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CYCLOMETALATION OF PHOSPHORUS LIGANDS BY UV IRRADIATION OF COMPLEXES HAVING TRANSITION METAL—SILICON BONDS

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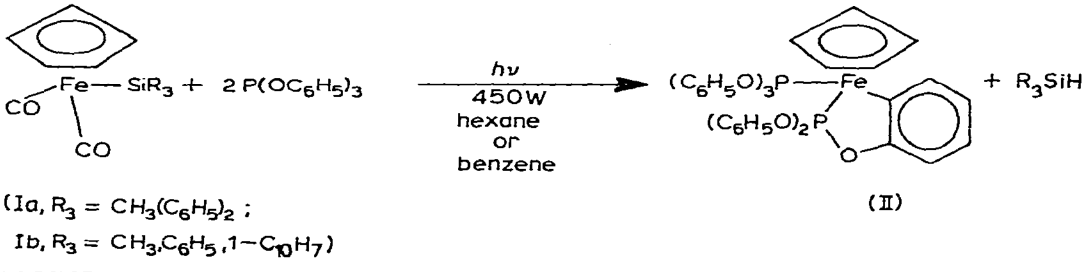
Summary

UV irradiation of complexes of the type $(\eta^5\text{-}C_5H_5)(CO)_nMSiR_3$ (n = 2, M = Fe; n = 3, M = Mo) in the presence of phosphorus ligands such as $P(XC_6H_5)_3$ (X = O, S, CH_2) and phosphines containing allyl, 1-naphthyl or tolyl groups gives cyclometalated complexes, R_3SiH being eliminated with retention of configuration at Si. In the cyclometalation five-membered rings are formed in preference to six-membered rings, and metalation occurs more easily at sp^2 than at sp^3 carbon atoms. Methylphenyl-1-naphthylphosphine undergoes rapid racemization upon UV irradiation at room temperature.

Introduction

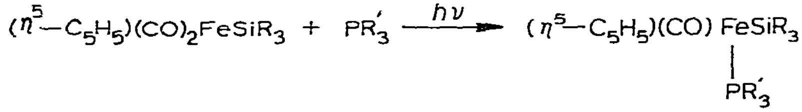
UV irradiation of $(\eta^5\text{-}C_5H_5)(CO)_2FeSiR_3$ complexes carried out in the presence of triphenyl phosphite is shown to give orthometalated complexes with cleavage of the iron—silicon bond and formation of silane (Scheme 1) [1].



SCHEME 1

In the case of the optically active Ib, the reaction occurred with complete retention of configuration (RN). No deuterated silane R_3SiD was obtained when benzene-d_6 was used as solvent; showing that the hydrogen atom came from the ligand and not the solvent.

In contrast triethyl phosphite, or triphenylphosphine, replaced one carbonyl ligand without cleavage of the iron—silicon bond [2] (Scheme 2).



$$(\eta^5\text{—}C_5H_5)(CO)_2FeSiR_3 + PR'_3 \xrightarrow{h\nu} (\eta^5\text{—}C_5H_5)(CO)Fe(SiR_3)(PR'_3)$$

