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MECHANISTIC INSIGHTS INTO CATALYTIC CYCLOPROPANATION BY COPPER(I) PHOSPHINE COMPLEXES. X-RAY CRYSTAL STRUCTURES OF $[Cu(F{-}BF_3)(PCy_3)_2]$ (Cy = cyclo-C_6H_{11}) AND $[Cu(MeCN)_2\{1,2\text{-}C_6H_4CH_2NMe_2(PPh_2)\}]BF_4$

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Abstract—The complexes $[Cu(PPh_3)_n(MeCN)_{4-n}]BF_4$ ($n = 0$, 2–3), $[Cu(F{-}BF_3)(PCy_3)_2]$, $[Cu(MeCN)_2\{1,2\text{-}C_6H_4CH_2NMe_2(PPh_2)\}]BF_4$ and species formed by *in situ* addition of various ligands to $[Cu(MeCN)_4]BF_4$ are all active catalysts for cyclopropanation reactions using $N_2{=}CH(CO_2Et)$. With styrene as a substrate the *trans/cis* selectivity in the product cyclopropane may be somewhat controlled by the appropriate choice of phosphine ligand. Catalysis by $[Cu(MeCN)_2(PPh_3)_2]BF_4$ and $[Cu(MeCN)_2\{1,2\text{-}C_6H_4CH_2NMe_2(PPh_2)\}]BF_4$ is proposed to involve alkene coordination, while that by $[Cu(MeCN)(PPh_3)_3]BF_4$ and $[Cu(F{-}BF_3)(PCy_3)_2]$ is not. The structures of the catalysts showing the highest selectivity have been determined. For monoclinic $[Cu(F{-}BF_3)(PCy_3)_2]$ the molecule contains an unusually large P—Cu—P angle (*ca* 160°).

Cyclopropanes constitute important structural fragments in many pharmaceutical and insecticidal molecules of economic importance.[1] One attractive cyclopropanation route to these targets is the decomposition of a diazo compound in the presence of an alkene.[2,3] Although many transition metals, in one form or another, show activity for this reaction, traditionally copper species are recognized as pre-eminent catalysts. A wide variety of copper sources, including activated copper powders,[4] simple copper(I) or copper(II) salts[5] and complexes such as $[CuCl\{P(OR)_3\}]_4$ (R = alkyl),[6,7] are active precatalysts. Recent studies have concentrated on reactions employing chiral ligands in the presence of labile copper(I) sources to fashion highly enantioselective (> 95% enantiomeric excess, e.e.) cyclopropanation reactions.[8–10]

It is popularly assumed, generally without proof, that in all these reactions unstable copper(I) carbenoid intermediates form and that these are trapped by substrate alkene resulting in cyclopropanation (Scheme 1). Alternatively, two carbene complexes may undergo binuclear C—C coupling to yield a substituted alkene, a commonly observed reaction by-product in catalytic cyclopropanation reactions. One reason for assuming copper(I) intermediates is that many diazo compounds show appreciable reductive ability and reduction of copper(II) sources to the lower oxidation state is facile under these conditions. Relatively few mechanistic studies in copper(I) catalysed cyclopropanation have been reported.[5,11] Whether a single reaction coordinate and set of common intermediates is responsible is unclear. These vagaries piqued our interest in the mechanism of catalytic cyclopropanation and led us to begin an investigation into the possibility of designing a cyclo-

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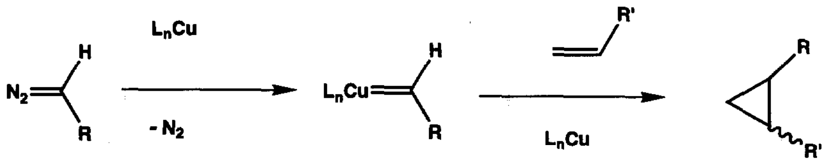

Scheme 1.

propanation reaction with well-defined catalytic intermediates, the preliminary results of which are the subject of this paper.

We selected the complex $[Cu(MeCN)_4]BF_4$ (**1**) as a versatile candidate with which to probe catalytic cyclopropanation for a number of reasons: complex **I** is easily prepared, fairly air-stable and the $[BF_4]^-$ anion can be systematically varied if necessary.[12] The cations $[Cu(MeCN)_4]^+$ are known to be active cyclopropanation catalysts.[10] The acetonitrile ligands in **1** are rather labile. For example, partial displacement with EPh_3 (E = P, Sb) forms the family of complexes $[Cu(MeCN)_{4-n}(EPh_3)_n]^+$ ($n = 2$–4).[13] Thus, steric and electronic modification of the copper(I) environment is possible. The presence of phosphine ligands also allows ^{31}P NMR reaction monitoring of such species on exposure to the catalytic reaction conditions.

