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Iron complexes of 1,1′-bis(diphenylphosphino)ferrocene (BPPF) as efficient catalysts in the synthesis of carbamates. X-ray crystal structure of (BPPF)Fe(CO)$_3$

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Abstract

1,1′-Bis(diphenylphosphino)ferrocene (BPPF) reacts with a 5–10 molar excess of Fe(CO)$_5$ to give three new iron complexes (η^2-BPPF)Fe(CO)$_3$ (**1**), (η^1-BPPF)Fe(CO)$_4$ (**2**), and (μ,η^1-BPPF)Fe$_2$(CO)$_8$ (**3**) with the product distribution depending upon reaction conditions. The structure of **1** has been determined. Crystals are monoclinic, space group $P2_1/c$, with a 9.708(1), b 16.195(2), c 19.869(5) Å, β 95.75(2)°, V 3108(1) Å^3, $Z = 4$, and D_{calc} 1.49 g cm^{-3}. The geometry around the central iron is a distorted trigonal bipyramid, with the two phosphorus atoms occupying axial and equatorial positions. All these compounds can catalyze efficiently the reaction of propargyl alcohol with secondary amines in the presence of CO_2 to provide corresponding carbamate esters. The yields of some carbamates are among the highest (~ 65%) ever reported in the literature.

Introduction

The catalytic incorporation of carbon dioxide into organic compounds has been an attractive goal in recent years since a number of functionalized substrates may be formed with this inexpensive, stable, and nontoxic reagent [1–3]. An important example is the catalytic formation of carbamates by the reactions of carbon dioxide and amines with alkynes as represented by the reaction in equation 1.

$$HC{\equiv}CR' + R_2NH + CO_2 \rightarrow H_2C{=}C(R')OC({=}O)NR_2 \quad (1)$$

This reaction provides a unique advantage over other preparative methods which include the conventional multistep synthesis based on toxic phosgene [4] and

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catalytic syntheses employing carbon monoxide in the presence of other reagents [5–7]. Prompted by recent reports that various ruthenium complexes [8–12] can catalyze the reaction in equation 1, we report the preparation of new iron(0) complexes of 1,1′-bis(diphenylphosphino)ferrocene (BPPF) along with our new findings that these complexes are good catalysts for the same reactions. We chose these systems because ferrocenylphosphines are well known as efficient ligands for metal complexes in a wide range of homogeneous catalytic reactions such as rhodium(I) catalyzed hydrogenation of olefins [13–18], palladium(II)- and nickel(II)-catalyzed Grignard cross-coupling reactions [19], platinum(II)-catalyzed hydrosilation of ketones [20], and gold(I)-catalyzed aldol condensation [21,22]. It was thus our desire to extend the utility of one of these ligands by preparing iron complexes which have hitherto received relatively little attention.

Experimental

All manipulations were conducted under argon using a double manifold vacuum system and Schlenk techniques. All commercial reagents were used as received unless otherwise mentioned. Solvents were purified by standard techniques [23], and distilled just prior to use.

Melting points were determined using a Gallenkamp melting point apparatus and are reported without correction. Microanalyses were performed by the Department of Chemistry, Kyungpook National University. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300, 80.15, and 121.5 MHz, respectively. Mass spectra were obtained using a Kratos MS-50 instrument. The capillary gas chromatography analysis was performed on an HP 5890A instrument with 30 m × 0.53 mm HP-5 capillary column and FID.

The ligand BPPF was prepared according to the standard method [24].

Preparation of (η^2-BPPF)Fe(CO)$_3$ (1), (η^1-BPPF)Fe(CO)$_4$ (2), and (μ,η^1-BPPF)Fe$_2$(CO)$_8$ (3) under thermal conditions

$Fe(CO)_5$ (4.8 ml, 36 mmol) and BPPF (2 g, 3.6 mmol) were dissolved in benzene (100 ml) in a 250-ml, two-necked, round bottom flask equipped with a condenser, a magnetic stirrer, and an argon inlet. The solution was refluxed with stirring for 10–13 h during which time the solution became dark-brown with deposit of black precipitates due to decomposition of $Fe(CO)_5$. The solution was then filtered on Celite to remove the precipitates, and the filtrate was evaporated to dryness. The remaining dark-brown oily residue was taken up in a small volume of THF to be chromatographed on silica gel. A trace amount of the unchanged ligand was eluted first with a mixture of hexane and ether (10/1). The three products were obtained by eluting the remaining three orange bands as follows: (1) band 1 was eluted with hexane/ether (5/1) to give **2** as orange crystals by standing the eluate at 4°C (0.13 g, 5%), (2) band 2 was eluted with hexane/ether (5/1) to give **1** as yellow crystals after usual workup followed by crystallization from a mixture of dichloromethane and cyclohexane (1/4) at room temperature (0.52 g, 20%), (3) band 3 was eluted with hexane/ether (3/1) to give **3** as orange crystals by cooling the eluate to 0°C (0.58 g, 18%). When the same reaction was carried out in toluene under reflux for 8–10 h, **2** and **3** were obtained as sole products with increased chemical yields for **2** after column chromatography: yield of **2** (1.04 g, 40%); yield of **3** (0.06 g, 2%).