$(R_3 = (C_6H_5)_3\ ; CH_3(C_6H_5)_2\ ;\ CH_3, C_6H_5, 1\text{-}C_{10}H_7$

$R' = C_6H_5, OC_2H_5)$

SCHEME 2

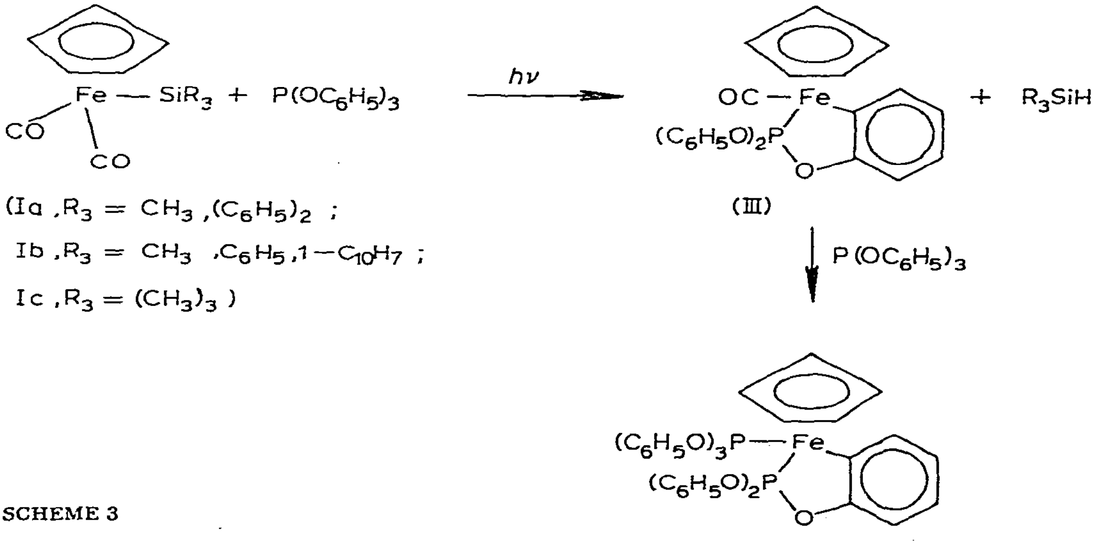
Although cyclometalation reactions are well known for 2nd and 3rd row transition metals [3—5], they are not usual for 1st row elements, and thus it was of interest to see to what extent they occurred with complexes of other transition metals [6].

Results and discussion

Since in some cases the cyclometalated complex could not be isolated, the criterion used to determine whether cyclometalation takes place or not is the quantitative formation of the silicon hydride R_3SiH with complete retention of configuration.

(i) *Ortho-metalation of triphenylphosphite with iron*

We reinvestigated the reaction described in Scheme 1 since disubstituted II and monosubstituted III complexes (Scheme 3) were previously obtained by photochemical cleavage of the iron—carbon bond [6]. Complexes Ia and Ib gave only II on irradiation with the 450 W lamp. However, with the 125 W lamp (see Experimental) a mixture of both II and III was obtained.



$(Ia, R_3 = CH_3, (C_6H_5)_2\ ;$

$Ib, R_3 = CH_3, C_6H_5, 1\text{-}C_{10}H_7\ ;$

$Ic, R_3 = (CH_3)_3\ )$

(III)

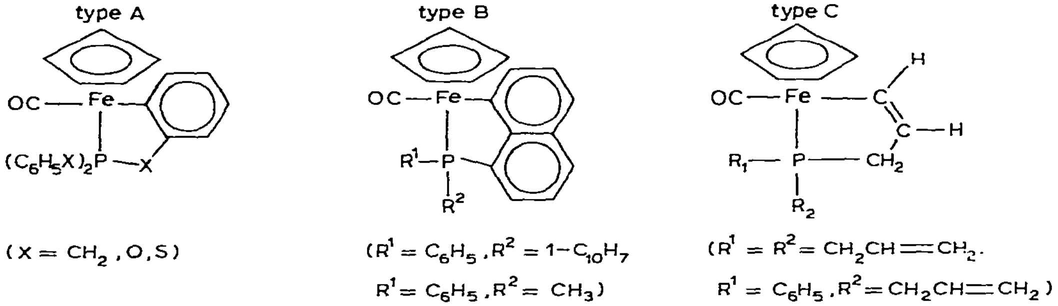
(II)

SCHEME 3

Furthermore complex Ic can also undergo cyclometalation and not only the carbon monoxide replacement which was previously described [7]. In this case irradiation with the 450 W lamp is necessary to give the same mixture of II and III.

(ii) Metalation of sp^2 carbon atoms

Cyclometalation of iron complexes also occurs easily (125 W lamp) with the corresponding ligands such as tribenzylphosphine or triphenyl trithiophosphite in which the O has been replaced by CH_2 or S. The silane is again formed quantitatively, but the complexes (type A) are too unstable to be isolated (Scheme 4).

