Cyclopropanation and Diels–Alder reactions catalyzed by the first heterobimetallic complexes with bridging phosphinooxazoline ligands†

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The bimetallic complex *trans*-[(OC)₃Fe(μ-**L**^{P,N})₂Cu]BF₄ (**2**), which contains two bridging phosphinooxazoline ligands, is the first metal–metal bonded six-membered ring system with P,N donors and its crystal structure shows a unique bimetallic cradle conformation. This complex is an efficient catalyst for the cyclopropanation of styrene by ethyl diazoacetate and for the Diels–Alder reaction between cyclopentadiene and methacrolein, these reactions being catalyzed for the first time by heterometallic complexes.

Introduction

Heterometallic complexes are extensively studied in the search for cooperative effects between metal centres of different natures, for metallosite selective reactions and/or chemical transformations occurring at both metal centres in sequence or in a concomitant manner.[1] Special interest arises of course when their reactivity is different from that of their homometallic or mononuclear analogues. Such differences may be related to the presence of a new chemical bond (direct metal–metal interaction), to changes in the coordination sphere of a metal centre resulting from the stereoelectronic properties of an adjacent metal, or to their combination.

Bi- or polyfunctional ligands, in particular functional phosphines, are often used as assembling ligands to stabilise bimetallic structures and have mostly led to the formation of five-membered metallocycles.[2] Metal–metal bonded systems with larger bimetallic cycles have been less studied[3] and in the case of (P,N) ligands there appears to be no six-membered ring system known and only one seven-membered macrocycle has been very recently reported.[4]

Although phosphinooxazoline ligands are being much investigated as P-monodentate or P,N-chelating ligands,[5] there is no reported example, to the best of our knowledge, of bridging behaviour for such ligands. We have now investigated their potential as assembling ligands to form metal–metal bonded six-membered ring systems.

Results and discussion

Using the ligand (2-oxazoline-2-ylmethyl)diphenylphosphine (**L**^{P,N}),[6] we have prepared *trans*-[Fe(CO)₃(**L**^{P,N})₂] **1** and used it to form the Fe–Cu complex *trans*-[(OC)₃Fe(μ-**L**^{P,N})₂Cu]BF₄ (**2**), with which the catalytic properties of heterometallic complexes have been examined for the first time in olefin cyclopropanation and Diels–Alder reactions. Complex **1**, whose structure has been determined by X-ray diffraction (Fig. 1), was reacted with a stoichiometric amount of [Cu(NC-Me)₄][BF₄] (Scheme 1) to afford the bimetallic complex **2** in 91% yield.
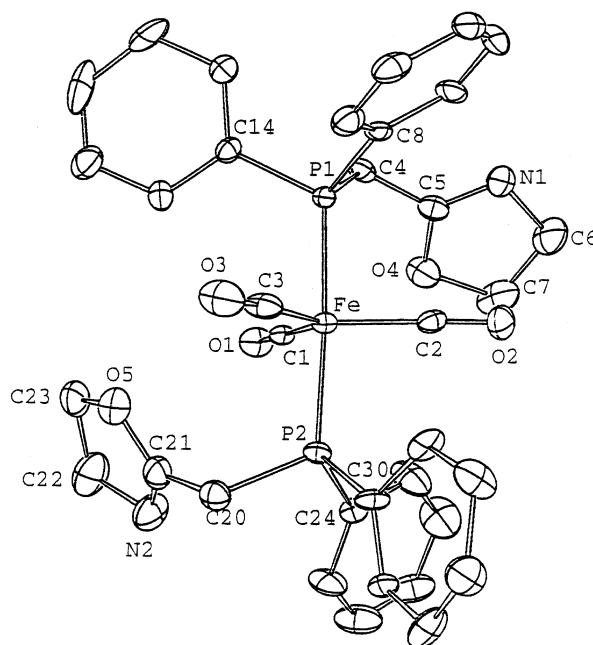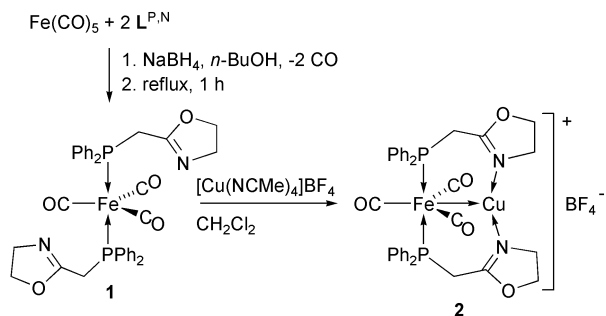

