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Preliminary Communication

PREPARATION OF A HETERODIFUNCTIONAL LIGAND POSSESSING BOTH PHOSPHINE AND CYCLOPENTADIENIDE FUNCTIONALITY

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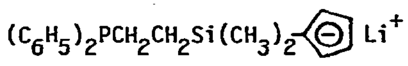
Summary

The difunctional ligand $(C_6H_5)_2PCH_2CH_2Si(CH_3)_2\text{-}\ominus\ Li^+$ (1) is readily prepared in three steps via photolytic addition of diphenylphosphine to vinyldimethylchlorosilane, followed by reaction with lithium cyclopentadienide and deprotonation. Ligand 1 is of value in the construction of molecules containing pairs of different transition metals indirectly linked but not metal-metal bonded.

Several recent reports have revealed intriguing and unusual chemistry resulting from the interaction of more than one metal center with reactive organic fragments (1). The construction of difunctional ligands having non-equivalent sites for metal complexation provides an entry into systems that may be useful for modeling such chemistry and, in general, studying the physical and chemical interactions of non-bonded but proximal metal centers.

We here report the convenient preparation of [dimethyl-(2-diphenylphosphinoethyl)silyl]cyclopentadienyllithium, 1, an isolable cyclopentadienide salt possessing a free, remote phosphine, and well-suited



$(C_6H_5)_2PCH_2CH_2Si(CH_3)_2\text{-}\ominus\ Li^+$

1

for use in the preparation of dinuclear compounds containing indirectly linked metal centers (2). In earlier work (3) we carried out the synthesis of the related ligand [dimethyl(diphenylphosphinomethyl)silyl]cyclopentadienyllithium, $(C_6H_5)_2$-$PCH_2Si(CH_3)_2C_5H_4^-Li^+$ and demonstrated its capabilities as a difunctional ligand for selective attachment to two different transition metals, e.g. ring-bonded Fe(II) and Zr(IV) and phosphine-linked Ni(II) and Fe(0). The synthesis of the latter, however, requires the preparation and isolation of the diphenylphosphinomethyllithium-TMEDA reagent (4), a procedure best carried out in a dry box, and the purity of final product is highly dependent on complete removal of non-ionic impurities at various stages in the synthesis. The synthesis of **1** described here avoids these difficulties and is well suited for large scale preparation of this useful ligand.

A benzene solution of diphenylphosphine and chlorodimethylvinylsilane (20% excess) is prepared under nitrogen in a stoppered quartz tube. Irradiation (450W Hanovia medium-pressure lamp) is carried out at 25°C for 48 h, and solvent and unreacted silane are removed under vacuum (5). The resultant white, semi-solid mixture is treated with a little dry petroleum ether, cooled to -40°C, and the supernatant collected. After removal of solvent, a 54% yield of chlorodimethyl(2-diphenylphosphinoethyl)silane, **2**, is obtained (6). Treatment of this chlorosilane with one equivalent of lithium cyclopentadienide in tetrahydrofuran under nitrogen instantaneously produces the neutral cyclopentadienylsilane which is separated from LiCl by removal of THF in vacuo, trituration with petroleum ether, and filtration. Treatment of the resultant solution with butyllithium gives rise to a gummy deposit of impure **1** which completely solidifies after trituration with fresh petroleum ether.

SCHEME I

$$(C_6H_5)_2PH + CH_2{=}CHSi(CH_3)_2Cl \xrightarrow[C_6H_6]{h\nu} (C_6H_5)_2PCH_2CH_2Si(CH_3)_2Cl$$

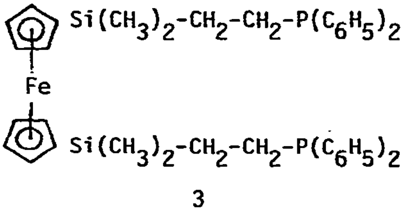
2

$$\xrightarrow[\text{2) } nC_4H_9Li,\ \text{pet. ether}]{\text{1) } LiC_5H_5,\ \text{THF}} (C_6H_5)_2PCH_2CH_2Si(CH_3)_2C_5H_4^{-}Li^{+}$$

1

Inasmuch as the latter two steps are virtually quantitative in yield, the overall yield of 1 based on diphenylphosphine is on the order of 50% (Scheme I). Both intermediate silanes appear to be stable at room temperature under nitrogen with the neutral silylcyclopentadiene showing no tendency to dimerize either neat or in hydrocarbon solvent.

Cyclopentadienide 1 is a pale yellow air- and water-sensitive solid, insoluble in hydrocarbon solvents, very soluble in tetrahydrofuran, and slightly soluble in diethyl ether. It is readily characterized spectroscopically as well as chemically; in the NMR it displays absorptions in THF-d_8 at δ0.13 (s,6H), ∿0.8 (m,2H), ∿2.0 (m,2H), 5.93 (br s,4H), and 7.1-7.7 (m,10H). The anion reacts readily with metal halides in appropriate solvents to give rise to the corresponding metallocene systems. Reaction with a slight excess of $FeCl_2$ in ether at 25°C, for example, affords 81% of ferrocene 3. The crude product, a brown oil, exhibits NMR absorptions that are not only broadened but shifted in position relative to the purified ferrocene itself, indicative perhaps of complexation of the free phosphine moieties with unreacted $FeCl_2$. Purification of 3 is effected by chromatography on alumina I with benzene, giving rise to an oil which slowly crystallizes upon standing under nitrogen (7). Compounds 1, 2, and 3 (when pure) all show similar pairs of characteristically complex NMR patterns for the P-CH_2-CH_2-Si proton systems, consistent with the comparable two- and three-bond $J_{P(C)_nH}$ values seen in a variety of acyclic compounds (8).



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In summary, ligand 1 is a stable, isolable reagent suitable for selective complexation at the cyclopentadienide function with a variety of transition metals. In all cases thus far investigated, the remote phosphine units in the purified complexes appear to be completely free from interaction with the central metal and behave normally in reactions aimed at complexation with a second metal atom. The ease of preparation and isolation of $\underset{\sim}{1}$ on a large scale makes it by far the most accessible of difunctional ligands of this type and the most valuable for the study of a variety of novel dinuclear systems, several of which are currently under investigation in our laboratory.

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6. Colorless oil, NMR (C_6D_6): δ0.17 (s,6H), 0.90 (m,2H), 2.16 (m, 2H), and 7.0-7.8 (m,10H).

7. Orange crystalline solid, mp 89-91°C. NMR (C_6D_6): δ0.20 (s,12H,CH_3Si), 0.92 (m,4H,$-CH_2-Si$), 2.13 (m,4H,$-CH_2-P$), 3.90 and 4.13 (apparent triplets, splittings ≃ 1.7Hz,4H ea.,Cp), 7.03-7.30 (m,12H,m- and p-Ph), 7.35-7.72 (m,8H,o-Ph). Anal: found: C,69.61; H,6.76; P,8.33. Calcd. for $C_{42}H_{48}P_2Si_2Fe$: C,69.41; H,6.66; P,8.52%.

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