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THE REACTION BETWEEN ORGANOSILYL DERIVATIVES OF $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ AND TRIPHENYL PHOSPHITE. NEW EVIDENCE FOR *ortho*-METALATED PHOSPHITE LIGANDS

GENEVIEVE CERVEAU, ERNESTO COLOMER and ROBERT CORRIU *

Laboratoire des Organométalliques, Equipe de Recherche associée au C.N.R.S. No. 554, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier-Cédex (France)

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Summary

UV irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiR}_3$ in the presence of triphenyl phosphite gives the *ortho*-metalation product $(\eta^5\text{-C}_5\text{H}_5)\overline{\text{Fe-}o\text{-C}_6\text{H}_4\text{OP}(\text{OC}_6\text{H}_5)_2\text{-[P}(\text{OC}_6\text{H}_5)_3]}$ with elimination of R_3SiH . Triethyl phosphite leads with substitution of one carbonyl group to $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(\text{OC}_2\text{H}_5)_3]\text{SiR}_3$. The optically active $R(+)-(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)(1\text{-C}_{10}\text{H}_7)$ yields $(-)\text{-CH}_3\text{C}_6\text{H}_5\text{-}(1\text{-C}_{10}\text{H}_7)\text{SiH}$ with complete retention of configuration. Mechanisms are suggested for these reactions.

Introduction

Studies on silicon—transition metal compounds carried out in our laboratory [1,2] led us to prepare complexes of the type $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})\text{SiR}_3$ in which L is a phosphorus ligand and R an alkyl or aryl radical. There is a good method of synthesis involving replacement of a carbonyl ligand in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiR}_3$ by a phosphine under UV irradiation [3], and we used this to prepare a number of these complexes [4]. Although the replacement of a carbonyl by triphenyl phosphite was also described for $\text{R} = \text{CH}_3$ [3], we could not obtain the expected compound for $\text{R}_3 = (\text{C}_6\text{H}_5)_2\text{CH}_3$, $(\text{C}_6\text{H}_5)_3$ or $(\text{CH}_3)(\text{C}_6\text{H}_5)(1\text{-C}_{10}\text{H}_7)$; the reaction proceeded very differently, as described below.