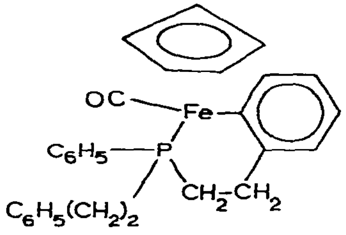


SCHEME 4

We isolated complexes of type B using phenyl-di-1-naphthyl- and methylphenyl-1-naphthyl-phosphines. Complexes metalated in the *peri* position were previously observed with iridium and rhodium [4].

In order to examine the possibility of cyclometalation with non aromatic sp^2 carbon atoms, we have investigated the behaviour of allylphosphines. Thus triallyl- and phenyldiallyl-phosphines readily give the silane (in 80 and 85% yield, respectively, from Ia). The corresponding cyclometalated complexes (type C) cannot be isolated. Surprisingly, methylphenylallylphosphine does not cleave the Fe—Si bond, but gives the monosubstituted complex (ν(CO) 1900 cm^{-1}); no silane is formed.

Metalation of ligands such as tribenzyl phosphite or phenyldiphenethylphosphine does not take place under these conditions. However, under more powerful irradiation (450 W lamp) the latter reacts and silane is formed in good yield (75%) from Ia. Complex IV has not been isolated.

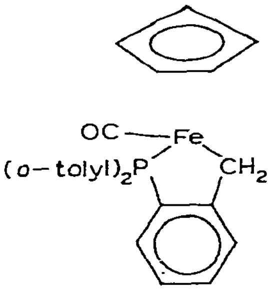


(IV)

These results show that five-membered rings are formed more easily than six-membered rings, as previously noted [8].

(iii) Metalation of sp^3 carbon atoms

Metalation of sp^3 carbon atoms occurs generally with sterically hindered phosphines [9,10]. Tri(*ortho*-tolyl)phosphine does not react with Ia when irradiation is carried out with the 125 W lamp, but a good yield of silane (82%) is isolated when the 450 W lamp is used. Again complex V cannot be isolated.

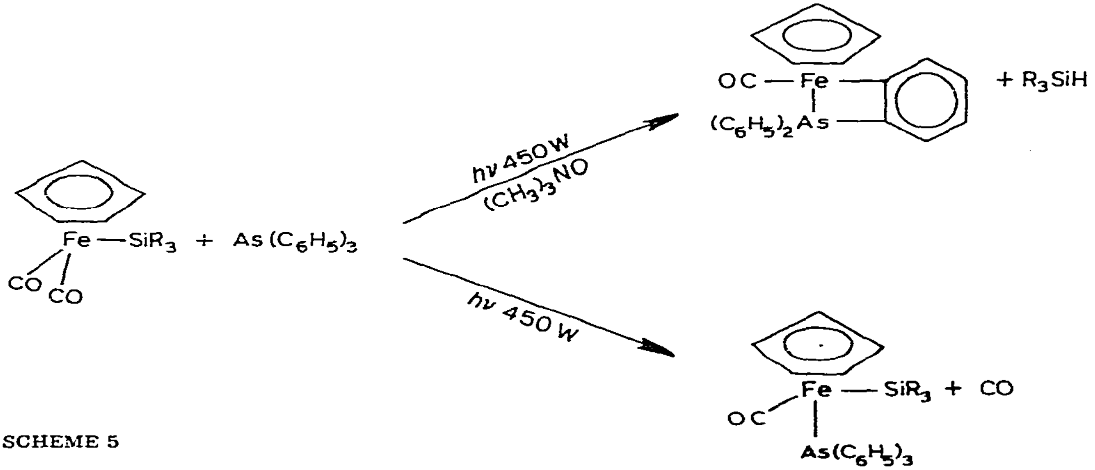


V

Metalation of sp^3 appears to be more difficult than that of sp^2 carbon atoms

(iv) Effect of trimethylamine oxide on the reactions

It is well known that trimethylamine oxide accelerates carbonyl replacement by phosphines under thermal activation [11,12], and so we examined the corresponding photochemical reaction. The presence of a stoichiometric amount of $(CH_3)_3NO$ did indeed cause a moderate acceleration of these cyclometalations metalation of tribenzylphosphine with Ic normally requires five hours with the 450 W lamp, but in the presence of $(CH_3)_3NO$ the reaction is complete in less than one hour. The presence of the amine oxide favours metalation of triphenylarsine with formation of a four-membered ring, rather than the substitution product normally obtained (Scheme 5).

