Novel Dialkyl Cobalt Derivatives

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Previously, we have reported[1] some stable alkyl nickel derivatives, with a formula of π-$C_5H_5Ni(PPh_3)R$, in which nickel metal attained the electronic configuration of krypton. The surprising stabilities of these compounds have now prompted us to prepare isoelectronic compounds of cobalt. Here we wish to report the preparation of the some dialkyl cobalt derivatives.

The treatment of a slurry of triphenylphosphine-π-cyclopentadienylcobalt diiodide[2,3] in benzene with a solution of methyl magnesium iodide in ether at room temperature gave an orange-red solution.* After the hydrolysis and evaporation of the solvent, the residue was separated on an alumina column, using benzene as the eluant. From the first red fraction, air-stable orange-red crystals of triphenylphosphine-π-cyclopentadienyl dimethylcobalt (I) (π-$C_5H_5Co(PPh_3)(CH_3)_2$) were obtained. (Yield, 54%. M. p. 142—143°C (decomp.). PMR (in CS_2)**: 2.65 τ ($C_6\underline{H}_5$), doublet (J=5 c. p. s.); 5.67 τ ($C_5\underline{H}_5$), sharp singlet; 10.02 τ ($C\underline{H}_3$), doublet (J_{PH}=6 c. p. s.).

Found: C, 71.80; H, 6.42. Calcd. for $C_{25}H_{26}PCo$: C, 72.11; H, 6.30%.) I is very stable in air, especially in the solid state, and it is soluble in most organic solvents.

From the second brown fraction, fine dark brown crystals of triphenylphosphine-π-cyclopentadienylmethylcobalt iodide (II) (π-$C_5H_5Co(PPh_3)(CH_3)I$) were obtained. (Yield, 1.3%. M. p. 112°C (decomp. without melting). Found: C, 54.35; H, 4.41. Calcd. for $C_{24}H_{23}IPCo$: C, 54.57; H, 4.39%.) Another experiment which was carried out employing an amount of methyl magnesium iodide equivalent to the diiodide and by the reverse addition method gave I in a 8% yield and II in a 13% yield.

According to the results of a similar procedure using benzyl magnesium chloride, dark red crystals of triphenylphosphine-π-cyclopentadienyldibenzylcobalt (III) (π-$C_5H_5Co(PPh_3)(CH_2Ph)_2$) were obtained. (Yield, 68%. M. p. 102°C (decomp.). PMR (in C_6D_6)***: 2.7 τ (P-$C_6\underline{H}_5$); 2.9 τ (CH_2-$C_6\underline{H}_5$); 5.67 τ ($C_5\underline{H}_5$); 6.85 and 7.15 τ (-$C\underline{H}_2$-), broad. Found: C, 77.96; H, 6.03. Calcd. for $C_{37}H_{34}PCo$: C, 78.16; H, 6.03%.)

The reaction of II with benzyl magnesium chloride resulted in the formation of triphenylphosphine - π - cyclopentadienylmethylbenzylcobalt (IV) (π-$C_5H_5Co(PPh_3)(CH_3)(CH_2Ph)$) as red crystals. (Yield, 51%. M. p. 112—113°C (decomp.). PMR (in C_6D_6)***: 2.5 τ (P-$C_6\underline{H}_5$); 2.95 τ (CH_2-$C_6\underline{H}_5$); 5.72 τ ($C_5\underline{H}_5$); 6.75 and 8.30 τ (-$C\underline{H}_2$-), broad; 9.17 τ (CH_3), doublet (J_{PH}= 6 c. p. s.). Found: C, 76.07; H, 6.13. Calcd. for $C_{31}H_{30}PCo$: C, 75.60; 6.14%.) This is the first example of a compound with two different alkyl groups bonded to a cobalt metal. The air sensitivities of I, IV and III increase in this order.

The proton magnetic resonance spectra of III and IV show that the methylenic protons of the benzyl group are not equivalent, suggesting the inhibition of the free rotation of the benzyl group. Attempts to isolate other dialkyl and diaryl derivatives were unsuccessful. The steric factor is essential for their stabilities.

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1) H. Yamazaki and N. Hagihara, This Bulletin, **37**, 907 (1964).
2) R. B. King, *Z. Naturforch.*, **19b**, 1160 (1964).
3) R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965).
* The reactions were all carried out under a nitrogen atmosphere, and melting points were measured in a nitrogen-filled capillary.

** Varian A 60. $Si(CH_3)_4$ was used as the external standard.
*** Japan Electron Optics, 100 Mc. $Si(CH_3)_4$ was used as the internal standard.