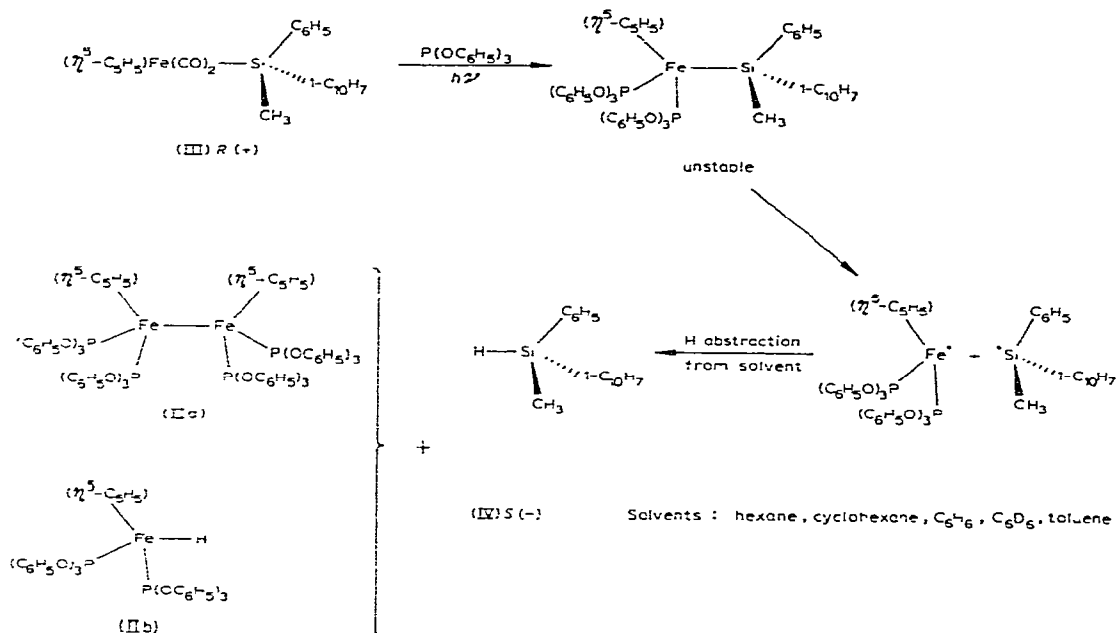
Results and discussion

UV irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiR}_3$ (Ia, $\text{R}_3 = \text{Ph}_2\text{Me}$; Ib, $\text{R}_3 = \text{Ph}_3$) with triphenyl phosphite in hexane or cyclohexane led to formation of the corresponding silane and a yellow crystalline material II. Similarly, $R(+)-(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)(1\text{-C}_{10}\text{H}_7)$ (III) yielded II and $S(-)\text{-CH}_3(\text{C}_6\text{H}_5)(1\text{-C}_{10}\text{H}_7)\text{-}$

SiH (IV) [5] with 95% retention of configuration. III was recently synthesized and its configuration established by chemical correlation [4]. The percentage of stereoselectivity was calculated as defined in ref. 6.

The results could be accounted for as in Scheme 1 in terms of a homolytic

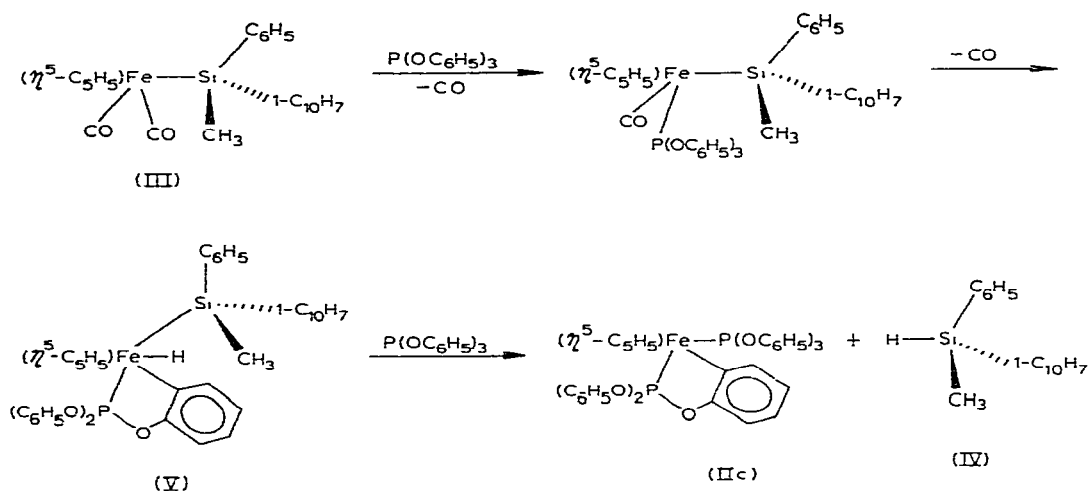
SCHEME 1



fission of the Fe—Si bond after substitution of both carbonyl ligands by triphenyl phosphite. The iron radical would dimerize into IIa, or abstract one hydrogen from the solvent giving IIb. The silyl radical would abstract another hydrogen atom giving the silane IV. This reaction would take place with retention of configuration, since it is known that silyl radicals, generated in several ways, are optically stable [7]. A radical mechanism was invoked by Nesmeyanov and coworkers [8] for the decomposition of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$ by irradiation in the presence of $\text{P}(\text{OC}_6\text{H}_5)_3$. Structure a was assigned to II on the basis of NMR and mass spectra, elemental analysis and molecular weight measurements.