RESULTS AND DISCUSSION

Preparation of the copper complexes

The preparation of $[Cu(MeCN)_4]BF_4$ (**1**), $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (**2**) and $[Cu(MeCN)(PPh_3)_3]BF_4$ (**3**) follows the routine literature preparations used for the related ClO_4 and PF_6 salts.[12,13] Attempts to prepare $[Cu(MeCN)_3(PPh_3)]BF_4$ deserve special comment. Addition of 1 equivalent of PPh_3 to **1** results in mixtures containing variable Cu : PPh_3 ratios. Fractional crystallization of the mixture from CH_2Cl_2–Et_2O leads to well-formed needles with a PPh_3 : MeCN ratio of 3 : 5, as judged by ^1H NMR spectroscopy. However, crystallographic investigation of these needles reveal them to be $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (**2**).* The hexafluorophosphate salt $[Cu(MeCN)_3(PPh_3)]PF_6$ is suggested on the basis of ^{31}P NMR spectroscopic evidence, but these claims are not yet substantiated crystallographically.[14] The versatility of acetonitrile replacement in **1** is further demonstrated by its reactions with PCy_3 (Cy = cyclo-C_6H_{11}), the nitrogen–phosphorus chelate **4** and other ligands in Scheme 2.

Reaction of PCy_3 and **1** in a 2 : 1 ratio affords colourless crystals. The toluene solubility of this material is inconsistent with the properties of a salt, suggesting the formula $[Cu(F—BF_3)(PCy_3)_2]$ (**5**). Consistent with this idea the ν(B—F) stretch observed in the solid-state IR spectrum is sharper than that observed for $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (**2**) and $[Cu(MeCN)(PPh_3)_3]BF_4$ (**3**) but different from that of $[Cu(F—BF_3)(PPh_3)_3]$ (**6**) prepared by pyrolysis of **3** under vacuum and subsequent recrystallization. The formation of **5** is confirmed by the absence of an MeCN signal in the ^1H NMR spectrum and by the results of an X-ray crystallographic study (see later).

The nature of tetrafluoroborate coordination in solutions of **5** is apparent from ^{19}F NMR studies. Two signals are seen for solutions of **5** in C_6D_6, acetone-d_6 or DMSO-d_6 in the range δ_F -145 to -150. The exact chemical shifts depend on the solvent, however, the integral ratio of the two signals shows the larger signal to be due to ^{10}B—F environments while the smaller signal represents ^{11}B—F. While the smaller signal remains a featureless envelope in all solvents the larger signal, in DMSO-d_6, shows the four-line multiplet [$J(^{10}BF) = 1.2$ Hz] expected for an uncoordinated $[BF_4]^-$ anion. For comparison, the $J(^{10}BF)$ coupling for $NaBF_4$ (δ_F -152.10) in D_2O is 2.2 Hz. These results indicate that the salt $[Cu(PCy_3)_2]BF_4$ is exclusively present in DMSO-d_6. In less polar solvents an equilibrium between **5** and $[Cu(PCy_3)_2]BF_4$ probably exists. A related anion exchange process has recently been characterized by ^{27}Al NMR spectroscopy for the complex $Ti(CH_2SiMe_3)(Cl—AlCl_3)(\eta\text{-}C_5H_5)_2$.[15]

The reaction of **4** with $[Cu(MeCN)_4]BF_4$ (**1**) affords a moderate yield (66%) of the complex $[Cu(MeCN)_2\{1,2\text{-}(Me_2NCH_2)(PPh_2)C_6H_4\}]BF_4$ (**7**) (Scheme 2). The purification procedure is complicated by the presence of yellow impurities and by the higher air-sensitivity of **7** compared to the bis-

