# New Hydrido- and Oxygen-complexes of Rhodium

Masahiko TAKESADA, Hiroshi YAMAZAKI and Nobue HAGIHARA

*The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka*

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Hydrido- and oxygen-complexes of transition metals have found attention in connection with their catalytic behavior.[1] We now wish to report the preparations of new hydrido- and oxygen-complexes of rhodium which were obtained during studies on the hydrogenation of olefins, and the oxidation of triarylphosphines catalyzed by phenyl-(1, 5-cyclooctadiene)-(triphenylphosphine)-rhodium (I)[*1].

During the treatment of a solution of I and triphenylphosphine (five molar equivalent to I) in toluene with hydrogen (1 atm) at room temperature for 30 min, approximately one mole of hydrogen was absorbed and yellow crystals were deposited. The reaction mixture was filtered and washed with toluene to give yellow crystals of hydrido-tetrakis-(triphenylphosphine)-rhodium, $HRh(PPh_3)_4$, (II) (Yield, 89%; mp 162—163°C (decomp). Found: C, 75.17; H, 5.31; P, 10.96%. Calcd for $RhC_{72}H_{61}P_4$: C, 75.00; H, 5.33; P, 10.74%.). II was unstable in air, especially in solution, and sparingly soluble in acetone, tetrahydrofuran, dichloromethane and benzene. II was diamagnetic and its infrared spectrum showed a sharp absorption at 2152 $cm^{-1}$ (in Nujol mull; at 2140 $cm^{-1}$ in KBr disk), which was assigned to the stretching vibration of the rhodium-hydrogen bond. The yellow deuterium analog was synthesized by a similar procedure with molecular deuterium, and its infrared spectrum showed an absorption at 1548 $cm^{-1}$ (Nujol mull). Confirmation of the presence of a Rh-H bond in II by NMR was unsuccessful due to the low solubility. Yellow crystals of hydrido-(triphenylphosphine) - tris(triphenylarsine)-rhodium, $HRh(PPh_3)(AsPh_3)_3$,(III), were also obtained by a similar procedure (Yield, 20%; mp 168—169°C (decomp). Found: C, 67.18; H, 4.88%. Calcd for $RhC_{72}H_{61}As_3P$: C, 67.30; H, 4.79%. IR (Nujol mull): 2118 $cm^{-1}$ with a shoulder at 2140 $cm^{-1}$). Hydrido-di(1, 2-bisdiphenylphosphinoethane)-rhodium[2] was also prepared by a similar treatment, obtaining a 67% yield.

Yellow crystals were obtained by a virtually similar method to that described for II except that molecular hydrogen was replaced with oxygen or air. Elemental analysis conformed to a composition, $Rh(PPh_3)_3O_2$, (IV) (Yield, 65%; mp 135—137°C (decomp). Found: C, 70.44; H, 4.96; P, 9.52%. Calcd for $RhC_{54}H_{45}O_2P_3$: C, 70.36; H, 4.92; P, 10.09%.). IV was explosive and sparingly soluble in common organic solvents. Its infrared spectrum showed an absorption at 815 $cm^{-1}$ (KBr disk), assignable to the stretching vibration of the peroxy group. The diamagnetism of IV seems to suggest that the complex has a dimeric structure, but X-ray analysis should be carried out to determine the exact structure. By a similar procedure, $Rh(PPh_3)(AsPh_3)_2O_2$ was also prepared (Yield, 3%; mp 137—139°C. Found: C, 64.45; H, 4.51%. Calcd for $RhC_{54}H_{45}As_2O_2P$: C, 64.24; H, 4.49%. IR (KBr disk): 810 $cm^{-1}$.).

Detailed studies of these complexes will be published in the near future.

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[*1] This compound was prepared by the treatment of chloro-(1, 5-cyclooctadiene) - (triphenylphosphine)-rhodium with phenylmagnesium bromide.

[1] a) J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. (A)*, **1966**, 1711; and the literatures therein; b) S. Takahashi, K. Sonogashira and N. Hagihara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 610 (1966); c) G. Wilke, H. Schott and P. Heinbach, *Angew. Chem.*, **79**, 62 (1967); d) S. Otsuka, A. Nakamura and Y. Tatsuno, *Chem. Commn.*, **1967**, 836.

[2] A. Sacco and R. Ugo, *J. Chem. Soc.*, **1964**, 3274.