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Preliminary communication

PREPARATION OF DICYCLOPENTADIENYLMETAL-BIS(TRIMETHYL PHOSPHITE) COMPLEXES OF TITANIUM(II) AND ZIRCONIUM(II) BY SODIUM ATOM REDUCTION

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Summary

The complexes $(C_5H_5)_2M[P(OCH_3)_3]_2$ (M = Ti and Zr) can be prepared by condensing sodium atoms at –100°C into tetrahydrofuran solutions containing $(C_5H_5)_2MCl_2$ and excess trimethyl phosphite.

Development of the coordination chemistry of dicyclopentadienyl derivatives of titanium(II) and zirconium(II) has been hindered by the limited availability of stable monomeric $(C_5H_5)_2ML_2$ derivatives other than the dicarbonyls $(C_5H_5)_2M(CO)_2$ (M = Ti [1,2] and Zr [3,4,5]). Gell and Schwarz [6] reported the formation of several $(C_5H_5)_2ZrL_2$ derivatives (L = $(C_6H_5)_2PCH_3$ and $C_6H_5P(CH_3)_2$ and $L_2 = R_2PCH_2CH_2PR_2$ [R = CH_3 and C_6H_5]) by reductive elimination of RH from $(C_5H_5)_2ZrHR$ on reaction with a stoichiometric amount of the trivalent phosphorus ligand. However, among these phosphine complexes only the zirconium(II) derivative of the strongly basic chelating ditertiary phosphine $(CH_3)_2PCH_2CH_2P(CH_3)_2$ was found to be sufficiently stable at room temperature for isolation in the solid state and complete characterization by chemical and spectroscopic methods. This communication describes the preparation and isolation of the stable metal(II) trimethyl phosphite complexes $(C_5H_5)_2M[P(OCH_3)_2]_2$ (M = Ti and Zr) using sodium atoms as a reagent for the reduction of the corresponding dichlorides $(C_5H_5)_2MCl_2$.

The sodium atom reduction was carried out in a rotating atom reactor described previously [7]. The sodium vapor was generated under vacuum ($< 10^{-2}$ torr) by electrically heating a quartz crucible containing a piece of sodium metal (ca. 1 g). The metal vapor was condensed into a tetrahydrofuran solution (200 cm^3) containing the $(C_5H_5)_2MCl_2$ complex (2 g, M = Ti or Zr)

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and excess trimethyl phosphite (10 cm^3), cooled to −100°C. These reaction conditions are similar to those in an earlier report on the use of potassium atoms to prepare bisarenemetal complexes [8], but in the present work sodium atoms are preferred since potassium atoms decompose trimethyl phosphite. As in the earlier paper [8], the progress of the metal atom reduction was monitored by the color changes of the solution. The "end-point" color, optimizing the yield of the desired $(C_5H_5)_2M[P(OCH_3)_3]_2$ was determined experimentally. In the case of $(C_5H_5)_2ZrCl_2$, upon addition of sodium atoms to the colorless original solution, the color changed to dark red through pink to green, which was found to be the optimum end-point color. Evaporation of solvent followed by crystallization from toluene gave 1.0 g (31% yield) of red air-sensitive $(C_5H_5)_2Zr[P(OCH_3)_3]_2$ identified by elemental analyses (C, H), its mass spectrum, and its proton NMR spectrum. Thus the proton NMR spectrum in C_6D_6 exhibits a cyclopentadienyl resonance at δ 4.70 ppm (10 H; triplet, J 2 Hz) and a methoxy resonance at δ 3.04 ppm (18 H; doublet, J 10 Hz). The mass spectrum exhibits the ions $(C_5H_5)_2Zr[P(OCH_3)_3]_n^+$ (n = 2 and 1) and $(C_5H_5)_2Zr(OCH_3)_n^+$ (n = 2 and 1). The latter ions are apparently formed through methoxy shift from phosphorus to zirconium, since the following process is supported by a strong metastable ion at $m/e \sim 231.5$;

$$(C_5H_5)_2ZrP(OCH_3)_3^+ \rightarrow (C_5H_5)_2Zr(OCH_3)_2^+ + CH_3OP$$

The observation of this process is consistent with the high affinity of zirconium for bonding to oxygen.

The titanium complex $(C_5H_5)_2Ti[P(OCH_3)_3]_2$ was prepared in an analogous manner although a different pattern of color changes (red → green → deep red) was observed. After stopping the sodium evaporation at the optimum deep red end-point color, solvent evaporation followed by crystallization from pentane gave 1.2 g (35% yield) of red-brown very air-sensitive $(C_5H_5)_2Ti[P(OCH_3)_3]_2$, identified by elemental analysis (C, H) and appropriate C_5H_5 (2 Hz triplet at δ 4.42 ppm) and CH_3O(10 Hz doublet at δ 2.93 ppm) resonances in its proton NMR spectrum (C_6D_6). This titanium compound appears to be less stable than its zirconium analogue. It is more air-sensitive and in its mass spectrum the ion of highest m/e corresponds to $(C_5H_5)_2TiOCH_3^+$ whereas the zirconium compound gives a molecular ion.

Attempts to prepare the phosphite complexes using sodium amalgam at −30°C or sodium sand dispersed in tetrahydrofuran at −78°C in place of sodium atoms, were not successful. Although reduction of the dihalides occurred, only traces of toluene soluble products were obtained. It seems that the low temperature of reduction and the close control of the amount of reductant which is possible in the atom technique, is essential to the success of these preparations.

The compounds $(C_5H_5)_2M[P(OCH_3)_3]_2$ (M = Ti and Zr) react with CO in pentane solution at 25°C/1 atm. The coordinated trimethyl phosphite is displaced cleanly to give high yields of the corresponding dicarbonyls, identified, after evaporation of the pentane solution and re-extraction with hexane, by comparison of their ν(CO) frequencies with those reported [3] in the literature.

The isolability of $(C_5H_5)_2M[P(OCH_3)_3]_2$ (M = Ti and Zr) in reasonable yields coupled with the apparent lability of the trimethyl phosphite ligands, suggests that these complexes might be useful starting materials for exploring novel dicyclopentadienyl-titanium(II) and -zirconium(II) chemistry. In this connection, some reactions of $(C_5H_5)_2M[P(OCH_3)_3]_2$ with various potential ligands (e.g., t-butyl isocyanide and 3-hexene) have been investigated and characterization of the products is in progress.

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