Compound **1** (m.p. 233–235 °C). Anal. Found: C, 64.00; H, 4.73. $C_{37}H_{28}Fe_2O_3P_2$ (MW = 693.7) calcd.: C, 64.01; H, 4.04%.

Compound **2** (m.p. 169–171 °C). Anal. Found: C, 56.00; H, 4.00. $C_{38}H_{28}Fe_2O_4P_2$ (MW = 721.7) calcd.: C, 63.22; H, 3.91%.

Compound **3** (m.p. 210–212 °C). Anal. Found: C, 56.00; H, 4.35. $C_{42}H_{28}Fe_3O_8P_2$ (MW = 889.5) calcd.: C, 56.67; H, 3.85%.

Preparation of 1–3 under photochemical conditions

A solution of $Fe(CO)_5$ (1.4 ml, 13 mmol) and BPPF (2.5 g, 4.5 mmol) in 100 ml of THF was irradiated at −78 °C for 3–4 h (high-pressure mercury lamp, 125 W). After removal of solvent under vacuum, the residue was dissolved in 10 ml of THF and the solution left to stand at room temperature to deposit **1** as yellow crystals (0.94 g, 30%). The mother liquor separated from the crystals was chromatographed on silica gel with hexane/ether (the ratio was slowly increased from 5/1 to 2/1). Recrystallization of the eluate (first band) from hexane/THF (4/1) gave **3** (0.16 g, 16%). The amount of **2** obtained from this reaction was negligibly small. When the same reaction was carried out at room temperature for 5–10 h, **3** was obtained as a major product in 45% yield with a trace amount of **1** and **2**.

Catalytic reactions

The catalytic reactions were run in a Parr type 4565 pressure reactor. In the 50-ml reactor cup was placed a solution of secondary amine (20 mmol), acetylenic alcohol substrate (10 mmol), and the catalyst precursor (0.1 mmol) in degassed acetonitrile (10 ml) under a stream of nitrogen, along with a stirring bar. After being flushed with CO_2, the reactor was then pressurized to the desired value ($P(CO_2)$ 30 atm) and placed in a stirred thermostatic oil bath (90 ± 2 °C) for 24 h. The resulting solution was reduced in volume to a minimum amount and chromatographed on a preparative TLC (silica gel) (eluent; acetone/chloroform, 1/1) to give the desired product. The product was characterized by conventional methods.

X-ray crystallographic analysis of 1

Crystals of X-ray diffraction quality of **1** were obtained from a mixture of CH_2Cl_2/C_6H_{12} (1/4). The deep yellow crystal was sealed in a 0.5-mm diameter thin-walled glass capillary and used for data collection. An Enraf–Nonius CAD-4 diffractometer with a graphite monochromator and Mo-K_α radiation (λ 0.71073 Å) was used for all X-ray experiments. The final unit cell parameters were determined to be a 9.708(1), b 16.195(2), c 19.869(5) Å, β 95.72(2)° by least-squares refinement of well-centred 25 reflections (20° < 2θ < 30°). The intensities of three check reflections were monitored over X-ray exposure time throughout the data collection and showed only small random fluctuations. The complete data set consisted of 2712 unique reflections with $I > 3\sigma(I)$ from the quarter sphere ($\pm h$, $\pm k$, l) such that 2° < 2θ < 50°. Lorentz and polarization correction was applied but absorption correction was not. The structure was solved in the space group $P2_1/c$. A starting set of atomic positions for the two Fe atoms was obtained from MULTAN-80 [25]. The program system, SHELX-76 [26] was used to locate the remaining non-hydrogen atoms by least-squares refinement and difference Fourier methods. The final least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms except carbon atoms of cyclopentadienyl and phenyl groups