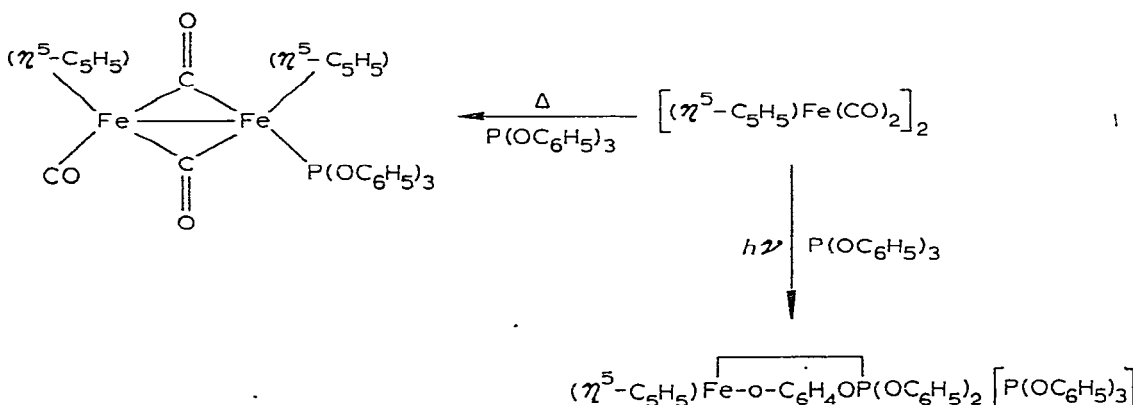
However, such a pathway is inconsistent with several experimental features. First of all, accurate measurement of the largest value m/e peak of the mass spectrum of II afforded a value of 740 (theoretical mass for IIb 742, lit. [8] for IIa 741). This observation is in excellent agreement with the results of Stewart et al. [9], who reformulated complex IIa as having the structure c (Scheme 2). UV irradiation of I or III with triphenyl phosphite in benzene, which is a poor hydrogen donor in radical reactions, led again to II and to hydrosilane; no formation of disilane was observed. When benzene- d_6 was used as solvent only hydrosilane, free of deuteriosilane, was formed. This showed unambiguously that the reaction did not follow a radical pathway since no deuterium was incorporated in the silane, and this was confirmed by the failure

SCHEME 2



to trap the silicon radical with alkenes or alkynes in various solvents (Table 1). When toluene was used as solvent no 1,2-diphenylethane was found, as would have been expected for a radical abstraction of hydrogen. In view of these results, including the appearance of the molecular ion peak at 740, we can conclude that II has the structure c.

Compound II was also obtained in moderate yield (63%) by UV irradiation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ with triphenyl phosphite in hexane. It is interesting to underline that only one carbonyl was replaced by thermal reaction between the dimer and the phosphite without cleavage of the iron-iron bond affording $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ [10].



We thus suggest the reaction pathway shown in Scheme 2. This involves elimination of one carbonyl ligand under UV light, replacement by phosphite, and a further elimination of carbon monoxide. Then, instead of association with another phosphite, the 16-electron complex would undergo insertion of the iron atom into an *ortho* aromatic C-H bond. Reductive elimination of hydrosilane would then lead to a new 16-electron complex which would combine with a molecule of phosphite to give compound IIc.

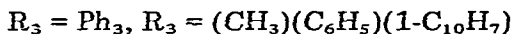
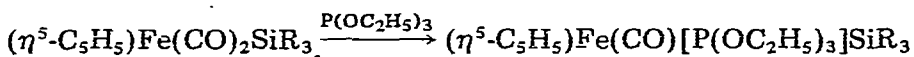
TABLE 1
UV IRRADIATION OF $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiR}_3$ UNDER VARIOUS CONDITIONS

R_3	Solvent	Reactant	Product ^a	Yield (%)
Ph_2Me	C_6H_6	—	Ph_2MeSiH	60
Ph_2Me	CH_3CN	—	$(\text{Ph}_2\text{MeSi})_2\text{O}$	12
Ph_2Me	Hexane	Cyclohexene	$(\text{Ph}_2\text{MeSi})_2\text{O}$ + Ph_2MeSiH	80 10
Ph_2Me	CH_3CN	Cyclohexene	$(\text{Ph}_2\text{MeSi})_2\text{O}$	60
Ph_2Me	Hexane	$\text{PhC}\equiv\text{CH}$	$(\text{Ph}_2\text{MeSi})_2\text{O}$	70
Ph_3	Benzene	$\text{PhC}\equiv\text{CH}$	$(\text{Ph}_3\text{Si})_2\text{O}$	56
Ph_3	Benzene		Ph_3SiH	67
Ph_3	Hexane		Ph_3SiH	96
Ph_3	C_6D_6		Ph_3SiH	69
Ph_3	Toluene		Ph_3SiH	74

^a Yields varying from 20 to 70% of II were obtained in all cases.

This mechanism takes account of the experimental observations, and the stereochemistry at silicon is easily explained. Indeed, reductive elimination of hydrosilanes is known to take place with retention of configuration [11]. The intermediate V may be compared to $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{H})\text{SiR}_3$ in which the hydrogen atom has a bonding interaction with the silicon atom [12]. In this case triphenylphosphite readily displaced R_3SiH with almost complete retention of configuration [13]. *ortho*-Metalation of metal triphenyl phosphite was previously reported for second and third row transition metals [14].