Fig. 1 View of the crystal structure of complex *trans*-[Fe(CO)₃(**L**^{P,N})₂] (**1**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Fe–C(1) 1.763(9), Fe–C(2) 1.78(1), Fe–C(3) 1.79(1), Fe–P(1) 2.197(3), Fe–P(2) 2.213(3), C(5)–N(1) 1.28(1), C(21)–N(2) 1.28(1), N(1)–C(6) 1.48(1), N(2)–C(22) 1.48(1), P(1)–C(4) 1.848(9), P(2)–C(20) 1.87(1), C(5)–O(4) 1.34(1), C(21)–O(5) 1.34(1); C(1)–Fe–C(2) 118.7(4), C(1)–Fe–C(3) 120.4(5), C(2)–Fe–C(3) 120.9(5), P(1)–Fe–P(2) 176.6(1), P(1)–C(4)–C(5) 116.1(6), P(2)–C(20)–C(21) 115.2(7).

Despite the "*anti*-type" spatial arrangement of the oxazoline groups in **1**, which minimizes steric repulsion, the **L**^{P,N} ligands can function as bridges and lead to two fused six-membered rings in **2**. The ν(C=N) vibration at 1643 cm^{-1} is consistent with the *N*-coordination of the oxazoline to Cu(I) and a singlet is observed in the ^{31}P{^{1}H} NMR spectrum at δ 71.71. No signal characteristic of MeCN was observed, indicating complete displacement from the precursor. The P*C*H₂ carbon atoms give rise in ^{13}C{^{1}H} NMR to an AA′XX′ multiplet from which a $^2J_{PP}$ coupling constant of 34.8 Hz was extracted

Scheme 1

Fig. 3 Perspective view of the structure of **2** along the P–Fe–P axis showing the curvature generated by the two, mutually eclipsed assembling phosphinooxazoline ligands. The Fe–Cu bond has been omitted for clarity and only the *ipso* carbons of the phenyl groups are shown.

(*g*NMRV3.6 simulation). This value is similar to those reported in the literature for related *trans*-[Fe(CO)₃LL′] complexes (L = tertiary phosphines).[7] The v(CO) vibrations (CH₂Cl₂) at 1986(w), 1915(s) and 1882(vs) cm^{-1} are consistent with a meridional arrangement of the carbonyls around the Fe centre. The structure of **2**·1.5CH₂Cl₂ was established by X-ray diffraction (Fig. 2). The molecule contains a mirror plane which includes the metals and the CO ligands. The coordination geometry about the Fe atom may be described as distorted octahedral with the P atoms *trans* to one another and the CO ligands in a *mer* arrangement. Alternatively, if one ignores the Fe–Cu bond, it may be viewed as trigonal bipyramidal, as in **1**, a geometry consistent with a formally zero-valent Fe centre. The Cu(I) atom exhibits a trigonal coordination involving the Fe atom and the two nitrogen atoms from the L^{P,N} ligands. The Fe–Cu distance of 2.5441(7) Å is longer than in a four-membered cycle with a bridging aminosilyl ligand [2.530(2) Å],[8] in five-membered ring complexes with bridging 2-(diphenylphosphino)pyridine (Ph₂PPy) [2.501(2) Å, 2.512(2) Å],[2d]

or bridging dppm [2.497(2),[9a] 2.540(2) Å[9b]] or in a bis-seven-membered macrocyclic compound [2.4572(7) Å],[4] but is similar to that in a complex with bridging *N*-(diphenylphosphino-methyl)morpholine [2.550(1) Å].[10] The Fe–Cu distance in **2** is equal to the sum of the atomic radii of iron and copper (2.54 Å). Owing to the presence of a mirror plane in the molecule, the P, CH₂ and oxazoline groups of one ligand are respectively eclipsed with those of the other ligand. This creates a sort of molecular cradle cavity (Fig. 3), which results from the ring size and the ligand conformation and contrasts with the generally rather flat structures exhibited by dinuclear complexes containing other types of assembling ligands, such as Ph₂PPy or dppm. The C(1)–Fe–C(2) angle of 131.0(2)° has opened up compared to **1** owing to the presence of the Cu centre and this leads to a C(1)–Cu separation of 2.339(4) Å and a Fe–C(1)–O(1) angle of 174.32(1)°.