Table 1

Crystal data collection and reduction parameters for **1**

Formula	$C_{37}H_{28}Fe_2O_3P_2$
Formular weight	693.7
Crystal system	Monoclinic
Space group	$P2_1/c$
a, b, c (Å)	9.708(1), 16.195(2), 19.869(5)
β (deg.)	95.75(2)
V (Å^3)	3108(5)
Z	4
$D_{calc.}$ (g cm^{-3})	1.483
F (000)	1423
Crystal size (mm)	0.30×0.50×0.56
Crystal shape	Tetragonal
μ (cm^{-1})	10.09
Radiation	Mo-K_α (0.71073 Å)
Scan type	$\omega/2\theta$
Scan rate (deg/min)	1.10–16.48
$2\theta_{max}$ (deg)	50
Data collected points	$-11 \le h \le 11, 0 \le k \le 18, 0 \le l \le 23$
No. of unique data $I > 3\sigma(I)$	2712
No. of variables	161
Over determination ratio	16.8
$R = (\Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma F_o)$	0.0586
$R_G = (\Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert)^2 / \Sigma F_o^2)^{1/2}$	0.0644

gave the final agreement factors of $R = 0.059$, $R_G = 0.064$. The phenyl and cyclopentadienyl carbons were refined as rigid bodies with idealized geometry (C–C 1.395 Å). Hydrogen atoms were not included in refinement. The crystal data collection and reduction of X-ray data, and refinement of **1** are given in Table 1. The maximum remaining electron density in the final difference map was 0.72 e/Å^3 at 2.39 Å from Fe(1) and 0.76 Å from C(25). No parameter shifted more than 10% of its estimated standard deviation. Atomic scattering factors for Fe from international tables for X-ray crystallography [27] and for P, C, and O from SHELX-76 system were used for all calculations. Final positional parameters and temperature factors are listed in Table 2.

Results and discussion

The three iron complexes **1–3** were prepared by the reaction of BPPF with a 5–10 molar excess of $Fe(CO)_5$ under reflux in an aromatic solvent or by UV irradiation as described in equation 2.

$$\text{BPPF} + Fe(CO)_5 \rightarrow$$

$$\underset{(1)}{(\eta^2\text{-BPPF})Fe(CO)_3} + \underset{(2)}{(\eta^1\text{-BPPF})Fe(CO)_4} + \underset{(3)}{(\mu,\eta^1\text{-BPPF})Fe_2(CO)_8} \quad (2)$$

The yields and the product distribution depended significantly on the reaction conditions as described in the Experimental section. Since the chromatographic

Table 2

Fractional atomic coordinates and thermal parameters for **1**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	0.5604(1)	0.2836(1)	0.9129(1)	0.0329(7)	0.0563(9)	0.0270(6)	−0.0022(6)	0.0039(5)	−0.0007(7)
Fe2	0.2853(1)	0.2023(1)	1.0551(1)	0.0371(7)	0.0386(8)	0.0277(6)	0.0034(6)	0.0003(5)	−0.0057(6)
P1	0.2363(2)	0.2347(1)	0.9456(1)	0.0304(12)	0.0370(14)	0.0271(11)	−0.0023(10)	−0.0010(9)	−0.0028(10)
P2	0.4856(2)	0.2724(1)	1.0776(1)	0.0337(12)	0.0357(13)	0.0249(11)	0.0004(10)	0.0005(9)	−0.0005(10)
C1	0.2944(11)	0.1627(6)	1.1388(5)	0.0561(65)	0.0483(64)	0.0429(60)	0.0002(52)	−0.0060(49)	−0.0072(52)
O1	0.2944(10)	0.1351(5)	1.1914(4)	0.1399(81)	0.0734(58)	0.0334(41)	0.0186(41)	0.0039(45)	−0.0154(55)
C2	0.1313(11)	0.2549(7)	1.0713(5)	0.0521(66)	0.0664(74)	0.0322(49)	0.0066(48)	0.0068(48)	−0.0044(56)
O2	0.0311(8)	0.2873(6)	1.0834(4)	0.0525(46)	0.1096(72)	0.0747(53)	0.0057(52)	0.0224(40)	0.0187(51)
C3	0.3110(10)	0.1004(7)	1.0280(5)	0.0562(66)	0.0493(69)	0.0351(53)	0.0054(48)	−0.0049(46)	−0.0104(54)
O3	0.3243(9)	0.0331(5)	1.0121(4)	0.1025(67)	0.0414(48)	0.0743(56)	−0.0091(41)	0.0069(47)	−0.0071(47)

