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Preliminary communication

A NEW REACTION OF FLUORINATED PHOSPHITES: THE PREPARATION OF η^5-CYCLOPENTADIENYLBIS[TRIS(2,2,2-TRIFLUOROETHYL)PHOSPHITO] IODOIRON(II)*

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Summary

The partially fluorinated phosphite, $P(OCH_2CF_3)_3$, has been found to replace carbon monoxide from certain metallocarbonyls and their derivatives under gentle reaction conditions with illumination. The preparation of the title compound is described as an example for this new usage for fluorinated phosphites.

The Lewis basicity of phosphines and phosphites has long been recognized and utilized in the development of a rich chemistry that follows from their interactions with transition metal and organometallic compounds. In comparison to the vast chemistry of $P(OCH_3)_3$ and $P(OC_2H_5)$, there has been minimal exploration of the chemistry of the partially fluorinated phosphite, $P(OCH_2CF_3)_3$, since its preparation [1].

Recent work in this laboratory on the preparation of $P[OC(CF_3)_3]_3$ [2], has focused our attention on the general chemistry of this class of compounds, including both the fully and partially fluorinated phosphites.

We find that when η^5-$C_5H_5Fe(CO)_2I$ and $P(OCH_2CF_3)_3$ react at 25°C in CH_2Cl_2 under illumination, a red solution is formed whether the initial stoichiometry is 1/2 or 1/3. The intensely deep red compound isolated corresponds to η^5-$(C_5H_5)Fe[P(OCH_2CF_3)_3]_2I$. M.p. 68—70°C (corrected); Calcd. C,

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*Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983. Both JMS and SMW had the privilege and pleasure of studying and working with Professor Emeléus while on sabbatical research leaves from their home universities, during the academic years 1967—68 and 1968—69, respectively.

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22.6; H, 1.88. $C_{17}H_{17}FeIO_6P_2$ found: C, 21.97; H, 1.82%. A molecular ion was observed in the mass spectrum. UV-VIS maxima observed at 535(w), 432(m), 365(sh) and 306(s) nm. The ^{31}P NMR spectrum shows a sharp resonance at +183.7 ppm (downfield) from 85% H_3PO_4. The resonance for the uncomplexed phosphite is +139.2 ppm. For the reaction, typically 2 h of illumination are required per millimole of starting material, using a quartz vessel and a Hanovia low pressure Hg lamp. The evolved carbon monoxide was measured in a gas buret. Within experimental error the gas to iron ratio was two. Care was taken to carry out all operations under dry N_2 or in a vacuum system where appropriate; however neither the phosphite nor the product seem unusually sensitive to oxygen or to the atmospheric humidity of Moscow, Idaho.

A solution of the compound in CH_2Cl_2 does not tarnish mercury, which attests to the non-lability of the iodine atom in the new coordination situation; however, treatment of the compound, dissolved in CH_3OH at 25° C, with KSCN gives a very intense red solution with new UV-VIS maxima at 515(m) and 297(s) nm which shows an upfield ^{31}P NMR shift of 1 ppm. The properties of this thiocyanato derivative are being investigated.

Reactions of this phosphite and the totally fluorinated tertiary butyl analogue with the Group VI and VII metal carbonyls are underway, and show that a variety of substitutions will be possible. When $Mn(CO)_5Br$ (1 mmol) was illuminated for 4.5 h with 2 mmol of $P(OCH_2CF_3)_3$, 2 mmol of CO evolved and the clear orange colored solution gave two new broad ^{31}P NMR resonances at +165 and +172 ppm (downfield from 85% H_3PO_4). Upon standing at room temperature for a day, another mmol of CO was evolved. Sublimation of the product mixture was attempted and there were clearly 2 compounds present, one solid and one liquid at room temperature.

When $Cr(CO)_6$ (2.4 mmole) was illuminated for 2.75 h with 2.4 mmol of $P(OCH_2CF_3)_3$, 2.6 mmol of CO were evolved and the clear lime-colored solution gave two new ^{31}P resonances at +183.9 and +190.8 ppm (downfield from 85% H_3PO_4) which were rather sharp but with structure. Even though roughly equivalent amounts of CO to phosphite were evolved some unreacted $Cr(CO)_6$ was recovered, which indicates that the substitution of CO may not be orderly. A similar pattern was observed in the thermal reaction up to 60° C in CH_2Cl_2 between equimolar amounts of $Cr(CO)_6$ and $P[OC(CF_3)_3]_3$, carbon monoxide being evolved and some $Cr(CO)_6$ recovered. The higher molecular weight product has not been successfully sublimed. It seems obvious that where several sites for substitution exist, the reaction will be complex.

We are interested in the differences in the chemistry and properties of organometallic derivatives with fluorinated phosphites in comparison with those containing the commonly used $P(OCH_3)_3$ and $P(OC_2H_5)_3$. Electronegativity and steric factors will obviously contribute. One major difference has already been seen. Towle [3] and co-workers have shown that a facile double Michaelis—Arbuzov rearrangement occurs with η^5-$C_5H_5CoI_2CO$ and $P(OCH_3)_3$ or $P(OC_2H_5)_3$ in CH_2Cl_2; the reaction occurring quickly and completely through substitution and rearrangement at 25° C without illumination. In contrast with our iron analogue, in reaction with the partially fluorinated phosphite, we did not observe any rearranged material under the conditions we used.

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