Complex **2** is an efficient catalyst for the cyclopropanation of styrene with ethyl diazoacetate [eqn. (1)]. The reaction was carried out in 1,2-dichloroethane at room temperature (1 mol% of **2** based on ethyl diazoacetate), with an olefin/ethyl diazoacetate ratio of 2:1. The ethyl diazoacetate was added very slowly over a period of 35 h.[11] *Trans*- and *cis*-ethyl 2-phenyl-1-cyclopropanecarboxylates were obtained, in 91% isolated yield in a 70:30 ratio, and complex **2** could still be detected after complete consumption of the ethyl diazoacetate. These results compare favourably with literature data for mononuclear copper catalysts.[12] However, we found that with [Cu(NCMe)₄][BF₄] as a catalyst under similar conditions, *trans*- and *cis*-ethyl 2-phenyl-1-cyclopropanecarboxylates were obtained in 97% isolated yield in a 64:36 ratio.

(1)

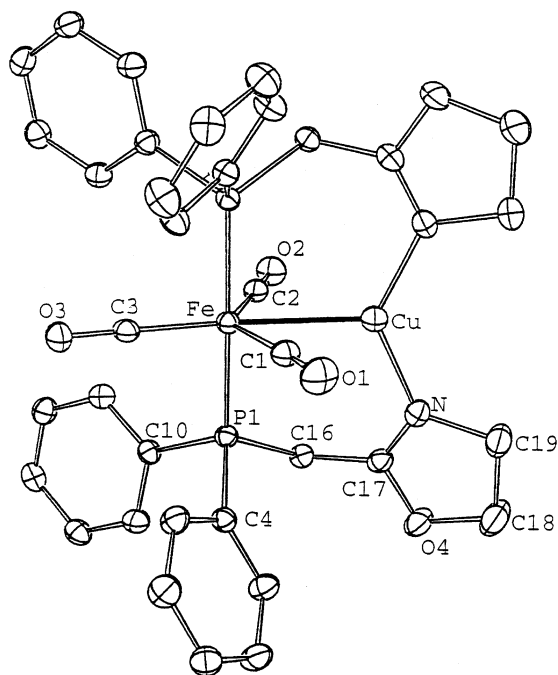**Fig. 2** View of the crystal structure of complex **2**. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Fe–Cu 2.5441(7), Fe–C(1) 1.795(4), Fe–C(2) 1.777(4), Fe–C(3) 1.786(4), Fe–P 2.230(1), Cu–C(1) 2.339(4), Cu–C(2) 2.514(4), Cu–N 1.939(2), C(17)–N 1.270(3); C(1)–Fe–C(2) 131.0(2), C(1)–Fe–C(3) 108.1(2), C(2)–Fe–C(3) 121.0(2), P(1)–Fe–P(1′) 173.75(4), Cu–Fe–C(1) 62.4(1), Cu–Fe–C(2) 68.5(1), Cu–Fe–C(3) 170.5(1), Cu–Fe–P 90.16(2), Fe–Cu–N 113.33(7), N–Cu–N′ 132.7(1), Fe–C(1)–O(1) 174.32(1), Fe–C(2)–O(2) 178.32(1), Fe–C(3)–O(3) 178.96(1).
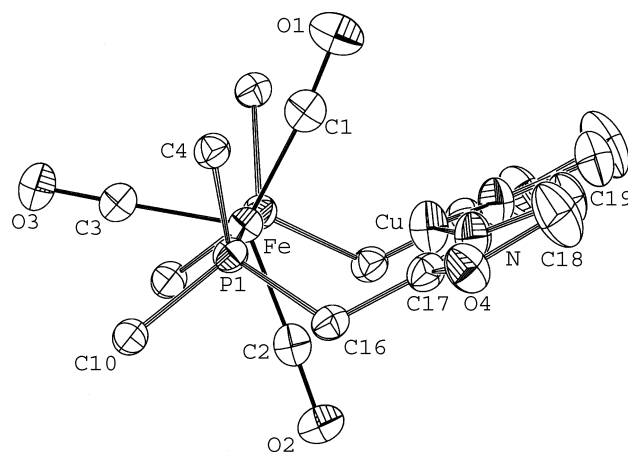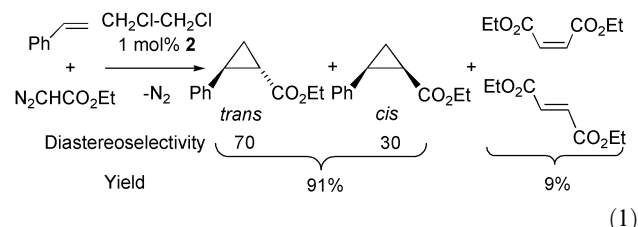
For further comparison, we prepared the new mononuclear complex (CuL^{N,P,N})BF₄ [L^{N,P,N} = bis(2-oxazoline-2-ylmethyl)-phenylphosphine)],[13] in which the coordination sphere of the Cu(I) ion contains two oxazoline ligands disposed similarly to those in **2** (in which additionally the Fe centre behaves like a metalloligand). With this complex as a catalyst, *trans*- and *cis*-ethyl 2-phenyl-1-cyclopropanecarboxylates were obtained in 91% isolated yield in a 68:32 ratio.