Atom	x	y	z	U	Atom	x	y	z	U
C11	0.3753(5)	0.2289(4)	0.8915(3)	0.0313(19)	C15	0.4820(5)	0.1685(4)	0.8960(3)	0.0466(25)
C12	0.3997(5)	0.2846(4)	0.8388(3)	0.0402(21)	C21	0.5855(6)	0.3157(4)	1.0119(3)	0.0333(20)
C13	0.5214(5)	0.2586(4)	0.8107(3)	0.0552(28)	C22	0.5512(6)	0.3861(4)	0.9711(3)	0.0412(22)
C14	0.5723(5)	0.1869(4)	0.8460(3)	0.0574(28)	C23	0.6552(6)	0.3961(4)	0.9263(3)	0.0509(26)
C24	0.7538(6)	0.3318(4)	0.9396(3)	0.0542(27)	C46	0.5896(6)	0.4209(3)	1.1389(3)	0.0462(24)
C25	0.7107(6)	0.2822(4)	0.9925(3)	0.0455(23)	C51	0.1057(6)	0.1662(4)	0.9004(3)	0.0426(23)
C31	0.6252(5)	0.2085(4)	1.1227(3)	0.0358(20)	C52	0.1057(6)	0.1529(4)	0.8310(3)	0.0496(26)
C32	0.7227(5)	0.2422(4)	1.1714(3)	0.0427(23)	C53	0.0046(6)	0.1028(4)	0.7970(3)	0.0630(31)
C33	0.8361(5)	0.1951(4)	1.1975(3)	0.0590(29)	C54	−0.0965(6)	0.0659(4)	0.8322(3)	0.0704(33)
C34	0.8521(5)	0.1144(4)	1.1748(3)	0.0622(30)	C55	−0.0964(6)	0.0792(4)	0.9016(3)	0.0718(34)
C35	0.7546(5)	0.0808(4)	1.1260(3)	0.0716(34)	C56	0.0047(6)	0.1293(4)	0.9357(3)	0.0562(28)
C36	0.6412(5)	0.1279(4)	1.1000(3)	0.0594(29)	C61	0.1627(6)	0.3386(3)	0.9254(3)	0.0323(19)
C41	0.4815(6)	0.3638(3)	1.1338(3)	0.0338(20)	C62	0.1897(6)	0.4027(3)	0.9718(3)	0.0408(22)
C42	0.3743(6)	0.3711(3)	1.1752(3)	0.0438(23)	C63	0.1373(6)	0.4816(3)	0.9570(3)	0.0495(25)
C43	0.3754(6)	0.4357(3)	1.2218(3)	0.0546(27)	C64	0.0577(6)	0.4964(3)	0.8957(3)	0.0545(28)
C44	0.4836(6)	0.4928(3)	1.2269(3)	0.0539(27)	C65	0.0307(6)	0.4323(3)	0.8493(3)	0.0517(26)
C45	0.5907(6)	0.4854(3)	1.1855(3)	0.0523(27)	C66	0.0832(6)	0.3535(3)	0.8642(3)	0.0413(23)

Table 3

Bond distances (A) and angles (°) for **1**

Bond	Distance	Bond	Angle
Fe1–C11	2.009(6)	P2–Fe2–P1	99.7(1)
Fe1–C12	2.035(6)	C1–Fe2–P1	168.2(3)
Fe1–C13	2.069(6)	C1–Fe2–P2	92.0(3)
Fe1–C14	2.063(6)	C2–Fe2–P1	87.9(3)
Fe1–C15	2.027(7)	C2–Fe2–P2	116.5(3)
Fe1–C21	2.028(6)	C2–Fe2–C1	88.1(5)
Fe1–C22	2.031(7)	C3–Fe2–P1	86.9(3)
Fe1–C23	2.046(6)	C3–Fe2–P2	112.7(3)
Fe1–C24	2.053(6)	C3–Fe2–C1	87.3(5)
Fe1–C25	2.041(6)	C3–Fe2–C2	130.7(5)
Fe2–P1	2.243(2)	C11–P1–Fe2	117.8(2)
Fe2–P2	2.256(3)	C51–P1–Fe2	113.6(2)
Fe2–C1	1.777(10)	C51–P1–C11	101.3(3)
Fe2–C2	1.778(11)	C61–P1–Fe2	117.5(2)
Fe2–C3	1.760(11)	C61–P1–C11	102.2(3)
P1–C11	1.810(5)	C61–P1–C51	102.0(3)
P1–C51	1.848(5)	C21–P2–Fe2	123.8(2)
P1–C61	1.855(5)	C31–P2–Fe2	112.8(2)
P2–C21	1.840(5)	C31–P2–C21	98.3(3)
P2–C31	1.861(5)	C41–P2–Fe2	116.7(2)
P2–C41	1.857(5)	C41–P2–C21	99.6(3)
O1–C1	1.137(11)	C41–P2–C31	102.2(3)
O2–C2	1.151(11)	O1–C1–Fe2	176.6(10)
O3–C3	1.145(11)	O2–C2–Fe2	177.9(9)
		O3–C3–Fe2	177.4(10)
		P1–C11–Fe1	123.7(3)
		P2–C21–Fe1	124.8(3)

separation of the three products was difficult and time-consuming, it was essential to find appropriate reaction conditions to ensure or at least to maximize the formation of any particular product(s) over others. The tricarbonyl derivative (**1**) was best obtained by photochemical reaction at −78°C for a short period of time (3–4 h). Although the octacarbonyl derivative (**3**) was also formed as minor product under these conditions, they could be readily separated and obtained pure by crystallizing out **1** first from the reaction mixture and subsequently chromatographing the mother liquor to obtain **3** with a small amount of **1** left in the column. The

Table 4

Some selected infrared and mass spectral data for **1–3** [a]

Compound	ν(CO) (cm^{-1})	Mass spectra (m/e)
1	2045(w), 1983(vs) 1913(vs), 1883(vs)	694, 666, 638, 610, 554
2	2045(s), 1975(s) 1973(vs), 1921(vs)	694, 666, 638, 610, 554
3	2052(vs), 1975(vs) 1944(vs), 1921(vs)	862, 806, 778, 750, 722, 694, 666, 638, 610, 554

[a] Key: w, weak; vs, very strong; s, strong.

