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UNUSUAL ROUTE TO AND REARRANGEMENT OF FOUR-MEMBERED RING COMPLEXES $C_5H_5Fe(CO)[(C_6H_5)_2PN(R)CH(C_6H_5)]$

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Summary

The amine substituted phosphines $(C_6H_5)_2PN(H)CH_2CH_3$ and $(C_6H_5)_2$-$PN(H)CH_2C_6H_5$ react with $C_5H_5Fe(CO)_2CH(C_6H_5)(OCH_3)$ photolytically to give moderate yields of the four-membered chelate ring complexes $C_5H_5Fe(CO)[(C_6H_5)_2PN(CH_2CH_3)CH(C_6H_5)]$ and $C_5H_5Fe(CO)[(C_6H_5)_2PN(CH_2$-$C_6H_5)CH(C_6H_5)]$, respectively. Photolysis of $C_5H_5Fe(CO)_2CH(C_6H_5)(OCH_3)$ in the presence of (S)-(-)-diphenyl(1-phenylethylamino)phosphine leads to the isolation of $C_5H_5Fe(CO)[(C_6H_5)_2PN{=}C(CH_3)(C_6H_5)]CH_2C_6H_5$ which is proposed to arise from a formally 1,3-hydrogen shift rearrangement of an intermediate four-membered chelate ring complex.

Introduction

In a continuing effort to study chiral transition metal complexes [1,2], we recently began attempts to synthesize an optically active derivative of the highly reactive carbene complex $[C_5H_5Fe(CO)_2CH$-$(C_6H_5)]PF_6$ [3]. This complex, synthesized by treatment of the methoxy substituted compound $C_5H_5Fe(CO)_2CH(C_6H_5)(OCH_3)$ I with trityl hexafluorophosphate, has been shown to react with substituted olefins in a stereospecific manner to produce cis substituted cyclopropanes [4]. We felt it would be of interest to synthesize an optically active complex $[C_5H_5Fe(CO)(PR_3)CH(C_6H_5)]PF_6$ chiral at the iron center in order to study the degree of optical induction in cyclopropane formation [5-9].

Our initial approach to this problem was to substitute a phosphine containing an optically active amino side-chain for a carbonyl in complex I. This would have been followed by generation of the phosphine substituted carbene complex and separation of diastereomers. However, in the process of experiments involving amine substituted phosphines, a unique reaction resulting in formation of a four-membered chelate ring and its opening by 1,3-hydrogen shift was discovered, the details of which are reported here.

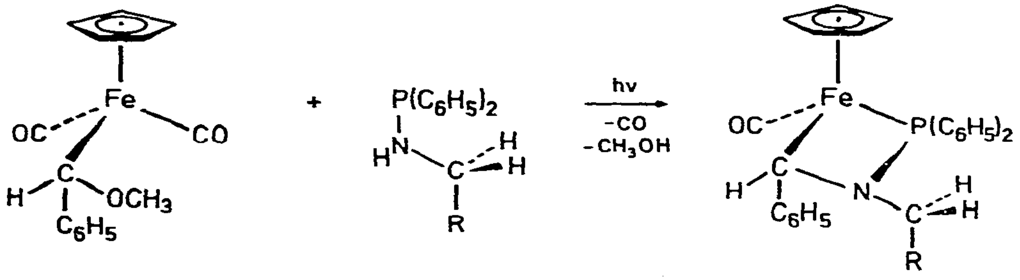
Results and Discussion

The readily available (S)-(-)-diphenyl(1-phenylethylamino)phosphine IIc, synthesized by reaction of $(C_6H_5)_2PCl$ with (S)-(-)-H_2N-$CH(CH_3)(C_6H_5)$, was allowed to react with I in solution under photolytic conditions. After 1 hour the pale brown solution had turned dark red, and no more carbon monoxide was evolved. Work up of the reaction solution afforded a dark red solid complex which exhibited no optical rotation. From this observation and the spectral data, it was clear that the desired product $C_5H_5Fe(CO)[(C_6H_5)_2PN(H)CH(CH_3)$-$(C_6H_5)]CH(C_6H_5)(OCH_3)$ had either rearranged or never been formed. To clearly identify the nature of this red complex, two simpler phosphines, $(C_6H_5)_2PN(H)CH_2CH_3$ IIa and $(C_6H_5)_2PN(H)CH_2C_6H_5$ IIb, were used in the same reaction.

