was triturated in succession with 300 ml of water, ethanol, and n-heptane to yield 50.0 g (37%) of a pale yellow solid mp 152-172°. After three recrystallizations from benzene, it afforded 20.0 g (15%) of 4-biphenylyl-1-naphthylphenylphosphine, (4), mp 190-191°, (Lit.[1] mp 191-192°). This material showed one spot on thin layer chromatography using Silica Gel G as the carrier and n-heptane-benzene (1:1) as the developing solvent; nmr ($CHCl_3$-d) δ 7.40 (m, aromatic); ir ν_{max}^{nujol} 830, 800, 760, 755, 740, and 690 (cm^{-1}) (aromatic).

Trichlorotris(4-biphenylyl-1-naphthylphenylphosphine)rhodium III (7)

4-Biphenylyl-1-naphthylphenylphosphine (1.20 g, 3.0 mmole) was suspended in 175 ml of hot absolute ethanol. This mixture was purged with a continuous stream of argon gas. Rhodium trichloride trihydrate (0.28 g, 1.0 mmole), dissolved in 75 ml of deoxygenated hot absolute ethanol, was added to the reaction mixture. The reaction mixture was refluxed for 20 minutes and after cooling to room temperature, filtered under an argon atmosphere to yield 1.00 g (73%), mp 180-186° of a brown powder. This material was purified by dissolving in warm ethanol and reprecipitating with n-heptane three times, mp 186°.

Anal. Calcd. for $C_{84}H_{63}Cl_3P_3Rh$: C, 73.39; H, 4.62; Cl, 7.74; P, 6.76.
Found: C, 72.95; H, 4.53; Cl, 7.62; P, 6.57.

Benzylethylphenylphosphine

Phenylphosphine was prepared in 64% yield from benzene phosphinic acid.[4] A solution of phenylphosphine (66.0 g, 0.60 mole) in ether (150 ml) was added to a four-necked flask containing liquid ammonia (500 ml) at -70° (Dry Ice-acetone bath). Small pieces of freshly cut sodium (13.8 g, 0.60 mole) were added to it during 1 hr. with vigorous stirring in the presence of nitrogen gas. A solution of ethyl bromide (65 g, 0.60 mole) in ether (100 ml) was added to the reaction mixture dropwise. Stirring was continued for 1.5 hr. after which a second equivalent of sodium metal (13.8 g, 0.60 mole) was added. Then a solution of benzyl bromide (76.2 g, 0.60 mole) in ether (100 ml) was added dropwise. All these reactions were conducted at -70° in an atmosphere of nitrogen. After all the additions were over, the reaction mixture was allowed to warm up to room temperature to expel excess ammonia. It was then diluted with ether (500 ml) and water (500 ml). The ether layer was separated dried (anhyd. $MgSO_4$) and evaporated under nitrogen to yield a crude oil (110 g Distillation of the oil under nitrogen afforded **8** as a clear colorless oil (94g. 74%) b.p. 115-120° (1mm), lit.[3] b.p. 145-150° (5mm).

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