Table 5

Selected NMR data for **1–3** [a,b,c]

Compound	^{1}H NMR		^{31}P NMR	^{13}C NMR (CO region)
	Cp	Phenyl		
1	4.28 (s, 4H), 4.20 (s, 4H)	7.40–7.64 (m, 20H)	64.85 (s)	220.7 (t, J(PC) 9.3)
2	4.46 (s, 2H), 4.38 (s, 2H), 3.88 (s, 2H), 3.68 (s, 2H)	7.22–7.49 (m, 20H)	68.45 (s), −15.65 (s)	213.2(d, J(PC) 19)
3	4.23 (b, 4H), 3.93 (b, 4H)	7.41–7.44 (m, 20H)	61.58 (s)	213.0 (d, J(PC) 19)

[a] In $CDCl_3$. [b] Chemical shifts are in ppm and coupling constants in Hz. [c] Key: s, singlet; b, broad single; m, multiplet; t, triplet; d, doublet.

formation of **3** under photochemical conditions increased with increasing reaction time or temperature. It is quite surprising that thermal reaction yielded **1** in no higher than 3%. The highest yield for **3** could be best achieved by simple UV irradiation at room temperature for at least 5 h. Thermal reactions in an aromatic solvent of high boiling point such as toluene always led to the formation of the tetracarbonyl derivative **2** as the major product. Judging from these observations, the BPPF ligand seems to prefer to form unidentate biphosphine complexes **2** and **3** as far as the reactions with $Fe(CO)_5$ are concerned. Thus special care must be taken to form the expected chelate diphosphine complex such as **1**. To the best of our knowledge, **2** and **3** are among the first examples [28,29] of this ligand functioning as a unidentate ligand although there are quite a few examples for unidentate diphosphine complexes incorporating such a chelate as 1,2-bis(diphenylphosphino)-ethane [30–39]. As **2** has a free phosphine group, it may function as another candidate for mixed-metal complexes containing BPPF. This subject will be addressed in our future communication.

The formation of **1–3** can be readily confirmed by their analytical and other spectroscopic data listed in Tables 4 and 5.

The tricarbonyl derivative **1** shows three strong CO stretching bands at 1983, 1913, and 1883 cm^{-1} in addition to a weak band at 2045 cm^{-1}. The pattern of the bands is similar to that found for other derivatives of the type (diphos)$Fe(CO)_3$ [40–42]. The presence of three carbonyls comes from the mass spectrum of this compound which shows the parent peak at $m/e = 694$ in addition to other peaks associated with the loss of up to three carbonyl groups. As expected, this pentacoordinate iron(0) complex should be quite fluxional in solution undergoing the Berry pseudorotation [42,43]. This is confirmed by the ^{13}C and ^{31}P NMR spectra of this compound. The ^{31}P NMR exhibits only a single phosphorus signal (δ 64.85 ppm) and the ^{13}C NMR pattern in the carbonyl region consists of a 1/2/1 triplet due to the coupling between two equivalent ^{31}P nuclei ($I = 1/2$) and three equivalent CO groups. This same behaviour has also been observed in the case of (dmpe)$Fe(CO)_3$ (dmpe = 1,2-bis(dimethylphosphino)ethane) [42]. In order to obtain more definitive structural information, the X-ray crystal structure has been determined. The structure labelling scheme of **1** is shown in Fig. 1. Relevant bond distances and angles are listed in Table 3.

