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STUDIES ON SOME MONO-η^5-CYCLOPENTADIENYLIRON DERIVATIVES WITH CHELATE DIPHOSPHINE LIGANDS

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Summary

The reactions between $Fe(\eta^5\text{-}C_5H_5)(L—L)I$ (where $L—L = Ph_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2PMe_2$ or (—)-DIOP) and $TlBF_4$ or $TlPF_6$ in presence of olefins are described. Evidence is presented that the diphosphine ligands give rise to steric restrictions against coordination of olefins to the metal center.

Rosenblum recently described some interesting reactions between iron—olefin and iron—σ-allyl derivatives, e.g. $\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\text{olefin}\}^+$ and $\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\text{-}\eta^1\text{-}C_3H_5\}$, which led to carbon—carbon bond formation [1,2]. Some chemistry of the diphosphine complexes $\{Fe(\eta^5\text{-}C_5H_5)(L—L)X\}$, where $L—L = Ph_2PCH_2CH_2PPh_2$ or $Me_2PCH_2CH_2PMe_2$, has been reported [3—6]. We were interested to see if it would be possible to use the synthetic methods of Rosenblum with complexes of the type $\{Fe(\eta^5\text{-}C_5H_5)(L—L)X\}$, where L—L was a chiral diphosphine such as (—)-DIOP ***. It was an objective to achieve asymmetric induction in the formation of a carbon—carbon bond. In order to gain further experience of the chemistry of the $\{Fe(\eta^5\text{-}C_5H_5)(L—L)X\}$ systems and since (—)-DIOP is expensive the initial studies were carried out using the more available ligands $P—P = Ph_2PCH_2CH_2PPh_2$ and $P'—P' = Me_2PCH_2CH_2PMe_2$ as model ligands.

Results and discussion

The iodide derivatives $\{Fe(\eta^5\text{-}C_5H_5)(P—P)I\}$ (I) and $\{Fe(\eta^5\text{-}C_5H_5)(P'—P')I\}$ (II) have been previously described [3,6]. However since experimental details for the synthesis of II are not given, we give our procedure here. In fact, we

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*** (—)-DIOP = (—)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [7].

found that treatment of the bisphosphite $\{Fe(\eta^5\text{-}C_5H_5)(P(OPh)_3)_2I\}$ with P′—P′ gave both II and the compound $\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')P(OPh)_3]^+I^-\}$ (III). The latter, after treatment with aqueous NH_4BF_4 leads to $\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')P(OPh)_3]^+BF_4^-\}$ (IV). It was found that irradiation of III in the presence of potassium iodide and an excess of P′—P′ in acetone gave conversion of III to II.

We have also prepared the new compound $\{Fe(\eta^5\text{-}C_5H_5)((\text{—})\text{-DIOP})I\}$ (V) by an analogous route, namely treatment of the bisphosphite $\{Fe(\eta^5\text{-}C_5H_5)[P(OPh)_3]_2I\}$ with a small excess of (—)-DIOP in toluene. No (—)-DIOP analogue of III was found in this thermal reaction.

Silverthorn has shown that complexes of the type $\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')L]^+BF_4^-\}$ (L = N_2 or Me_2CO) may be prepared by treatment of the iodide II with thallium tetrafluoroborate in the presence of the ligand L [6]. We verified this procedure by carrying out the reaction between I and $TlBF_4$ in the presence of CO giving the compound $\{[Fe(\eta^5\text{-}C_5H_5)(P\text{—}P)CO]^+BF_4^-\}$ (VI) in high yield. However when the reaction between I and $TlBF_4$ or $TlPF_6$ is carried out in the presence of ethylene, propene, cyclohexene, 1-heptene, diethylmaleate, methylacrylate, then in each case the same crystalline product VII was obtained in which the olefin had not been incorporated. The characterisation of VII has proved elusive. Treatment of VII with CO in acetone gives quantitative yield of VI. Also reduction of VII with sodium borohydride gives the known hydride $\{Fe(\eta^5\text{-}C_5H_5)(P\text{—}P)H\}$ (VIII) [4]. Further, treatment of VII with potassium iodide in acetone immediately reforms I in high yield. The ^{1}H NMR and IR spectra of VII are consistent with the presence of the moiety $\{[Fe(\eta^5\text{-}C_5H_5)P\text{—}P]^+BF_4^-\}$ or PF_6^-, however the analytical data varied according to the solvent of recrystallisation.

It has recently been shown that treatment of I with $AgPF_6$ gives the paramagnetic cation $\{[Fe(\eta^5\text{-}C_5H_5)(P\text{—}P)I]^+PF_6^-\}$ (IX) [8]. However, iodide is absent in our complex VII also, the Tl^+ cation is rather less reducing than the Ag^+ cation, so that IX would not be expected as a product from I and Tl^+. We conclude that VII probably contains the 16-electron cation $[Fe(\eta^5\text{-}C_5H_5)P\text{—}P]^+$ together with varying solvent incorporation, either as weak ligands, or, in the lattice; a crystal structure determination is in progress.