Formation of Four-membered Ring Complexes

Photolysis of I in the presence of $(C_6H_5)_2PN(H)CH_2CH_3$ IIa yielded after work up a pale orange crystalline complex showing only one strong metal CO band at 1923 cm^{-1} (benzene solution). From the ^1H and ^{13}C nmr data (tables 1 and 2) we assigned its structure to be that of the four-membered ring complex IIIa (R = CH_2CH_3) (scheme 1).

Scheme 1



I IIa,b IIIa,b

Table 1. ^{1}H nmr Parameters [a] for Complexes IIIa, IIIb, IVc, and V

	$C_5\underline{H}_5$	$C\underline{H}(C_6H_5)$	$C\underline{H}_2C_6H_5$	$C_6\underline{H}_5$	$C\underline{H}_3$, $C\underline{H}_2CH_3$
IIIa	$^{2}4.06$ $J(\underline{P}-C_5\underline{H}_5)=1.4$	$^{2}5.11$ $J(\underline{P}-C\underline{H})=5.6$	-	$^{m}6.98-7.83$	$2.77\ (CH_2)^{b}$ $J(C\underline{H}_2-C\underline{H}_3)=7$ $J(\underline{P}-C\underline{H}_2)=10.2$ $^{3}0.77\ (CH_3)$
IIIb	$^{2}4.07$ $J(\underline{P}-C_5\underline{H}_5)=1.5$	$^{2}5.22$ $J(\underline{P}-C\underline{H})=4.5$	CH_2 [c] $J(\underline{H}_a-\underline{H}_b)=13.5$	$^{m}6.76-7.72$	-
IVc	$^{2}4.01$ $J(\underline{P}-C_5\underline{H}_5)=3.1$		$^{3}2.43^{d}$, $^{4}2.77^{e}$ $J(\underline{H}_a-\underline{H}_b)=8.6$	$^{m}7.02-7.93$	$^{2}1.89$ $J(\underline{P}-C\underline{H}_3)=1.2$
V	$^{2}4.23$ $J(\underline{P}-C_5\underline{H}_5)=2$			$^{m}7.0-8.2$	2.02

[a] C_6D_6, i-TMS; Bruker-WH 90; values in ppm, coupling constants in Hz.
[b] This CH_2 group appeared as a doubled quartet.
[c] This methylene group exhibited an AMX pattern where the two AB quartets are centered at 3.95 and 3.98 ppm.
[d] Proton H_a, $J(\underline{P}-\underline{H}_a)=8.6$ Hz.
[e] Proton H_b, $J(\underline{P}-\underline{H}_b)=4.6$ Hz.

The ^{1}H nmr spectrum revealed that the methoxy group had been lost, but the benzylic hydrogen $C\underline{H}(C_6H_5)$ (δ 5.11) had been retained displaying a chemical shift in the area expected for complex IIIa. The phosphorus coupling to that proton $\underline{P}-C\underline{H}(C_6H_5)$ is smaller than that reported for the corresponding coupling in the triphenylphosphine substituted derivative of I (5.6 Hz as compared to 9 Hz) [4)]. Even though the methylene protons in the ethyl group are diastereotopic, they are degenerate in the ^{1}H nmr spectrum and appear as a doubled quartet due to coupling to phosphorus and the methyl group. The ^{13}C nmr spectrum (table 2) is in complete agreement with the assigned structure, and using off resonance decoupling, the signals for $\underline{C}H(C_6H_5)$ and the ethyl carbons were readily identified. Further support for the assigned structure came from the field desorption mass spectrum which showed the correct molecular ion at m/e 467.

In an analogous manner photolysis of I with $(C_6H_5)_2PN(H)CH_2C_6H_5$ IIb produced after work up an orange crystalline complex. The ^{1}H nmr

Table 2. ^{13}C nmr Parameters a) for Complexes IIIa and IVc

	C_5H_5	$\underline{C}H(C_6H_5)$	CH_2 b)	$N{=}\underline{C}$
IIIa	81.04	40.85 c) J(C–P)=39.81	46.27 J(C–P)=6.63	
IVc	84.94	5.47 b) J(C–P)=17.69		171.79 d) J(C–P)=8.85

