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Preliminary communication

NUCLEOPHILIC ADDITIONS OF PHOSPHINES TO A π-CYCLOBUTADIENE LIGAND

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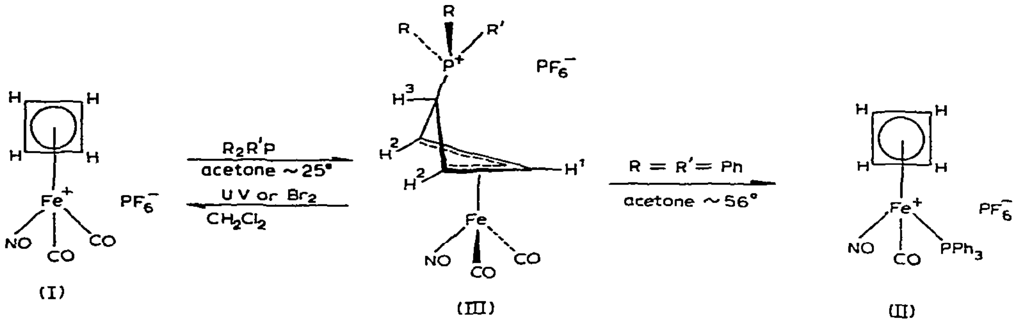
Summary

Nucleophilic addition of phosphines to the cyclobutadiene ring in $[(h^4\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$ leads to the formation of (*exo*-phosphonium-h^3-cyclobutenyl)dicarbonylnitrosyliron hexafluorophosphate.

Recently, we reported [1] the preparation of $[(h^4\text{-}C_4H_4)Fe(CO)_2NO]^+$-$PF_6^-$ (I) and several monocarbonyl substitution products $[(h^4\text{-}C_4H_4)Fe(CO)$-$(NO)L]^+PF_6^-$ (II) obtained from (I) by reaction with Lewis bases (L) such as $(C_6H_5)_3P$, $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$. In this communication, we describe some unusual reactions involving nucleophilic addition of tertiary phosphines to the $h^4\text{-}C_4H_4$ ring in (I).

The complex (I) reacts spontaneously with R_2R^1P ($R = R^1 = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5; $R = CH_3$, $R^1 = C_6H_5$; $R = C_6H_5$, $R^1 = CH_3$) in acetone at 22°C to give orange-red crystalline products of empirical formula $R_2R^1C_6H_4O_3NP_2F_6Fe$. Selected spectroscopic and analytical data for the $(C_6H_5)_3P$ derivative, obtained in quantitative yield, include: m.p. 118—119°C (Found: C, 47.72; H, 2.94; F, 19.30; Fe, 9.34; N, 2.54; P, 9.87; mol.wt. (osmometric in acetone), 433. $C_{24}H_{19}F_6FeNO_3P_2$ calcd.: C, 47.90; H, 3.08; F, 18.90; Fe, 9.34; N, 2.33; P, 10.32%; mol.wt., 601.) Infrared (CH_2Cl_2), ν(CO), 2070 and 2025; ν(NO), 1774; ν(PF), 840 cm^{-1} (in KBr); PMR (CD_2Cl_2), τ(ppm): 2.13(m, 15H); 4.84(t, 1H, J 4Hz); 4.96(s, 2H); 5.51(d of d, 1H, J 4Hz, J^1 14Hz); ^{31}P NMR(acetone), δ(ppm relative to H_3PO_4): —16[s, 1P, width at 1/2 height~2ppm]; +143[t, 1P, J(P—F) 668Hz]; Mössbauer(~80 K): *IS*, 0.0967 ± 0.001 (with respect to NBS SRM metallic iron spectrum at ~25°C); *QS*, 1.057 ± 0.006; line width (uncorrected for thickness broadening) 0.3155 ± 0.005 mm/sec; conductance (CH_3NO_2), Λ_∞, 95 ohm^{-1}; slope$[(\Lambda_\infty - \Lambda)/\sqrt{c}]$,



(I) (III) (II)

240. Spectroscopic and physical properties* of the other new iron complexes are closely related or identical to those of the $(C_6H_5)_3P$ derivative. For example, infrared carbonyl and nitrosyl stretching frequencies are identical within ± 1.0 cm^{-1} while the PMR(olefinic region) and ^{31}P NMR spectra show the same resonance patterns with virtually identical coupling constants (±0.5 Hz). These similarities are presented as evidence that the complexes are structurally related.

The crystal structure of the $(CH_3)_3P$ derivative, determined by single-crystal X-ray diffraction methods [2], revealed an *exo*-trimethylphosphonium-h^3-cyclobutenyl ligand bonded to $Fe(CO)_2(NO)$ [III; $R = R^1 = CH_3$]. In view of the near equivalence of their spectroscopic properties, the structure (*exo*-phosphonium-h^3-cyclobutenyl) dicarbonylnitrosyliron hexafluorophosphate (III) is believed to be general for all of the new iron complexes reported here.

The PMR spectra of (III) in the olefinic region are consistent with the following assigments: triplet (1H), singlet (2H) and doublet of doublets (1H) for H^1, H^2 and H^3 respectively. Here, we have assumed that $J = J(H^3—H^1) = J(P—H^1) = 4$Hz and $J^1 = J(P—H^3) = 14$Hz. The H^2 degeneracy would require the presence of a symmetry plane for the cations in solution. While the absence of $H^1—H^1$ vicinal coupling in cyclobutenyl rings has been noted in previous investigations [3,4], long range $H^1—H^3$ and $H^1—P$ couplings have not been observed previously in a cyclobutenyl system. The ^{31}P NMR spectra of (III) consist of a singlet (1P) and a triplet[1P, $J(P—F)$668Hz] assigned to the P(phosphonium) and P(phosphate) atoms respectively; absence of the expected doublet and heptet is attributed to resolution and solubility limitations. While the P(phosphate) chemical shift for the different derivatives (III) remains virtually unchanged(±0.5ppm), that due to P(phosphonium) depends critically upon the substituents present. In general, the P(phosphonium) chemical shift is 22—87ppm downfield from that of the respective free tertiary phosphine used in the preparation of (III).

Mössbauer data are consistent with the presence of one unique iron atom in (III) and the results of conductometric and molecular weight measurements are in accord with an ionic formulation. Carbonyl and nitrosyl stretching frequencies in (III) are lower than the corresponding frequencies in (I)

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*Satisfactory elemental analyses were obtained for all the new complexes reported in this communication.

[1] suggesting an enhancement of $d_\pi(Fe) \rightarrow p_\pi^\star(CO, NO)$ back bonding interactions in the former compounds.

Nucleophilic addition of phosphines to acyclic [5,6] or cyclic π-ligands is rare. The above results demonstrate the ease with which such addition of phosphines to the h^4-C_4H_4 ring in (I) occurs. Attempts to effect similar reactions with $(C_6H_5)_3As$, $(C_6H_5)_3Sb$ and $(RO)_3P$, R = C_6H_5, C_2H_5 were unsuccessful, possibly because of the lower relative nucleophilicity of these reagents. Cleavage of the P(phosphonium)—C(cyclobutenyl) bond in (III) (R = R^1 = C_6H_5) may be induced thermally, photolytically or chemically. For example, in boiling acetone, (III, R = R^1 = C_6H_5) converts to (II, L = $(C_6H_5)_3P$) in about 50% yield, while photolysis or attempted bromination of (III, R = R^1 = C_6H_5) in CH_2Cl_2 leads to low yield regeneration of (I). Further studies of the reactions between (I), (II) and various nucleophiles are in progress.

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