Since P—P is a better donor to a transition metal than two CO ligands, it might have been expected that olefin complexes of the type $[Fe(\eta^5\text{-}C_5H_5)(P\text{—}P)\text{olefin}]^+$ would have a stronger Fe—olefin bond than in the known dicarbonyl analogues. Therefore we attribute our failure to prepare even the ethylene compound $[Fe(\eta^5\text{-}C_5H_5)(P\text{—}P)C_2H_4]^+$ to the greater steric requirements of the P—P ligand compared with two CO ligands. For this reason we explored the reactivity of the compound II in the hope that substitution of the two phenyl groups by methyls would result in reduction of the steric inhibition to addition of olefin to the metal center in II.

Treatment of II with $TlBF_4$ in the presence of an activated olefin L, gave the anticipated olefin complexes $\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')L]^+BF_4^-\}$ (X, L = diethylmaleate and XI, L = methylacrylate) respectively in good yields. The data for these compounds is given in Table 1. We were however unable to obtain analogues of X and XI with olefins, such as heptene, cyclopentene, cyclohexene. Therefore, it appears that stereoelectronic requirements of $Me_2PCH_2CH_2PMe_2$ are more suitable than those of $Ph_2PCH_2CH_2PPh_2$ with respect to the ability of olefins to complex to the metal center. On the other hand, clearly $Ph_2PCH_2CH_2$-

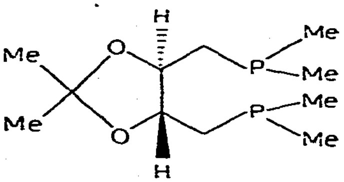
TABLE 1

ANALYTICAL AND ^{1}H NMR DATA OF COMPOUNDS III, IV, V, X AND XI

Compound (no.)	Colour	Analysis: Found (calcd.) (%)		^{1}H NMR ^{a}
		C	H	
$\{Fe(\eta^5\text{-}C_5H_5)((-)\text{-}DIOP)I\}$ (V) ^{b}	Black-red	57.9(57.9)	5.2(5.0)	6.20($CDCl_3$)
$\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')P(OPh)_3]^+I^-\}$ (III)	Yellow	48.8(49.1)	4.9(5.1)	5.62($CDCl_3$)
$\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')P(OPh)_3]^+BF_4^-\}$ (IV)	Yellow	51.9(52.1)	5.5(5.4)	5.65($CDCl_3$)
$\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')EtOCOCH{=}CHCOOEt]^+BF_4^-\}$ (X)	Gold-yellow	42.5(43.0)	5.9(6.2)	5.35(D_2O)
$\{[Fe(\eta^5\text{-}C_5H_5)(P'\text{—}P')CH_2{=}CHCOOMe]^+BF_4^-\}$ (XI)	Brick-red	39.6(40.5)	5.7(6.1)	5.20(DMSO-d_6)

[a] Given as the chemical shift (τ) in ppm for $\eta^5\text{-}C_5H_5$ hydrogens only. [b] $[\alpha]_D^{20}$ − 518° (c 0.27, $CHCl_3$).

PPh_2 is a closer model to (—)-DIOP than $Me_2PCH_2CH_2PMe_2$. It therefore seemed unlikely that the (—)-DIOP complex V would lead to a chemistry suitable for extensive studies in asymmetric induction, and as was expected, preliminary attempts to prepare olefin complexes of the type $[Fe(\eta^5\text{-}C_5H_5)((-)\text{-DIOP})\text{olefin}]^+$ were unsuccessful. So the dimethyl analogue XII of the DIOP would be more



(XII)

promising. The synthesis of this compound and its metal complexes is in progress.

Experimental

Preparation and manipulations were made under vacuum or in an inert atmosphere. ^{1}H NMR spectra were determined on a 60 MHz Japan Electron Optics Laboratory instrument at probe temperature.

η^5-Cyclopentadienyliodo[1,2-bis(dimethylphosphino)ethane]iron (II) and η^5-cyclopentadienyl[1,2-bis(dimethylphosphino)ethane] triphenylphosphite iron iodide (III) and tetrafluoroborate (IV)

(a) The iodide $\{Fe(\eta^5\text{-}C_5H_5)(P(OPh)_3)_2I\}$ (5.8 g) in toluene (40 ml) and 1,2-bis(dimethylphosphino)ethane (0.95 g) were stirred at 60°C for 6 h and then overnight at room temperature. Evaporation of toluene yield a grey brown solid which was washed with light petroleum (b.p. 30—40°C) (80 ml), then extracted with dichloromethane (2 × 40 ml), giving a black solution and a yellow residue. After evaporation of the solvent from the filtered solution the resulting black solid was recrystallised from dichloromethane/light petroleum (b.p. 60—80°C) giving black crystals of pure II. (Yield 1.10 g, 41%.)