	CH_3 e)	C_6H_5	CO
IIIa	141.18 J(C–P)=2.65	126.37–132.86 136.08–154.34 f)	221.09 J(C–P)=33.17
IVc	23.64 J(C–P)=12.38	121.43–132.53 139.33–157.42 g)	222.97 J(C–P)=33.61

a) $CDCl_3$, Bruker 90 FT, in ppm downfield from TMS, coupling constants in Hz, proton decoupled.

b) Triplet in the off-resonance spectrum.

c) Doublet in the off-resonance spectrum.

d) The 171.9 ppm signal was assigned due to its larger P-C coupling constant as compared to the 157.42 ppm resonance.

e) Quartet in the off-resonance spectrum.

f) The two ipso carbons adjacent to phosphorus were assigned as four signals ranging from 136.03 to 139.07 ppm. The ipso carbon of $CH(C_6H_5)$ was assigned to the signal at 154.34 ppm [J(C-P)= 11.94 Hz].

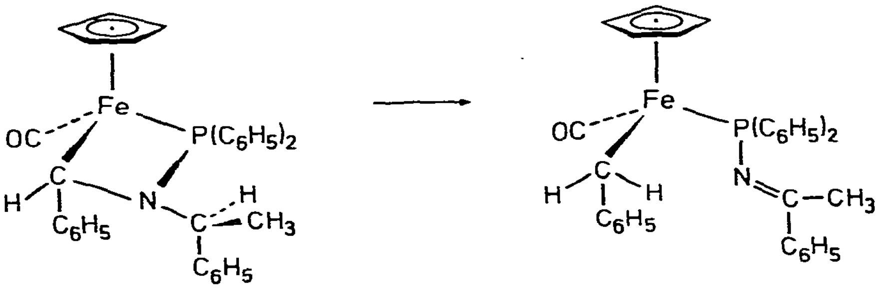
g) Three of the ipso carbons appear as six signals ranging from 139.33 to 142.84 ppm. The other ipso carbon, adjacent to the azomethane carbon, appears at 157.42 ppm [J(C-P)=5.31 Hz].

spectrum (table 1), ir spectrum (one strong ν(CO) band at 1939 cm^{-1}, benzene) and elemental analysis showed this to be the four-membered ring complex IIIb (R = $CH_2C_6H_5$) (scheme 1). The most identifying feature was the doublet in the ^{1}H nmr spectrum for $C\underline{H}(C_6H_5)$ at δ 5.22 [J(P-H) = 4.5 Hz]. In the case of compound IIIb the diastereotopic methylene hydrogens adjacent to nitrogen exhibited an eight line AMX pattern in which the two protons were coupled to one another (13.5 Hz) and differently to phosphorus. Thus, for the amine substituents R = CH_2CH_3 and $CH_2C_6H_5$ four-membered ring complexes IIIa and IIIb are stable compounds. Refluxing solutions of IIIa or IIIb in benzene for 24 hours caused no detectable rearrangement and very little decomposition of either complex.

1,3-Hydrogen Shift

From the above results it seemed likely that the aforementioned dark red product, obtained by reaction of I with IIc, arose as a result of rearrangement of the four-membered ring complex IIIc, and we were able to identify the compound as the ring-opened complex IVc (scheme 2).

Scheme 2



IIIc IVc

The infrared spectra showed strong ν(C≡O) and ν(C=N) bands at 1955 cm^{-1} and 1680 cm^{-1} (KBr), respectively. In the ^1H nmr spectrum of IVc (table 1), the diastereotopic methylene hydrogens of the $CH_2C_6H_5$ group appeared as a triplet (δ 2.43) and quartet (δ 2.77). The $C\underline{H}_2C_6H_5$ hydrogens were coupled to one another (8.6 Hz) and differently to phosphorus (8.6 and 4.6 Hz, respectively). The ^{13}C nmr spectrum (table 2) was in agreement with the assigned structure, and the field desorption mass spectrum contained the expected peak at m/e 543. Finally, reaction of a solution of IVc in CH_2Cl_2 with iodine gave after work up a dark green solid complex V which must be formulated as $C_5H_5Fe(CO)[(C_6H_5)_2PN=C(C_6H_5)(CH_3)]I$. Its ir spectrum showed that the C≡O and C=N groups were still present with bands at 1920 cm^{-1} and 1680 cm^{-1} (KBr), respectively. However, from the ^1H nmr spectrum (table 1) of the iodo complex V it was obvious that the signals for the benzylic group attached to iron had disappeared in accord with the assumption that iodine had replaced the $CH_2C_6H_5$ group in IVc to produce $C_5H_5Fe(CO)[(C_6H_5)_2PN=C(CH_3)(C_6H_5)]I$ V.