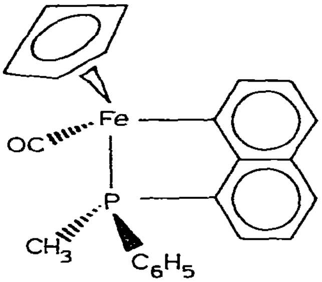


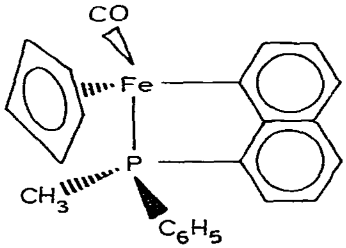
SCHEME 5

Once again the orthometalated complex is too unstable to be isolated, but the silane is formed in good yield.

(v) Metalation of methylphenyl-1-naphthylphosphine

The metalation of this phosphine leads to a mixture of diastereoisomers since both iron and phosphorus atoms are chiral:





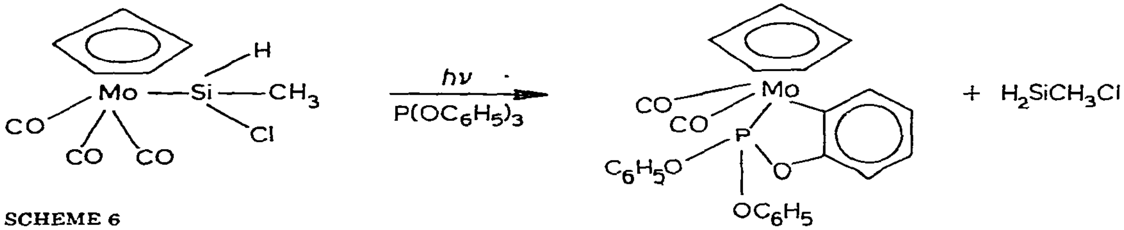
The two complexes are easily distinguished by ^{1}H (δ 5.26 and 5.53 ppm, C_5H_5; 7.89 and 7.93 ppm, CH_3) and ^{31}P NMR spectroscopies (δ —81.3 and —79.7 ppm). We have succeeded in isolating one of the diastereoisomers. It would be of interest to isolate the corresponding optically active complex, and so we synthesized the optically active phosphine [13,14] but, unfortunately, it racemizes under the UV irradiation in the time needed for cyclometalation, affording a mixture of racemic diastereoisomers. The photochemical racemization of the phosphine was examined separately and found to take place in 10 min.

Although the substitution is faster in the presence of $(CH_3)_3NO$ the product is still racemic.

The results are summarized in Table 1.

(vi) Metalation of triphenyl phosphite with molybdenum

The complex (η^5-C_5H_5)$(CO)_3MoSiHCH_3Cl$ [15] when treated with triphenyl phosphite gives the cyclometalated complex in moderate yield (Scheme 6),



SCHEME 6

though the volatile silane was not isolated. This result suggests the possibility of a general reaction for complexes with transition metal—silicon bonds of the type (η^5-C_5H_5)$(CO)_nMSiR_3$ (M = transition metal).

The following rules governing cyclometalation of phosphorus ligands in reactions with iron complexes can be formulated.

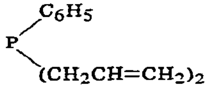
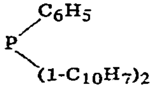
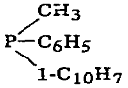
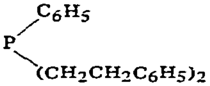
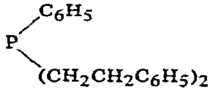
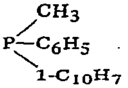
(a) five-membered rings are formed with more facility than four- or six-membered rings, as is usual [5].

(b) sp^2 carbon atoms, even when not in aromatic rings, are metalated more easily than sp^3 carbon atoms.