In agreement with these results, UV irradiation of III with triethyl phosphite led to the replacement of only one carbonyl ligand without cleavage of the iron—silicon bond [4]. In this case, *ortho*-metalation was obviously impossible and the reaction followed its "normal" course.



Failure to prepare $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(\text{OC}_6\text{H}_5)_3]\text{SiR}_3$ by direct replacement of carbonyl by $\text{P}(\text{OC}_6\text{H}_5)_3$, led us to an attempt at an alternative synthesis as previously described for analogous iron—carbon compounds [9,15]. However, treatment of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{SiR}_3$ with $\text{P}(\text{OC}_6\text{H}_5)_3$ in refluxing benzene led to decomposition.

Experimental

All experiments were carried out under nitrogen, using a vacuum line, in Schlenk tubes. Photochemical reactions were performed in a Pyrex reaction vessel with a 125W Hanovia medium pressure mercury lamp. Solvents were dry, distilled and deoxygenated. Iron—silicon compounds were prepared by published methods [4].

Melting points of iron compounds were taken under vacuum in a Dr. Tottoli's apparatus and were uncorrected. IR spectra were recorded in a Perkin—Elmer 257 spectrophotometer and NMR spectra in a Varian A60 spectrograph. Optical rotations were measured in a Perkin—Elmer 141 polarimeter.

UV irradiation of (η^5 -cyclopentadienyl)(dicarbonyl)(diphenylmethylsilyl)iron (Ia) with triphenyl phosphite

A solution of Ia (2.5 mmol) and 1550 mg of $P(OC_6H_5)_3$ (5 mmol) in 40 ml of cyclohexane was irradiated for 8 h, at 20–30°C. After this time the solvent was pumped off and the residue dissolved in CH_2Cl_2 and chromatographed on acid alumina. Hexane eluted 297 mg of diphenylmethylsilane (yield 60%) (identical with an authentic sample [16]); hexane/ CH_2Cl_2 50/50 eluted 740 mg of II (yield 40%), yellow crystals, recrystallized from ether/hexane m.p. 124–125°C with decomposition.

1H NMR spectrum in $CDCl_3$: 2.94 (aromatic H, multiplet) and 5.88 (C_5H_5 , triplet $J(PH) \sim 1.5$ Hz) with relative intensities 6/1. Mass spectrum (m/e assignment): 740 ($\eta^5-C_5H_5$) $FeC_6H_4OP(OC_6H_5)_2P(OC_6H_5)_3^+$, 430 ($\eta^5-C_5H_5$) $FeC_6H_4OP(OC_6H_5)_2^+$, 310 $P(OC_6H_5)_3^+$, 217 $P(OC_6H_5)_2^+$. Anal. Found C, 66.66; H, 4.89; P, 8.59. $C_{41}H_{34}O_6P_2Fe$ calcd.: C, 66.48; H, 4.59; P, 8.38%.

UV irradiation of R(+)-(η^5 -cyclopentadienyl)dicarbonyl(methylphenyl-1-naphthylsilyl)iron (III) with triphenyl phosphite

A solution of 950 mg of III, $[\alpha]_D^{25} + 28^\circ$ (2.25 mmol) and 1.4 g of $P(OC_6H_5)_3$ (4.5 mmol) were irradiated for 6 h. Work-up as above yielded S(–)-methylphenyl 1-naphthylsilane, 396 mg (71%), $[\alpha]_D^{25} - 20.5^\circ$ and II 999 mg (60%).

From the maximum rotations of III ($[\alpha]_D^{25} + 41^\circ$) and of the silane ($[\alpha]_D^{25} - 34^\circ$), the stereochemistry can be shown to be 94% retention of configuration.

Other irradiations of iron–silicon compounds

($\eta^5-C_5H_5$) $Fe(CO)_2SiPh_2Me$ (Ia) and ($\eta^5-C_5H_5$) $Fe(CO)_2SiPh_3$ (Ib) were irradiated in various solvents (Table 1). The molar ratios added reactant/Fe–Si compound varied from 1 to 10.

UV irradiation of (η^5 -cyclopentadienyl)dicarbonyliron dimer

A solution of 708 mg of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ (2 mmol) and 2.48 g of $P(OC_6H_5)_3$ (8 mmol) in 300 ml of hexane was irradiated for 15 h. The usual work-up afforded 1.86 g of II m.p. 124°C (yield 63%).

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