[Cu(L^{N,P,N})][BF$_4$]
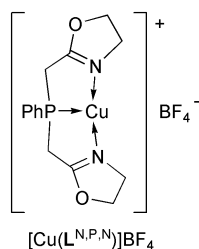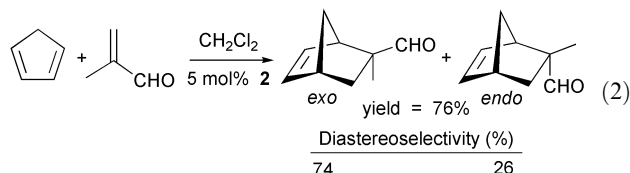
However, to the best of our knowledge, **2** is the first metal–metal bonded heterometallic catalyst to be used in olefin cyclopropanation.

Furthermore, **2** was found to catalyze the Diels–Alder reaction of methacrolein with cyclopentadiene [eqn. (2)]. The reaction reached 76% convertion after stirring for 162 h at −20 °C.[14]

$$\text{Diastereoselectivity (\%)}$$

74	26

The *exo*:*endo* ratio of 74/26 (determined by ^{1}H NMR)[15] compares favourably with the best copper systems reported in the literature,[14] amongst which we could not find any Cu(I) system. For a better comparison, we therefore evaluated [Cu(NC-Me)$_4$][BF$_4$] as a catalyst for this reaction under the same conditions. The reaction reached 70% convertion after stirring for 162 h at −20 °C and the *exo*:*endo* ratio was 85/15 (determined by ^{1}H NMR). In contrast, (CuL^{N,P,N})BF$_4$ did not catalyze this reaction, although the utilization of phosphinooxazoline ligands and Cu(I) salts has been reported for the catalytic enantioselective aza-Diels–Alder reaction of imines.[16]

Conclusion

The complex *trans*-[Fe(CO)$_3$(L^{P,N})$_2$] **1** is a readily available precursor for the construction of new bimetallic complexes with phosphinooxazoline assembling ligands, as exemplified with the formation of *trans*-[(OC)$_3$Fe(μ-L^{P,N})$_2$Cu]BF$_4$ (**2**), a formally Fe(0)→Cu(I) complex. The latter appears to be the first metal–metal bonded heterometallic complex successfully tested in olefin cyclopropanation and Diels–Alder reactions. Although our preliminary catalytic results do not demonstrate a clear advantage of the bimetallic system over a well-chosen mononuclear Cu(I) catalyst, we had to resort to different Cu(I) precursors to observe catalysis in each reaction. We expect further developments in the context of bimetallic effects in catalysis[1] and of enhanced selectivity properties associated with the unique "bimetallic cavity-like" shape of complex **2**. Current extensions include the use of chiral systems and we have already prepared the Fe–Cu complex **2*** (see Experimental) containing the enantiopure ligand L$^{P,N_{Ph}}$.[17] Its evaluation in catalysis will be the subject of further studies.