(c) $(CH_3)_3NO$ accelerates these reactions and facilitates the formation of less favoured ring sizes.

TABLE 1

REACTIONS OF COMPLEX Ia (Ib was used for stereochemical determinations)

Lamp (time)	Ligand	R_3SiH yield (%) [a]	Retention (%) [b]	Cyclometalated complex	$\delta(^{31}P)$ (ppm) (in $CDCl_3$)
125 W (8 h)	$P(OC_6H_5)_3$	80	94	ref. 5	—203.7
125 W (8 h)	$P(CH_2C_6H_5)_3$	85	90	not isolated	—96
125 W (8 h)	$P(SC_6H_5)_3$	75	87	not isolated	
125 W (8 h)	$P(CH_2CH=CH_2)_3$	80	87	not isolated	
125 W (8 h)	 $P(C_6H_5)(CH_2CH=CH_2)_2$	85		not isolated	—58
125 W (8 h)	 $P(C_6H_5)(1\text{-}C_{10}H_7)_2$	90		isolated	—90
125 W (8 h)	 $P(CH_3)(C_6H_5)(1\text{-}C_{10}H_7)$	90	88	isolated	—81.3 —79.7
125 W (8 h)	 $P(C_6H_5)(CH_2CH_2C_6H_5)_2$	0		no cyclo-metalation	—54 [c]
450 W (24 h)	 $P(C_6H_5)(CH_2CH_2C_6H_5)_2$	75		not isolated	—71
450 W (24 h)	$P(o\text{-}CH_3C_6H_4)_3$	82		not isolated	
450 W $(CH_3)_3NO$ (1 h)	$P(CH_2C_6H_5)_3$	[d]		not isolated	
450 W $(CH_3)_3NO$ (1 h)	 $P(CH_3)(C_6H_5)(1\text{-}C_{10}H_7)$	[d]		isolated	
450 W $(CH_3)_3NO$ (1 h)	$As(C_6H_5)_3$	85		not isolated	

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[a] Diphenylmethylsilane recovered from Ia after chromatography on acid alumina eluted with hexane.
[b] Calculated from the maximum rotation of Ib ($|\alpha|_D^{25}$ + 41°) and of the silane ($|\alpha|_D^{25}$ —36°) as in ref. 16.
[c] Chemical shift for the substituted complex. [d] From $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_3$; $(CH_3)_3SiH$ not isolated.

The fast racemization of the optically active phosphine by UV irradiation is noteworthy.

Experimental

The experiments were carried out under nitrogen using a vacuum line and Schlenk tubes. Photochemical reactions were performed with a 125 or 450 watt Hanovia mercury lamp in a Pyrex reaction vessel. Solvents were dried, distilled and deoxygenated. IR spectra were recorded on a Perkin—Elmer 257 spectrophotometer, ^1H NMR spectra on a Varian EM 360 spectrograph and ^{31}P NMR spectra on a Bruker FT WP 80 spectrospin (32.37 MHz) (δ is negative for chemical shifts downfield from H_3PO_4). Optical rotations were measured on a Perkin—Elmer 141 polarimeter. Melting points of complexes were taken under vacuum in a Dr. Tottoli's apparatus and are uncorrected.

The iron—silicon and molybdenum—silicon complexes were described previously [2,15]. The phosphines were prepared by standard procedures: tribenzylphosphine [17], tri-*o*-totylphosphine [18], trithiophosphites [19], tribenzylphosphite [20], triallylphosphine [21] and racemic methylphenyl-1-naphthylphosphine [4]. Phenyl-dialkenyl- or -diaryl-phosphines were obtained by condensation of an excess of the corresponding Grignard reagent with phenyldichlorophosphine at room temperature. After careful hydrolysis with ammonium chloride and removal of the solvent from the organic layer, the following phosphines were isolated as oils or solids. Their purities were checked by ^1H NMR: phenyldiphenethylphosphine b.p. 210°C/0.005 mmHg; phenyldihomoallyl-phosphine b.p. 145°C/0.1 mmHg [21]; phenyldiallylphosphine b.p. 130°C/0.1 mmHg [21]. phenyldi-1-naphthylphosphine m.p. 215°C.

