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# PRELIMINARY NOTES

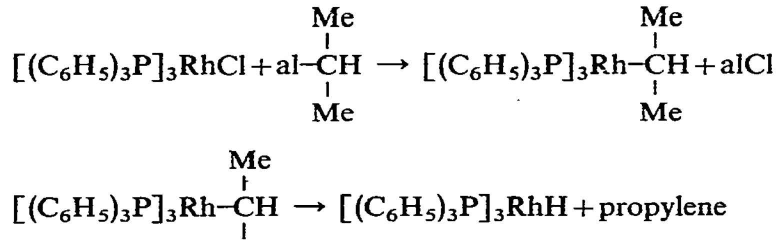
## Tris(triphenylphosphine)rhodium(I) complexes

There has been considerable interest in recent years in the properties of low-valent $\sigma$-bonded complexes of transition metals as catalysts. To our knowledge no organometallic rhodium(I) complexes containing a Rh–carbon bond have been described in the open literature.

We now wish to report the synthesis and characterization of $\sigma$-bonded rhodium(I) complexes of the general formula $RhL_3R$ (L = triphenylphosphine; R = methyl, phenyl, hydride).

Methyltris(triphenylphosphine)rhodium and phenyltris(triphenylphosphine)-rhodium have been obtained by reaction of a suspension of $[(C_6H_5)_3P]_3RhCl$* in ether with a two-fold excess of the corresponding Grignard reagent. At 0°C the reaction time was 24 hours. The orange complexes which formed were filtered and washed several times with abs. ether. The yields ranged from 80–90%. The IR spectra of these complexes are characterized by the $(C_6H_5)_3P$ absorption bands. The NMR spectrum of $[(C_6H_5)_3P]_3RhCH_3$ is in agreement with the proposed structure in which the methyl group is bound directly to the rhodium. The methyl resonance centered at $\delta(CH_3) = 0.35$ ($\delta(P) = -41$) is split by interaction with the three equivalent $^{31}P$ nuclei into a symmetrical quartet with relative intensities 1:3:3:1 ($J(P\text{–}H) = 3.6$ Hz). Each line is further split by $^{103}Rh$ into a doublet ($J(Rh\text{–}H) = 1.4$ Hz). These results strongly imply a tetrahedral structure for $[(C_6H_5)_3P]_3RhCH_3$.

Hydridotris(triphenylphosphine)rhodium has been prepared by treating a suspension of $[(C_6H_5)_3P]_3RhCl$ in hexane with the stoichiometric amounts of aluminumtriisopropyl at room temperature. The orange $[(C_6H_5)_3P]_3RhH$ could be isolated in 80% yield by filtration. The reaction mechanism can be visualized as follows:



$$[(C_6H_5)_3P]_3RhCl + al\text{–}\overset{\text{Me}}{\underset{\text{Me}}{CH}} \rightarrow [(C_6H_5)_3P]_3Rh\text{–}\overset{\text{Me}}{\underset{\text{Me}}{CH}} + alCl$$

$$[(C_6H_5)_3P]_3Rh\text{–}\overset{\text{Me}}{\underset{\text{Me}}{CH}} \rightarrow [(C_6H_5)_3P]_3RhH + \text{propylene}$$

$[(C_6H_5)_3P]_3RhH$ could also be prepared in 60% yield by treating $[(C_6H_5)_3P]_3RhR$ ($R = CH_3, C_6H_5$) in toluene solution with hydrogen (600 psig) at room temperature.

$$[(C_6H_5)_3P]_3RhR + H_2 \rightarrow [(C_6H_5)_3P]_3RhH + RH \qquad R = CH_3, C_6H_5$$

Methane and benzene have been isolated in nearly quantitative yields.

The infrared spectrum of $[(C_6H_5)_3P]_3RhH$ shows a very weak band at 2020

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* This compound has been obtained independently by several workers, see ref. 1–4.

cm$^{-1}$ attributable to the Rh–H stretching vibration. The NMR spectrum shows a doublet at $\delta(\mathrm{H}) = -8.3$ ($\delta(\mathrm{P}) = -19$) with a rhodium–hydrogen coupling constant of $J(\mathrm{Rh{-}H}) = 12.4$ Hz. The described complexes readily react in toluene solution at 100°C with an excess of $C_6H_5OH$ to form dark red solutions. The reddish-brown complex $[(C_6H_5)_3P]_3RhOC_6H_5$ crystallized upon addition of n-hexane and was isolated in 60% yield. The corresponding hydrocarbons or hydrogen have been obtained in nearly quantitative yield.

$$[(C_6H_5)_3P]_3RhR + C_6H_5OH \rightarrow [(C_6H_5)_3P]_3RhOC_6H_5 + RH \qquad (R = H, CH_3, C_6H_5)$$

The recrystallization of $[(C_6H_5)_3P]_3RhOC_6H_5$ in toluene led to the dissociation of $(C_6H_5)_3P$, and the compound $[(C_6H_5)_3P]_2RhOC_6H_5$ was isolated in 70% yield. The bis(phosphine) complex is presumably dimeric, analogous to $Rh_2(CO)_4Cl_2$[5].

All of the described compounds are air-sensitive and soluble in benzene or other aromatic solvents, and they decompose upon heating between 150–200°C. Satisfactory analyses were obtained for all complexes.

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