2*
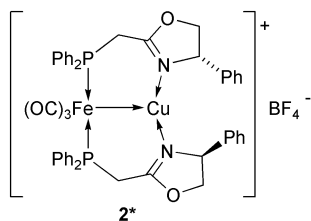
Experimental

All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional

methods. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a FT Bruker AC300 instrument, ^{13}C NMR spectra at 75.477 or 100.628 MHz on FT Bruker AC300 or AC400 instruments, respectively, and the IR spectra in the 4000–400 cm^{-1} range on a Bruker IFS66 FT spectrometer. The ligands (L^{P,N}),[6] (L^{N,P,N})[13] and (L$^{P,N_{Ph}}$)[17] were prepared according to the literature.

Synthesis of the complexes

Synthesis of *trans*-[Fe(CO)$_3${(2-oxazoline-2-ylmethyl)diphenylphosphine}$_2$] (1). [Fe(CO)$_5$] (0.942 mL, 7.11 mmol) was added over 5 min to a stirred mixture of L^{P,N} (6.15 g, 22.9 mmol) and NaBH$_4$ (0.271 g, 7.11 mmol) in 150 mL of *n*-BuOH. Vigourous gas evolution occurred and a yellow solution resulted. The reaction mixture was refluxed for 2 h (longer reaction times did not increase the yield), and cooled to room temperature. A yellow precipitate was already observed after 15 min under reflux. After concentration of the solution and addition of hexane, large quantities of crystals formed upon cooling the mixture in a freezer for 12 h. The precipitate was collected by filtration and washed with cold methanol (3 × 10 ml) to remove the borate salts. The solid product was dried under vacuum. The IR and ^{31}P{^{1}H} NMR spectra showed the isolated product to be exclusively *trans*-[Fe(CO)$_3$(L^{P,N})$_2$] (4.82 g, 90%). IR (CH$_2$Cl$_2$): v(CO) 1974 (w), 1886 (vs), v(C=N) 1661(m) cm^{-1}; (KBr): v(CO) 1973 (vw), 1931 (sh), 1876 (vs), v(C=N) 1658 (ms) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 7.78–7.42 (m, 20H, aromatics), 4.06 (t, 4H, $^3J_{HH}$ = 9.0 Hz, OCH$_2$), 3.75 (t, 4H, $^3J_{HH}$ = 9.0 Hz, NCH$_2$), 3.60 (m, 4H, J_{PH} = 7.9 Hz, PCH$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 213.2 (t, 3CO, $^2J_{PC}$ = 22 Hz), 162.7 (s, C=N), 137.0 (d, $^1J_{PC}$ = 22 Hz, *ipso*-aryl), 132.8 (s, *m*-aryl), 130.6 (s, *p*-aryl), 128.6 (s, *o*-aryl), 67.9 (s, OCH$_2$), 55.2 (s, NCH$_2$), 34.1 (m, PCH$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 78.4 (s) Anal. Calcd. for C$_{35}$H$_{32}$FeN$_2$O$_5$P$_2$: C, 61.94; H, 4.76; N, 4.13. Found: C, 61.81; H, 5.01; N, 3.89%.

Synthesis of 2. Solid [Cu(NCMe)$_4$]BF$_4$ (0.464 g, 1.47 mmol) was added to a solution of **1** (0.997 g, 1.47 mmol) in CH$_2$Cl$_2$ at 25 °C. The mixture was stirred vigorously for 20 min, the yellow solution became deeper almost immediately. The mixture was concentrated and slow diffusion of pentane afforded yellow crystals (1.11 g, 91%). IR (CH$_2$Cl$_2$): v(CO) 1986 (mw), 1915 (s) 1882 (vs), v(C=N) 1643 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 7.58–7.52 (m, 20H, aromatics), 4.46 (t, 4H, $^3J_{HH}$ = 9.7 Hz, OCH$_2$), 4.17 (t, 4H, $^3J_{HH}$ = 9.7 Hz, NCH$_2$), 3.56 (appearance of "filled-in d" analyzed as an AA'XX' spin system (X = P), 4H, $^{2+4}J_{PH}$ = 9.1, $^2J_{PP}$ = 34.8 Hz, PCH$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 210.0 (t, 3CO $^2J_{PC}$ = 25 Hz), 168.7 (s, C=N), 133.9–128.9 (aromatics), 68.6 (s, OCH$_2$), 55.3 (s, NCH$_2$), 31.6 (m, AA'XX' spin system (X = P), $^{2+3}J_{PC}$ = 19.6, J_{PP} = 34.8 Hz, PCH$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 71.7 (s). Anal. Calcd. for C$_{35}$H$_{32}$BCuF$_4$FeN$_2$O$_5$P$_2$·1.5CH$_2$Cl$_2$·0.5MeCN: C, 46.12; H, 3.77; N, 3.59. Found: C, 46.15; H, 3.57; N, 3.87%.

