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ALTERNATIVE SYNTHESIS OF ENANTIOMERIC 1-DIPHENYLPHOSPHINO-2-DIMETHYLAMINOMETHYLFERROCENE (KUMADA'S LIGAND)

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Summary

A novel facile synthesis of enantiomeric 1-diphenylphosphino-2-dimethylaminomethylferrocene (III), an important ligand for asymmetric catalysis using metal complexes, has been developed. This substance is prepared in a two-step procedure starting with dimethylaminomethylferrocene (I), in 40% overall yield. The absolute configuration and maximum optical rotation of III are determined through the correlation with the previously described cyclopalladated amine derived from I.

At present, there are few metals whose complexes have proved to be effective as homogeneous catalysts. Among them are, in the first place, rhodium, palladium, nickel and cobalt. Much effort has been directed toward the search for new optically active ligands which can be effective in homogeneous asymmetric catalysis. Ligands which possess planar chirality are of special interest due to their large bulk and high resistance to racemization.

Recently, Kumada and co-workers proposed as ligands optically active aminoalkylferrocenylphosphines which appeared to be effective in asymmetric hydrogenation [1], hydrosilylation [2] and coupling [3]. Their synthetic routes, however, involve resolution of racemates as a necessary step.

We propose now an alternative one-step synthesis of enantiomeric III from optically active organopalladium II, the preparation of which as either of two enantiomers by way of asymmetric cyclopalladation of I has already been published [1]. This is another example of the utility of organopalladium(I) for enantioselective synthesis as has been previously demonstrated [5].

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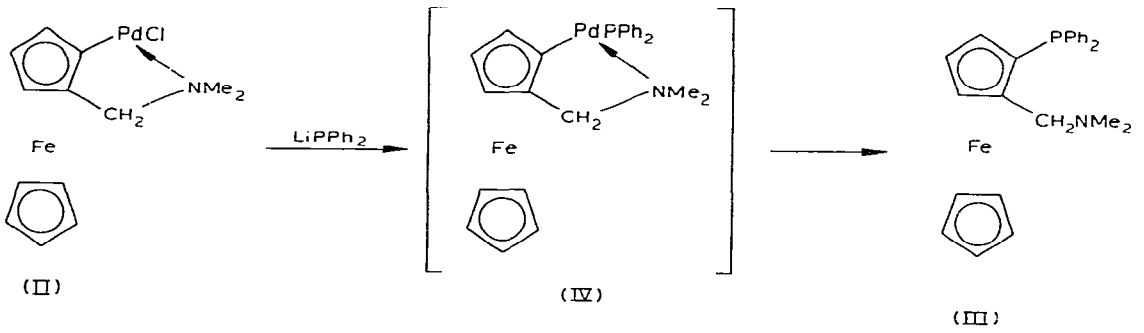

(II) (IV) (III)

The reaction of chelated organopalladiums of the arene series with organolithium reagents to afford *ortho*-alkyl(aryl) derivatives was investigated thoroughly by Murahashi et al. [6]. They found, in part, that added triphenylphosphine (4 eq) suppressed side processes and increased the yield of the alkylation product to 90%. So a similar reaction with lithium diorganophosphides looked quite possible. In fact, the treatment of II with Ph_2PLi in THF results in replacement of palladium with the Ph_2P group to give the desired aminophosphine III. The probable intermediate complex IV undergoes decomposition without isolation. This process is probably homolytic because some quantity of I is always formed as a result of hydrogen extraction from solvent by ferrocenyl radicals. The more soluble enantiomeric II gives a better yield than racemic II, which has low solubility in THF and requires much solvent. The addition of 2 mol eq of PPh_3 increases the yield of enantiomeric III to 50%. This additive may favour the heterolytic reaction pathway. Palladium is removed as a soluble phosphine complex, presumably low-valent, not as the metal itself.

Since the absolute configuration and the absolute rotation of II have been established previously [4], the above-mentioned reaction allows us to assign the absolute configuration and enantiomeric purity of aminophosphine III. Starting with *R*(+)II, $[\alpha]_D$ + 552° (±—2%) (CH_2Cl_2), enantiomeric excess 87.3%, in three independent runs *R*(+)III was obtained having $[\alpha]_D$ + 277.4°, 275.0° and 294.0° ($CHCl_3$), respectively, corresponding to absolute rotations $[A]_D$ + 317.8°, 315.0° and 336.8°, average value is 323.2°. This value is identical to that reported by Hayashi et al. [3] who resolved racemic III as its sulphide. To summarize, the approach outlined here allows one to prepare aminophosphine III of high enantiomeric purity in a two-step procedure from the easily accessible I in 40% overall yield.

Racemic 1-diphenylphosphino-2-dimethylaminomethylferrocene (+) III. To a solution of Ph_2PLi prepared from 4.75 g of Ph_3P and 0.2 g of lithium in 15 ml of THF [7] was added at 10°C a suspension of racemic II (2.0 g) in 40 ml of THF. After stirring under argon for 4 h benzene and water were added. To a benzene solution of the product heptane was added, the precipitate was removed and the filtrate was chromatographed on silica gel, eluents being benzene (for Ph_3P and Ph_2PH) and then the mixture benzene/hexane/triethylamine 5/5/1, (for I and III). The yield of (±) III was 0.4 g (19%), pale yellow crystals.

^1H NMR (CCl_4): δ 1.88 (6H, NMe_2), 2.97, 3.11, 3.49, 3.62, 3.77, 4.07,

(10H, CH_2N, C_5H_5, C_5H_3); broad multiplet centered 7.25 ppm (10H, Ph_2P). Found: C, 70.72; H, 6.18; P, 6.96. $C_{25}H_{26}NFeP$ calcd.: C, 70.29; H, 6.13; P, 7.25%.

Enantiomeric R(+)III. To a solution of Ph_2PLi, prepared from 1.2 g of Ph_3P and 0.1 g of lithium in 4 ml of THF, was added at 10°C a solution of 0.5 g of *R*(+)II* and 0.65 g of Ph_3P in 1 ml of THF. After the above-mentioned work-up 0.254 g of *R*(+)III (51%) was obtained, $[\alpha]_D^{20}$ + 277.4°; $[\alpha]_D^{20}$ + 304° ($CHCl_3$, *c* 0.86). ^1H NMR spectra of enantiomeric and racemic III are identical.

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*The sample used exhibited $[\alpha]_D^{20}$ + 543° (CH_2Cl_2, *c* 1.9) and according to its NMR spectrum and elemental analysis contained ca. 10% of heptane occluded during crystallization, the calculated enantiomeric purity was 87.3%.