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

A solution of Ia (935 mg, 2.5 mmol) and $P(OC_6H_5)_3$ (775 mg, 2.5 mmol) in 300 ml of hexane was irradiated with the 125 W lamp for 12 h at 20—30°C. The solvent was then pumped off and the residue was dissolved in CH_2Cl_2, and subjected to chromatography on acid alumina with hexane as eluant. The solvent was pumped off leaving a yellow solid. This solid was a mixture of II and III (66 and 33% respectively) as shown by ^1H NMR ($CDCl_3$) δ (TMS) 4.62 and 4.12 ppm. The mass spectrum showed both molecular peaks 458 and 740 (*m/e* assignment). The IR spectrum shows a ν(CO) absorption at 1940 cm^{-1} due to complex II.

UV irradiation of (η^5-cyclopentadienyl)(dicarbonyl)(trimethylsilyl)iron, Ic, with triphenyl phosphite

A solution of Ic (500 mg, 2 mmol) and triphenyl phosphite (620 mg, 2 mmol) in 200 ml of hexane were irradiated for 15 h with the 450 W lamp. Work-up as above yielded a mixture (62 and 38% respectively) of II and III. Their ratio was determined as before.

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

A solution of Ia (2.5 mmol) and 1.55 g of tribenzylphosphine (5 mmol) in 300 ml of hexane was irradiated with the 125 W lamp for 8 h at 20—30°C. The solvent was then pumped off, and a solution of the residue in CH_2Cl_2 was chromatographed on acid alumina with hexane as eluant. 400 mg of $(C_6H_5)_2$-CH_3SiH were obtained (yield 85%), and found to be identical to an authentic sample [22]. The brown orthometalated complex decomposed on the column.

The same procedure was used in all cases in which the cyclometalated complex could not be isolated (see Table 1 for conditions).

UV irradiation of Ia with phenyldi-1-naphthylphosphine

A solution of 1.1 g (3 mmol) of Ia and 1.1 g (3.1 mmol) of phosphine in 300 ml of benzene/hexane (1/1) was irradiated with the 125 W lamp for 8 h. After the usual work up, recrystallization gave 350 mg (CH_2Cl_2/hexane) of orange crystals, m.p. 218°C. ^1H NMR ($CDCl_3$) δ 8.10 (multiplet, 1 H, peri), 7.87 and 7.40 (multiplets, aromatics, 17 H) and 4.67 ppm (doublet J(P—H) 1.5 Hz, C_5H_5, 5 H) relative to TMS. ^{31}P NMR δ —90 ppm. ν(CO) 1920 cm^{-1} (CH_2Cl_2). Mass spectrum (*m/e* assignment) 510 (molecular peak) 482 (M — CO). Analysis. Found: C, 74.58; H, 4.87; P, 5.81. $C_{32}H_{23}FeOP$ calcd.: C, 74.51; H, 4.61; P, 6.07%.

UV irradiation of Ia with methylphenyl-1-naphthylphosphine

A solution of Ia (2.5 mmol) and 800 mg of phosphine in 300 ml of a mixture of hexane/benzene (1/1) was irradiated for 8 h. After the same work-up, 460 mg of silane (90% yield) and 860 mg (85% yield) of an orange oil were obtained. The latter was a 1/1 mixture of diastereoisomers as shown by ^1H and ^{31}P NMR spectra in $CDCl_3$: ^1H NMR δ 7.87—7.41 (aromatic multiplet, 11 H), 4.74 and 4.41 (J(P—H) 1.5 Hz C_5H_5 signals of the diastereoisomeric mixture, 5 H), 2.11 and 2.07 ppm (doublets, J(P—H) 5 Hz, CH_3 signals, 3 H), relative to TMS. ^{31}P NMR δ —79.7 and —81.3 ppm. By crystallization from toluene/hexane, the diastereoisomer δ 4.41 (C_5H_5) and 2.07 ppm ($P — CH_3$) was isolated. ^{31}P NMR δ —81.3 ppm. ν(CO) 1910 cm^{-1} (CH_2Cl_2). Mass spectrum (*m/e* assignment) 398 (molecular peak) 370 (M — CO). Analysis. Found: C, 69.34; H, 4.53; P, 7.82. $C_{23}H_{19}FeOP$ calcd.: C, 69.34; H, 4.77; P, 7.78%.