Synthesis of [Cu(L^{N,P,N})]BF$_4$. Solid [Cu(NCMe)$_4$]BF$_4$ (0.781 g, 2.48 mmol) was added to a solution of L^{N,P,N} (0.686 g, 2.48 mmol) in CH$_3$CN at 25 °C. The mixture was stirred vigorously for 20 min and a white precipitate formed after hexane was added (1.04 g, 98%). IR (KBr): v(C=N) 1644 (vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.97 (s, 3H, CH$_3$CN), 3.17 (m, 2 H, part A of an ABX system (A = B = H, X = P), PCH$_A$H$_B$), 3.45 (m, 2 H, part B of an ABX system, PCH$_A$H$_B$), 3.74 (m, 2 H, part A of an ABFG system (A = B = F = G = H), NCH$_A$H$_B$), 3.89 (m, 2 H, part G of an ABFG system, NCH$_A$H$_B$), 4.48 (m, 2 H, part F of an ABFG system, OCH$_F$H$_G$), 4.55 (m, 2H, part B of an ABFG system, OCH$_F$H$_G$), 7.58–7.89 (m, 5 H, aromatics), ^{31}P{^{1}H} NMR (DMSO-d_6):

δ −22.3 (s). Anal. Calcd. for $C_{14}H_{17}BCuF_4N_2O_2P\cdot CH_3CN$: C, 41.11; H, 4.32; N, 8.99. Found: C, 40.57; H, 4.30; N, 9.00%. At this stage, we cannot state whether the molecule of acetonitrile found in solution and in the solid (elemental analysis) corresponds to a molecule of solvation or to a Cu(I)-bound ligand.

Synthesis of *trans*-[Fe(CO)$_3$(L$^{P,N_{Ph}}$)$_2$] (1*). To a stirred mixture of $L^{P,N_{Ph}}$ (5.33 g, 15.4 mmol) and $NaBH_4$ (0.181 g, 4.76 mmol) in 150 mL of *n*-BuOH, [Fe(CO)$_5$] (0.630 mL, 4.76 mmol) was added over 5 min. Vigourous gas evolution occurred and a yellow solution resulted. The reaction mixture was refluxed for 2 h (longer reaction times did not increase the yield), and cooled to room temperature. After concentration of the solution and addition of hexane, a yellow powder formed upon cooling the reaction mixture in a freezer for 12 h. The precipitate was filtered and washed with cold methanol (3 × 10 ml) to remove the borate salts. The solid product was dried under vacuum. Both IR and ^{31}P NMR spectra showed the isolated product to be exclusively *trans*-[Fe(CO)$_3$(L$^{P,N_{Ph}}$)$_2$] (0.382 g, 9.70%). IR (CH$_2$Cl$_2$): v(CO) 1970 (w), 1882 (vs), v(C=N) 1657 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 8.10–6.90 (m, 30H, aromatics), 5.09 (dd, 2H, A part of an AB spin system $^2J(H_AH_B)$ = 9.8 Hz, $^3J(H_AH)$ = 8.6 Hz, OCH$_A$H$_B$), 4.45 (dd, 2H, B part of an AB spin system $^2J(H_AH_B)$ = 9.8 Hz, $^3J(H_BH)$ = 8.6 Hz, OCH$_A$H$_B$), 3.89 (t, 2H, $^3J(H_AH) \approx$ $^3J(H_BH)$ = 8.6 Hz, NCH), 3.75 (m, 2H, A part of an AB spin system, PCH$_A$H$_B$), 3.64 (m, 2H, B part of an AB spin system, PCH$_A$H$_B$). ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 77.7 (s). Anal. Calcd. for $C_{47}H_{40}FeN_2O_5P_2$: C, 67.94; H, 4.86; N, 3.37. Found: C, 67.99; H, 4.86; N, 3.39%.

