

Alkyl Derivatives of Nickel, Palladium, and Platinum stabilized by Chelation with Phosphorus

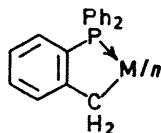
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Summary The synthesis of 2-(diphenylphosphino)benzylpotassium and of the related chelated organometallic compounds of nickel(II), palladium(II), and platinum(II) is reported.

We report a new synthesis of some phosphorus-chelated organometallic compounds, which provides new possibilities for the growing field of chelated organometallic compounds of transition metals.¹

The starting reagent was prepared by metallation of diphenyl-*o*-tolylphosphine with *n*-butyl-lithium in hexane in the presence of potassium *t*-butoxide. 2-(Diphenylphosphino)benzylpotassium (I) was obtained in 60–70%



- (I) M = K, brick-red.
 (II) M = Ni, $n = 2$, yellow.
 (III) M = Pd, $n = 2$, colourless, m.p. 257° dec.
 (IV) M = Pt, $n = 2$, colourless, m.p. 306° dec.

yield as a brick-red air-unstable powder, containing lithium *t*-butoxide as an impurity (*ca.* 20%). Compound (I) is soluble in tetrahydrofuran, but the solution decomposes slowly at room temperature (about 50% decomposition in 48 h). The metallation is also promoted by addition of *NNN'*-tetramethylethylenediamine, but in this case a complex between the amine and (I) is obtained. In both

cases n.m.r. studies of the phosphine recovered after decomposition with D₂O demonstrate that metallation takes place at the methyl group.

By treating benzene solutions of the compounds L₂MCl₂ (where L = SEt₂ or PBu₃ when M = Pt; L = SEt₂, or PEt₃ when M = Pd; and L = PEt₃ when M = Ni) with (I) we have obtained the crystalline compounds (II), (III), and (IV) in which the transition-metal-carbon bond is stabilized by chelation with a phosphorus atom. The solubility of compounds (II), (III), and (IV) decreases on descending the subgroup, and the platinum derivative is only slightly soluble in a few solvents such as pyridine. The i.r. spectra (Nujol mull) of (II), (III), and (IV) are practically identical. ¹H n.m.r. spectra have been obtained in C₅D₅N at 100° for (III) and (IV). Both spectra consist of a doublet, (III) at τ 6.54 and (IV) at τ 6.24, which in the latter case is split by the platinum atom. Both doublets disappear on irradiation of the phosphorus atoms; the P–H coupling constant in both cases is 7.5 Hz. From the Pt–H coupling constant (75 Hz) and the shape of the spectra it is possible to assign a *cis*-structure to these compounds,² assuming no substitution by the perdeuterio-pyridine. Evidence for this assumption, as well as a comparison of the reactivity of these phosphorus-chelated complexes and of similar nitrogen-chelated complexes, will be presented elsewhere.³

The potassium derivative (I) seems to be a reagent of general applicability, particularly in cases in which the alkyl derivatives show low stability, and we are at present characterising the corresponding copper(I) derivative.

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² J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 2801, and references therein.

³ G. Longoni, P. Chini, F. Canziani, and P. Fantucci, to be submitted to *J. Organometallic Chem.*