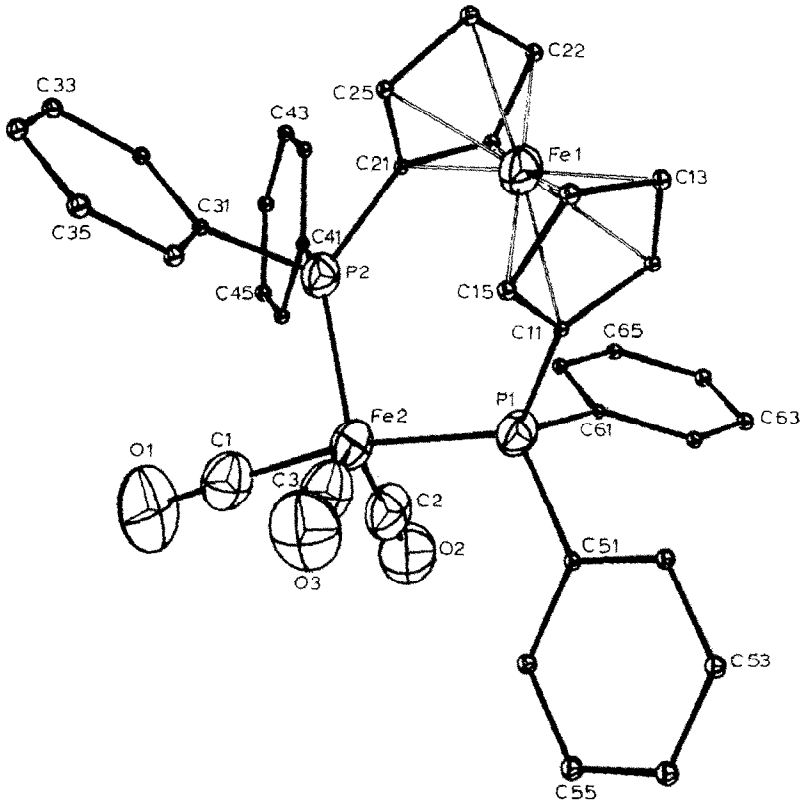


Fig. 1. ORTEP drawing of the molecular structure of **1** with 50% probability thermal ellipsoids. Thermal ellipsoids of the C atom in the pH and Cp are reduced for clarity.

The metrical parameters with the BPPF ligand moiety are similar to those found in $[(BPPF)Rh(NBD)]ClO_4$ [16], $(BPPF)MX_2$ (M = Pd, Ni; X = Cl, Br) [44], $(BPPF)Mo(CO)_4$ [44]. Cyclopentadienyl rings are rotated by 28.5(3)° from the exact eclipsed conformation, and parallel within the limits of experimental error (2.2°). P atoms are slightly displaced from the ring planes toward the Fe(1) atom by 0.042(2) and 0.034(2) Å. The geometry around Fe(2) is a distorted trigonal bipyramid. Fe(2), P(2), C(2), and C(3) are regarded as being in the plane since the deviation of the Fe(2) atom from the plane consisting of P(2), C(2), and C(3) is only 0.034(2) Å. Two axial ligands are slightly bent by 12.8° from the linear configuration. The bond distances of Fe(2) to P(1) and P(2), 2.243(3) and 2.256(3) Å, respectively, are similar to those in $(dppe)Fe(CO)_3$ [45]. The distances between Fe(2) and carbonyl ligands are nearly normal and are comparable with the values for other iron carbonyl compounds [45,46].

The tetracarbonyl derivative **2** exhibits two singlets with the uncoordinated phosphorus resonance (δ −15.65 ppm) almost the same as that recorded from the free ligand while the coordinated phosphorus signal is found downfield at 68.45 ppm. There is no coupling between the two phosphorus atoms. The mass spectral pattern for **2** is identical with that for **1** except that the parent peak is missing in the case of **2**. The ^{13}C NMR in the carbonyl region and the pattern in the carbonyl stretching band are as expected.

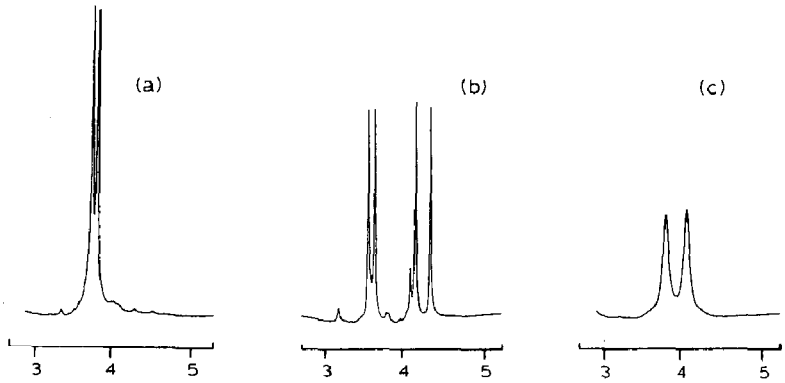


Fig. 2. ^{1}H NMR (300 MHz) spectra of (a) **1**, (b) **2**, and (c) **3** in the cyclopentadienyl region.