(b) The yellow solid residue after purification on column chromatography (alumina, acetone) leads to the compound III. (Yield 2.4 g, 51%.)

(c) The compound III (2 g), 1,2-bis(dimethylphosphino)ethane (0.3 g) and potassium iodide (0.5 g) in acetone (100 ml) were irradiated with stirring through Pyrex apparatus with a medium-pressure mercury lamp (Hanovia 500 W) for 24 h at room temperature. After filtration from a reddish insoluble solid, the solvent was evaporated under reduced pressure, the resulting black solid was recrystallised from dichloromethane/light petroleum (b.p. 60—80°C) giving black crystals of II. (Yield 0.3 g, 27%.)

(d) The complex III (0.3 g) in acetone (20 ml) was added to a saturated aqueous solution of ammonium tetrafluoroborate. The resulting light-yellow precipitate was filtered, washed with water (2 × 50 ml) and recrystallised from acetone/water to give yellow crystals of IV. (Yield 0.23 g, 82%.)

η^5-Cyclopentadienyliodo(—)-DIOP iron (V)

The iodide {$Fe(\eta^5\text{-}C_5H_5)(P(OPh)_3)_2I$} (1.74 g) in toluene (30 ml) and (—)-DIOP (1 g) were stirred at 80° C during 15 h. Then the solvent was evaporated to dryness and the resulting solid washed three times with 20 ml of light petroleum (b.p. 30—40° C). The pure complex V was obtained after a further recrystallisation from dichloromethane/light petroleum (b.p. 60—80° C). (Yield 1.05 g, 69%.)

Complex VII

(a) The compound I (0.130 g) in acetone (20 ml) and thallium tetrafluoroborate (0.2 g) were stirred for 3 days at room temperature. The filtrate from the yellowish precipitate of thallium iodide was evaporated to dryness leaving an orange-brown solid. Recrystallisation from dichloromethane/toluene, gave 0.095 g of yellow orange crystals of VII. The product was recrystallised a second time from acetone/water.

(b) In an attempt to obtain olefin complexes, we carried out the same reaction as above in the presence of an olefin. The following experimental conditions have been used: passage of ethylene or propene into a mixture of compound I and thallium tetrafluoroborate in acetone for 24 h, or addition of a large excess of an olefin (cyclohexene, heptene, diethylmaleate, methylacrylate) to the same mixture of the compound I and thallium tetrafluoroborate in acetone and stirring for 3 days at room temperature. The reactions have also been carried out with the pure olefins as the solvent.

The reaction products were in all cases characterized as VII.

(c) The anion BF_4^- can be changed for PF_6^- by using thallium hexafluorophosphate. The experimental procedure was the same as described above.

Reactions of the compound VII

(i) With carbon monoxide. Carbon monoxide was bubbled through a solution of VII in acetone at room temperature for 15 h. The carbonyl compound VI was isolated and characterized as previously reported [3].

(ii) With potassium iodide. The compound VII in acetone (100 ml) was treated with an excess of potassium iodide. The mixture was refluxed for 2 h. After evaporation to dryness, redissolution in dichloromethane, filtration from the insoluble salts and evaporation of the solvent, compound I was obtained in essentially quantitative yield.

(iii) With sodium borohydride. A suspension of VII (1.0 g) in anhydrous tetrahydrofuran (10 ml) was treated with sodium borohydride (0.3 g). The mixture was refluxed and stirred for 3 h. After filtration and evaporation of the solvent, the orange residue was extracted with toluene (20 ml). After filtration the filtrate was concentrated under vacuum (5 ml) and light petroleum (b.p. 30—40° C) (20 ml) was slowly added causing precipitation of a pale yellow product. After cooling to —20° C, filtration and washing with cold light petroleum, the product was shown to be the hydride VIII, as previously described.

η^5-Cyclopentadienyl[1,2-bis(dimethylphosphino)ethane] (diethylmaleate)iron tetrafluoroborate

The iodide {$Fe(\eta^5\text{-}C_5H_5)(Me_2PCH_2CH_2PMe_2)I$} (5.85 g) in acetone (80 ml) was treated with thallium tetrafluoroborate (2.51 g) and freshly distilled diethylmaleate (13 g) at room temperature with stirring for 100 h. The resulting mixture was filtered from the yellow precipitate and the solvent was removed from the filtrate under reduced pressure. The resulting solid was recrystallised from acetone/toluene giving golden-yellow crystals of the compound X. (Yield 6.9 g 89%.)

The compound $\{[Fe(\eta^5\text{-}C_5H_5)(Me_2PCH_2CH_2PMe_2)CH_2{=}CHCOOMe]^+BF_4^-\}$ was prepared in an essentially identical manner. (Yield ca. 80%.)

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