Synthesis of *trans*-[(OC)$_3$Fe(μ-L$^{P,N_{Ph}}$)$_2$Cu]BF$_4$ (2*). Solid [Cu(NCMe)$_4$]BF$_4$ (0.145 g, 0.46 mmol) was added to a solution of *trans*-[Fe(CO)$_3$(L$^{P,N_{Ph}}$)$_2$] (1*) (0.382 g, 0.46 mmol) in CH$_2$Cl$_2$ at 25 °C. The yellow solution became deeper almost immediately and the mixture was stirred vigorously for 20 min. Concentration and slow diffusion of pentane afforded a yellow powder (0.411 g, 91%). IR (CHCl$_3$): v(CO) 1988 (mw), 1919 (s) 1885 (vs), v(C=N) 1640 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 8.00–6.70 (m, 30H, aromatics), 4.68 (br, 4H, OCH$_2$), 4.11 (br, 2H, NCH), 3.45 (m, 2H, A part of an AB spin system, PCH$_A$H$_B$), 3.61 (m, 2H, B part of an AB spin system, PCH$_A$H$_B$). ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 69.65 (s). Anal. Calcd. for $C_{47}H_{40}BCuF_4FeN_2O_5P_2\cdot CH_3CN$: C, 57.58; H, 4.24; N, 4.11. Found: C, 58.00; H, 4.07; N, 4.03%.

Catalytic reactions

Cyclopropanation. The reaction was carried out in 1.5 mL of 1,2-dichloroethane at room temperature using 1 mol% catalyst (based on ethyl diazoacetate), activated with phenylhydrazine (0.2 mL of a 1% solution in 1,2-dichloroethane).[11] In order to minimize the formation of diethyl fumarate and maleate (which result from carbene dimerization), an olefin:ethyldiazoacetate ratio of 2:1 was used and the ethyl diazoacetate was added very slowly over a period of 35 h. The yields and diastereoselectivities were determined by ^{1}H NMR analysis after total consumption of ethyl diazoacetate.

Diels–Alder reaction. The Diels–Alder addition of methacrolein to cyclopentadiene was performed in 4 mL of CH$_2$Cl$_2$ with 2.0 mmol (0.168 mL) dienophile, 2.4 mmol (0.20 mL) cyclopentadiene freshly cracked, and 5 mol% catalyst. The reaction mixture was stirred at −20 °C for 162 h and then filtered through silica gel with Et$_2$O elution to give after concentration (*exo*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde and (*endo*)-2-methyl bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde as a clear colourless oil.

Crystallographic analysis of 1 and 2·1.5CH$_2$Cl$_2$

Single crystals were selected and mounted on a Kappa CCD diffractometer. Data were collected using phi-scans and the structure was solved using direct methods and refined against F^2 using SHELX 97 software.[18,19] No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C–H} = 0.95$ Å, $U_{11} = 0.04$).

Crystal data for **1**: $C_{35}H_{32}FeN_2O_5P_2$, $M = 678.45$, orthorhombic, $a = 41.966(1)$ Å, $b = 34.575(1)$ Å, $c = 9.741(1)$ Å, $V = 14\,133(2)$ Å^3, $T = 173$ K, space group: *Fdd*2, $Z = 16$, μ(Mo-Kα) = 0.559 mm^{-1} ($\lambda = 0.71073$ Å), 17 857 reflections measured, 2614 reflections with $I > 3\sigma(I)$, $R = 0.046$ and $Rw = 0.079$.

For **2·1.5CH$_2$Cl$_2$**: $C_{35}H_{32}BCuF_4FeN_2O_5P_2\cdot1.5CH_2Cl_2$, $M = 956.2$, monoclinic, $a = 24.4623(7)$ Å, $b = 14.3872(6)$ Å, $c = 12.4708(4)$ Å, $\beta = 111.598(4)$,° $V = 4080.9(5)$ Å^3, $T = 173$ K, space group $C2/m$, $Z = 2$, μ(Mo-Kα) = 1.213 mm^{-1} ($\lambda = 0.71073$ Å), 13 114 reflections measured, 4571 reflections with $I > 3\sigma(I)$, $R = 0.046$ and $Rw = 0.057$.

CCDC reference numbers 177707 and 177708.

See http://www.rsc.org/suppdata/nj/b2/b206410n/ for crystallographic data in CIF or other electronic format.

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