The octacarbonyl derivative **3** also shows four characteristic carbonyl stretching bands at 2052, 1975, 1944, and 1921 cm^{-1}. The local symmetry of the $PPh_2Fe(CO)_4$ unit in **3** can be either C_{3v} or C_{2v} depending upon whether the phosphine group is coordinated in an axial or equatorial manner. The number and intensities of these bands suggest that each PPh_2 group in BPPF is coordinated to the $Fe(CO)_4$ moiety in an equatorial manner. Axial substitution (C_{3v} symmetry) usually requires three active carbonyl stretching modes (2A + E) [47]. However, due to the possible decrease in symmetry of the complex, axial C_{3v} symmetry may also give rise to four absorption bands, and differentiation between the two structures is hard to make with certainty, except by counting bands. The mass spectrum shows the parent peak at $m/e = 890$ and other peaks corresponding to the loss of up to eight carbonyl groups as well as the ligand peak at $m/e = 554$. The ^{31}P NMR spectrum give an expected downfield singlet at 61.58 ppm for the equivalent pair of coordinated phosphines. The ^{13}C NMR in the carbonyl region is as expected, giving rise to a doublet.

Finally, regarding the ^{1}H NMR pattern for the cyclopentadienyl ring protons in the three complexes, all exhibit a simple A_2B_2 pattern with the coupling constants ^4J(HH) and ^3J(PH) being negligibly small. Thus, as shown in Fig. 2, a two-line pattern in **1** and **3** and a fourline pattern in **2** are exhibited for the AB portions. The lower two singlets in **2** are considered to be from the Cp ring where P is coordinated with iron carbonyl and the higher two singlets from the uncoordinated Cp ring [48*].

Catalytic formation of carbamates

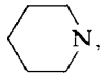
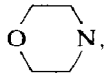
The use of acetylene alcohols such as 2-methyl-3-butyn-2-ol (**4**) and propargyl alcohol (**5**) in the ruthenium catalyzed synthesis of carbamates is well-established [8–12]. In the present work the same substrates and a series of secondary amines

* Reference number with asterisk indicates a note in the list of references.

were used employing our new iron complexes **1**–**3** as catalysts (eq. 3).

$$HC{\equiv}CC(R')_2OH + R_2NH + CO_2 \xrightarrow{[Fe]} R_2NCO_2C(R')_2C(=O)CH_3 \quad (3)$$

(**4**: $R' = CH_3$; **5**: $R' = H$) (**6** (A–I): $R' = CH_3$; **7** (A–I): $R' = H$)

(R'_2N = ,  , ,  , Et_2N, $(C_6H_{12})NMe$,

(A) (B) (C) (D) (E) (F)

, , $(CH_3H_5)_2N$)

(G) (H) (I)

Tables 6 and 7 present the yields of 1,1-dimethyl-2-oxopropyl-*N*,*N*-dialkylcarbamates (**6A**–**6I**) and 2-oxopropyl-*N*,*N*-dialkylcarbamates (**7A**–**7I**) obtained from the reactions of **4** and **5**, respectively, under a standard set of conditions.

The most notable result is that our iron complexes are highly efficient catalysts in terms of chemical yields of the carbamates isolated after the work-up described in the Experimental section. In addition there is no significant formation of any side product. The yields from the reactions of aliphatic cycloamines such as pyrrolidine (run 1), piperidine (runs 2/10), perhydroazepine (runs 3/11), morpholine (runs 4/12) are higher than any previously reported [8–12]. Of the four cyclic amines, the particularly low yields recorded with morpholine have been explained in terms of its low basicity [11]. The importance of the basicity of amine is best demonstrated by the observations that aromatic amines do not react to give the corresponding carbamates (runs 7–9/15–17). This may be due to the inability of these aromatic amines of lowered basicity to form the ammonium carbamate intermediates as

Table 6

Yields of carbamates **6A**–**6I** from **4** [a]

Run	R_2N	Substrate	Product	Catalyst		
				1	**2**	**3**
1	**A**	**4**	**6A**	50	49	45
2	**B**		**6B**	66	64	54
					24 [b]	
					43 [c]	
3	**C**		**6C**	43	40	26
4	**D**		**6D**	18	16	5
5	**E**		**6E**	45	42	20
6	**F**		**6F**	25	20	17
7	**G**		**6G**	0	0	0
8	**H**		**6H**	0	0	0
9	**I**		**6I**	0	0	0

[a] Isolated yield (%) based on the substrate. Reaction conditions: [substrate] 10 mmol; [amine] 0.1 mmol in 10 ml of CH_3CN; $P(CO_2)$ 30 atm; reaction temperature 90 °C; reaction time 24 h. [b] [catalyst] 0.2 mmol. [c] [catalyst] 0.05 mmol.