UV irradiation of R(+)-(η^5-cyclopentadienyl)(dicarbonyl)(methylphenyl-1-naphthylsilyl)iron (Ib) with methylphenyl-1-naphthylphosphine

140 mg of Ib (0.33 mmol) $[\alpha]_D^{25}$ +30° with 90 mg of phosphine in 50 ml of benzene were irradiated for 8 h. Work up as above yielded 72 mg of S(—)-methylphenyl-1-naphthylsilane (90%) $[\alpha]_D^{25}$ —18.9°. From the maximum rotation of Ib $[\alpha]_D^{25}$ +41° and of the silane $[\alpha]_D^{25}$—36°, the deduced stereochemistry is 88% of retention [16].

UV irradiation of (η^5-cyclopentadienyl)(dicarbonyl)(trimethylsilyl)iron (Ic) with methylphenyl-1-naphthylphosphine and trimethylamine oxide

A solution of 500 mg of Ic (2 mmol), 500 mg of phosphine (2 mmol) and 250 mg of trimethylamine oxide in 200 ml of benzene was irradiated for 1 h with the 450 W lamp. The solvent was pumped off and a solution of the residue in CH_2Cl_2 was chromatographed as usual. 700 mg of an orange oil (85% yield, mixture of diastereoisomers described above) was obtained.

Preparation of R(+)-methylphenyl-1-naphthylphosphine

4 g (10 mmol) of R(—)-menthyl-1-naphthylphenylphosphinate $[\alpha]_D^{25}$ —21.1° (hexane), m.p. 98°C (prepared by the method of [13] were added to 50 mmol

of methyllithium in ether at room temperature. After 30 min, the solution was slowly poured into 50 ml of aqueous 4 *N* HCl. The aqueous layer was twice washed with 20 ml of CH_2Cl_2. The organic layer was dried and concentrated. The oily residue was then eluted on silica gel with CH_2Cl_2; menthol was first eluted, and then 2 g of methylphenyl-1-naphthylphosphine oxide $[\alpha]_D^{25}$ −22° (methanol) m.p. 139°C. The *R*(—)-phosphine oxide was dissolved in 50 ml of benzene and treated with 1.7 ml of Si_2Cl_6 at 80°C for 30 min. The mixture was then cooled and hydrolyzed by cautious addition of 30% aqueous NaOH (20 ml). The organic layer was dried and concentrated, and the air-stable phosphine was eluted with benzene on a silica gel column. The solvent was removed and 1.8 g of *R*(+)-methylphenyl-1-naphthylphosphine $[\alpha]_D^{25}$ + 143° (benzene), m.p. 73° C were obtained

UV irradiation of (η^5-cyclopentadienyl)(tricarbonyl)(methylchlorohydridosilyl)-molybdenum with triphenylphosphite

750 mg (2.3 mmol) of the title compound were irradiated in 100 ml of hexane in the presence of 900 mg (2.9 mmol) of $P(OC_6H_5)_3$ (125 W lamp) for 10 h. Usual work-up and column chromatography on acid alumina (elution with CH_2Cl_2) gave 500 mg of orange crystals of $(\eta^5\text{-}C_5H_5)(CO)_2MoP(OC_6H_5)_2O\text{-}o\text{-}C_6H_4$, m.p. 105—107°C. ^1H NMR ($CDCl_3$) δ 7.1—7.5 (multiplet, aromatic, 14 H) and 4.80 ppm (singlet, C_5H_5, 5 H) relative to TMS. ν(CO) 2060w, 1980vs and 1905vs cm^{-1} ($CHCl_3$). Mass spectrum (*m/e* assignment) 526 (molecular peak) 498 (*M* — CO). Analysis. Found: C, 56.85; H, 3.94; P, 6.14. $C_{25}H_{19}MoO_5P$: calcd.: C, 57.03; H, 3.61; P, 5.89%.

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