We feel that IVc probably arises through rearrangement of an intermediate four-membered ring complex IIIc according to scheme 2. The fact that reaction with both the ethyl and benzyl substituted amino phosphines IIa and IIb gives the stable four-membered ring complexes IIIa and IIIb, indicated that steric factors probably play the major role in the transformation IIIc → IVc, which formally represents a 1,3-hydrogen shift.

The ^{31}P nmr spectra of complexes IIIa, IIIb, and IVc were recorded. Proton decoupled spectra for IIIa and IIIb were very similar each showing a single signal at 85.02 and 89.56 ppm downfield from external 80 % H_3PO_4, respectively. However, as would be expected, complex IVc exhibited a singlet at a substantially different chemical shift of 110.56 ppm.

Experimental

All operations were carried out in a nitrogen atmosphere, using standard Schlenk techniques. The solvents were dried and distilled before use. Ir spectra were recorded either on a Beckman IR-33 or Beckman IR-4240. All photolysis reactions were performed with a Philips HPK 125 W lamp in a 80 ml capacity well. The ^1H and ^{13}C nmr spectra were recorded on a Bruker WH90 instrument, and the ^{31}P nmr spectra on a Varian XL 100 instrument.

$C_5H_5Fe(CO)[(C_6H_5)_2PN(CH_2CH_3)CH(C_6H_5)]$ IIIa

Complex I [3,4] (1.1 g, 3.6 mmol) and $(C_6H_5)_2PNH(CH_2CH_3)$ IIa (0.84 g, 3.6 mmol) were dissolved in a photolysis well with 10 ml of benzene, and the solution diluted to 80 ml with pentane. After photolysis for 1 hour at 25°C no more CO evolution was observed, and the pale orange solution had turned to a dark red-orange color. The solution was concentrated in vacuo, and the residue chromatographed on silica gel in benzene. Elution with benzene developed two bands, first an orange and then a red band. When evaporated to dryness the solution from the orange band yielded a solid material which was recrystallized from ether/pentane to give 720 mg (43 %) of red-orange crystalline IIIa with m.p. 134–136°C ($C_{27}H_{26}FeNOP$ calc.: C, 69.41; H, 5.50; N, 3.00 %. Found: C, 69.33; H, 5.62; N, 3.09 %.). The more slowly eluted red band proved by ir and ^1H nmr to be $[C_5H_5Fe(CO)_2]_2$.

$C_5H_5Fe(CO)[(C_6H_5)_2PN(CH_2C_6H_5)CH(C_6H_5)]$ IIIb

This compound was synthesized in a completely analogous manner as complex IIIa using $(C_6H_5)_2PNH(CH_2C_6H_5)$ IIb instead of IIa. Work up as above resulted in a 40 % yield of the orange crystalline IIIb with m.p. 62-64°C ($C_{32}H_{28}FeNOP$ calc.: C, 72.62; H, 5.30; N, 2.65 %. Found: C, 72.91; H, 5.38; N, 2.24 %).

$C_5H_5Fe(CO)[(C_6H_5)_2PN{=}C(CH_3)(C_6H_5)]CH_2C_6H_5$ IVc

Complex I [3,4] (1.0 g, 3.4 mmol) and (S)-(-)-$(C_6H_5)_2PNH[CH(CH_3)-(C_6H_5)]$ IIc (1.0 g, 3.4 mmol) were photolyzed for 1 hour in a pentane/benzene solution. After this time no more CO evolved, and the light orange solution had turned dark red. The solution was concentrated, and the residue chromatographed on silica gel eluting with benzene. Two red bands developed. The first band was collected, concentrated, and the resulting oil was treated with pentane to yield 800 mg (43 %) of red, powdery IVc with m.p. 119-121°C ($C_{33}H_{30}FeNOP$ calc.: C, 72.93; H, 5.52; N, 2.58 %. Found: C, 72.41; H, 5.64; N, 2.60 %.). The second red band proved to be $[C_5H_5Fe(CO)_2]_2$.

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