Table 7

Yields of carbamates **7A–7I** from **5**

Run	R_2N	Substrate	Product	Catalyst		
				1	**2**	**3**
10	**B**	**5**	**7B**	27 10 [b]	25	16
11	**C**		**7C**	25	23	18
12	**D**		**7D**	12	10	5
13	**E**		**7E**	28	25	20
14	**F**		**7F**	15	14	12
15	**G**		**7G**	0	0	0
16	**H**		**7H**	0	0	0
17	**I**		**7I**	0	0	0

[a] Reaction conditions are the same as described in Table 6. [b] [catalyst] 0.2 mmol.

illustrated in Fig. 3 (see below). The yields with non-cyclic amines such as diethylamine (runs 5/13) and cyclohexylmethylamine (runs 6/14) are lower than those obtained with cyclic amines. The reversed trends, however, have been reported with ruthenium complexes [8,11]. The catalytic efficiency of **1–3** in terms of chemical yields decreases in the order **1** > **2** > **3** in all reactions investigated, for unknown reasons. The amount of catalyst also plays a role, yields being highest when the catalyst concentration is 0.1 mmol (runs 2/10). Comparing the two substrates, propargyl alcohol gives poorer yields in all cases. The formation of the iron-acetylene intermediate (Fig. 3) might have been accelerated by the increased electron-donating

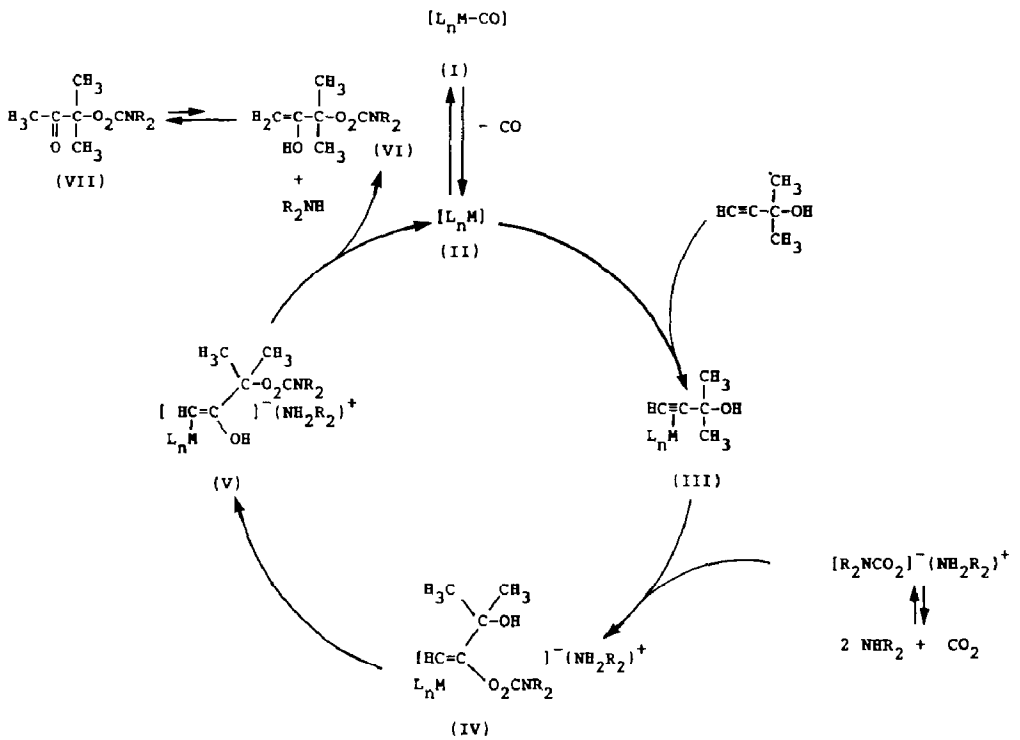


Fig. 3. A possible cycle for the catalytic formation of carbamates catalyzed by the complexes **1–3**.

ability of the substrate (4) due to two methyl groups as compared with propargyl alcohol (5). As would be expected from the nature of the carbamates produced, all reactions proceed in a totally regioselective manner, directing the addition of ammonium carbamate onto the terminal position of the acetylenic alcohol as is the case in ruthenium catalyzed reactions [8–12].

These observations, coupled with other well documented facts concerning the catalytic formation of carbamates [8,11], lead us to propose a possible catalytic cycle as shown in Fig. 3.

The first step of the cycle involves coordination of the acetylenic alcohol substrate to the active catalyst II generated by loss of a carbonyl from precursor I. Though less common and less stable than their corresponding metal olefin complexes, the formation of metal alkyne complexes is well-documented and finds numerous synthetic applications [49,50]. An alternative route to this first step may be suggested involving an iron-vinylidene intermediate similar to the ruthenium-vinylidene mechanism proposed by Dixneuf et al. [12]. Nucleophilic addition to this iron-acetylene π complex (III) of ammonium carbamate, produced from the reaction of carbon dioxide and amine, forms the iron-olefin intermediate. Transesterification in IV followed by protonation of V generates the enol carbamate VI and amine with concomitant regeneration of the active catalyst II. Tautomerization of VI finally yields the carbamate VII. Obviously, isolation and spectroscopic studies of the intermediates species involved in this catalytic cycle would help to understand these reactions. Further studies are being made to clarify these points.

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