SHORT COMMUNICATIONS

Synthesis of a New δ-Bonded Dimethyl Rhodium Derivative, π-$C_5H_5Rh(CH_3)_2[P(C_6H_5)_3]$

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(Received December 19, 1966)

Recently, some stable δ-bonded alkyl derivatives of transition metals have been prepared[1] and a few examples of δ-bonded organo-rhodium compounds have been reported.[2] Here we wish to report the preparation of a stable δ-bonded dimethyl-rhodium derivative containing cyclopentadienyl and triphenylphosphine groups as ligands.

The treatment of a solution of bis(cycloocta-1,5-diene)-μ, μ'-dichlorodirhodium[3] in ether with a solution of iodine under cooling with ice water resulted in the formation of black crystals of π-cyclopentadienyl-diiodorhodium, (yield, 80%; decomp. p. >260°C. Found: C, 14.10; H, 1.43%. Calcd for $C_5H_5RhI_2$: C, 14.24; H, 1.20%). This compound was insoluble in all common organic solvents. Its infrared spectrum showed only a few weak bands except those characteristic of the cyclopentadienyl group and agreed with similar descriptions on the spectrum of $[(C_5H_5)RhBr_2]_x$ and $[(C_5H_5)RhI_2]_x$[4] which had been prepared from π-cyclopentadienyl-(1-*exo*-phenylcyclopentadiene)-rhodium and bromine or iodine. The reaction between π-cyclopentadienyl diiodorhodium and triphenylphosphine in boiling chloroform yielded dark brown air stable triphenylphosphine-π-cyclopentadienyl-rhodium diiodide π-$C_5H_5RhI_2P(C_6H_5)_3$ in nearly quantitative yield, (mp >260°C (decomp.). Found: C, 40.52; H, 3.10%. Calcd for $C_{23}H_{20}RhI_2P$: C, 40.39; H, 2.95%). Slurry of this compound in anhydrous tetrahydrofuran was treated with a large excess of methylmagnesium iodide in ether at 0°C, followed by hydrolysis in aqueous solution of ammonium chloride and chromatography on alumina. Triphenylphosphine-π-cyclopentadienyl-dimethylrhodium π-$C_5H_5Rh(PPh_3)(CH_3)_2$ (yield, 35%; mp 115—119°C. Found: C, 65.07; H, 5.91%; mol wt, 456 (in benzene). Calcd for $C_{25}H_{26}RhP$: C, 65.22; H, 5.71%; mol wt, 460.) was separated as pale yellow crystals. It was stable in air and was soluble in most organic solvents. The NMR spectra of the compound in deuterochloroform showed lines at 2.63 τ (unresolved singlet), 4.60 τ (double doublet, $J_{Rh-H}=1.8$ cps, $J_{P-H}=9.6$ cps), and 9.72 τ (double doublet, $J_{Rh-H}=2.4$ cps, $J_{P-H}=4.8$ cps), corresponding to fifteen phenyl protons, five cyclopentadienyl protons, and six methyl protons, respectively supporting the foregoing formula.

Further, more detailed studies are now in progress.

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