## Trialkyl Phosphite Addition to the Bis(benzene)-iron(11) and -ruthenium(11) Dications: Catalysed Hydrolysis to Dialkyl Phosphites

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Summary Phosphite addition to  $[(C_6H_6)_2M]^{2+}$  (M = Fe,Ru) yields cyclohexadienyl phosphonium and phosphonate adducts that catalyse the conversion of excess of phosphite into HP(O)(OR)<sub>2</sub> and RP(O)(OR)<sub>2</sub>.

The addition of alkyl phosphites to co-ordinated cyclic  $\pi$ -hydrocarbons, in contrast with the analogous reaction with phosphines,<sup>1</sup> has not been widely investigated. There are three reports of phosphite addition:  $[(C_6H_7)Fe(CO)_3]BF_4$  and  $[(C_7H_7)Cr(CO)_3]BF_4$  react with  $P(OBu^n)_3$  to give the phosphonium salt,<sup>2</sup> but addition of  $P(OMe)_3$  to  $[(C_6H_6)Rh-(C_5Me_4Et)](PF_6)_2$  is accompanied by an Arbuzov rearrangement to the phosphonate.<sup>3</sup>

We report here that  $[(C_6H_6)_2Fe](PF_6)_2$  (1a) and  $[(C_6H_6)_2 \operatorname{Ru}_{(\operatorname{PF}_6)_2}(\mathbf{1b})$  react with  $\operatorname{P(OMe)_3}$  and  $\operatorname{P(OBu^n)_3}$  to yield the phosphonium adducts  $[\{C_6H_6P(OR)_3\}(C_6H_6)M](PF_6)_2$ (2) which, at least with  $P(OMe)_3$ , are readily converted in solution into the phosphonates  $[{C_6H_6P(O)(OR)_2}(C_6H_6)M]$  $(PF_6)$  (3). We also found that (1a) and (1b) are effective homogeneous catalysts for the conversion of P(OR)<sub>3</sub> into  $HP(O)(OR)_2$ . For example, the addition of a large excess of  $P(OBu^n)_3$  or  $P(OMe)_3$  to a slurry of (1a) in acetone or acetonitrile produced a deep red solution from which (1a) reprecipitated after ca. 5-10 min. <sup>1</sup>H N.m.r. spectra taken before reprecipitation showed that one of the benzene rings was attacked to give a cyclohexadienyl ring adduct which was fairly rapidly reconverted into (1a) as the excess of phosphite was hydrolysed to the dialkyl phosphite, HP(O)- $(OR)_2$ . Solutions containing (1a) and phosphite generally gave broad n.m.r. resonances owing to a slight decomposition into paramagnetic iron species. This problem did not exist with complex (1b).

The ruthenium compound (1b) and  $P(OMe)_3$  reacted rapidly in  $CD_3CN$  to yield a cyclohexadienyl ring adduct which gives n.m.r. resonances at  $\delta$  6.23 (benzene ring) and 4.00 and 4.20 [ $P(OMe)_3$ ] which we ascribe to the phosphonium adduct (2b). Within minutes all the excess of  $P(OMe)_3$  was hydrolysed to  $HP(O)(OMe)_2$  and MeOH, and the  $\delta$  4.00 and 4.20 resonances disappeared, being replaced by bands at 3.50 and 3.68 which are assigned to (3b). Depending on the experimental conditions, complex (3b) persists or is converted into the starting complex (1b). There was normally sufficient water in the solvent to ensure complete hydrolysis. However, in the absence of sufficient water the  $P(OMe)_3$  was catalytically converted into MeP(O)(OMe)\_2.

Depending on the concentrations and time after mixing, the addition of ether to a solution of  $P(OMe)_3$  and (1b) gave mixtures of (1b), (2b), and (3b). A mixture of (2b) and (3b) in dry CD<sub>3</sub>CN was converted into pure (3b) by the addition of a small amount of water. Assignment of the resultant white product as the phosphonate (3b) is supported by satisfactory analyses for C and H and <sup>1</sup>H n.m.r. data:  $\delta 6.48$  (H-4), 6.22 (C<sub>6</sub>H<sub>6</sub>), 5.14 (H-3 and -5), 3.60 (H-2 and -6), and 3.50 and 3.68 [P(O)(OMe)<sub>2</sub>]. Area ratios are consistent with these assignments. The H-1 *endo*-resonance was probably obscured by the phosphoryl methyl resonances and baseline noise. The phosphonium adduct (2b) could not be isolated in a pure state. However, its ready conversion into (3b) (with liberation of MeOH) is strong support for the proposed formulation.

Reaction of (1a) with P(OMe)<sub>3</sub> gave results similar to those with (1b), but gave less well defined <sup>1</sup>H n.m.r. spectra and analytical results.

Hydrolysis of phosphites by water in MeCN is a well known reaction.<sup>4</sup> However, under our experimental conditions neither hydrolysis nor Arbuzov rearrangement to  $MeP(O)(OMe)_2$  occurred over 24 h in the absence of (1a) or (1b).

The catalytic cycle we suggest for the hydrolysis reaction reported here is given in the Scheme. The final complex remaining after the  $P(OR)_3$  has given  $HP(O)(OR)_2$  [or  $RP(O)(OR)_2$ ] can be (1a) and (1b) and/or (3), depending on the concentrations of the various species.

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The Scheme suggests that the phosphorus in (2) is activated to nucleophilic attack by water. The less electrophilic complex  $[(C_6H_6)Mn(CO)_3]^+$  was found to be inactive as a catalyst, suggesting that only the most electrophilic ring systems will work. An alternative mechanism would be for (2) to activate  $P(OR)_{a}$  by allowing phosphite attack at the metal. Evidence against this pathway is provided by the observation that the phosphine adducts [(C,H,PBu3)- $(C_6H_6)M]^{2+}$  (M = Fe, Ru) do not function as phosphitehydrolysis catalysts.

The stopped-flow method was used to measure the rate of reaction (1) with P(OBu<sup>n</sup>)<sub>3</sub>. At 25 °C in MeCN the rate constants are  $k_1(M^{-1}S^{-1})$  1530 (Fe), 69 (Ru), and 24 (Os) and  $k_{-1}(s^{-1}) 0.09$  (Ru) and 0.06 (Os). These results illustrate the strong metal dependence of the electrophilicity as previously observed<sup>1</sup> for phosphine addition to these complexes.

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<sup>4</sup>G. Aksnes and D. Aksnes, Acta Chem. Scand., 1964, 18, 38, 1623.