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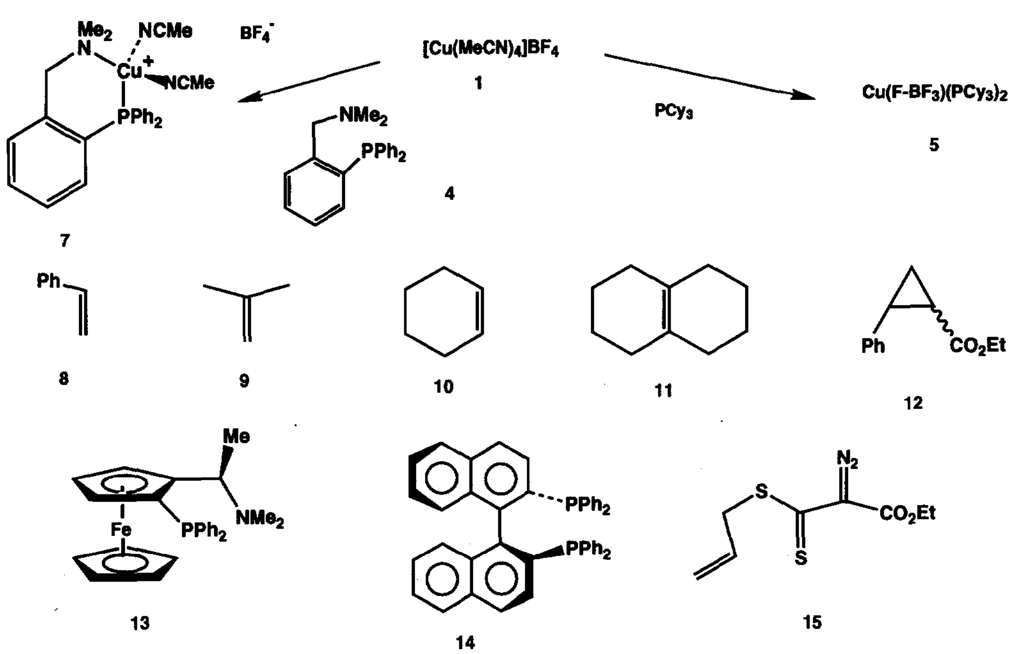
* $[Cu(MeCN)_2(PPh_3)_2]BF_4$ crystallizes from CH_2Cl_2–Et_2O as monoclinic colourless prisms. Space group $P2_1/n$, $a = 9.211(3)$, $b = 26.864(9)$, $c = 15.397(4)$ Å, $\beta = 94.60(2)°$, $V = 3798(2)$ Å^3, $Z = 8$. Full details are deposited in the Cambridge crystallographic database. The structure of the copper cation is essentially identical to the known perchlorate salt. See also ref. 20.



Scheme 2.

phosphine complexes. The spectroscopic properties of **7** and the results of a crystallographic study (see later) are fully consistent with the formula proposed.

Catalytic and mechanistic studies

At the outset of this project information regarding cyclopropanation reactions using **1** was rather limited. We, therefore, undertook some initial screening reactions to identify the catalytic activity of **1** and the related phosphine complexes **2**, **3**, **5** and **7** for cyclopropanations using ethyl diazoacetate and the alkenes **8**–**11** (Scheme 2). In addition cyclopropanation reactions of **1** in the presence of added ligands were performed. Ethyl diazoacetate is an excellent test compound as known literature compounds are formed in most cases. In all cases, after a short induction period (*ca* 10–30 s), prompt decomposition of $N_2{=}CH(CO_2Et)$ at room temperature is observed (Table 1). The complexes are highly active compared to traditional catalysts.

Table 1. Catalytic cyclopropanation results

Catalyst[a]	Alkene [Conc.]	Reaction time	Cyclopropane[b] yield	Isomer[c] ratio	Alkene[b] yield	*E*/*Z*[c] ratio
$[Cu(MeCN)_4]^+$	**8** [1.5 M]	10 min	60%	1.65	30%	1.35
$[Cu(MeCN)_4]^+$	**8** [0.35 M]	20 min	34%	1.95	43%	1.55
$[Cu(MeCN)_2(PPh_3)_2]^+$	**8** [1.5 M]	2.25 h	55%	2.50	31%	1.80
$[Cu(MeCN)(PPh_3)_3]^+$	**8** [1.5 M]	16 h	27%	2.38	34%	1.75
$[Cu(MeCN)_2(\mathbf{4})]^+$	**8** [1.5 M]	15 h (at 4°C)	65%	2.75	32%	1.60
$[Cu(MeCN)_2(\mathbf{13})]^+$ [d]	**8** [1.3 M]	45 min	47%	2.50	34%	4.10
$[Cu(F{-}BF_3)(PCy_3)_2]$	**8** [1.5 M]	4.5 h	29%	4.00	49%	4.20
$[Cu(MeCN)_4]^+$	**9** [3.5 M]	20 min	71%	—	30%	1.25
$[Cu(MeCN)_4]^+$	**10** [1.5 M]	10 min	30%	5.50[e]	44%	3.90
$[Cu(MeCN)_4]^+$	**11** [1.5 M]	10 min	7%	—	46%	1.35

[a] Reactions performed on a 1–2 mmol scale in CH_2Cl_2 using 2 mol% catalyst ($[BF_4]^-$ counter-anion) at ambient temperature.

[b] Isolated by column or preparative TLC.

[c] *Trans*/*cis* ratio (cyclopropane) or *E*/*Z* ratio (alkene) determined by GC on the crude reaction mixture, error ±0.05.

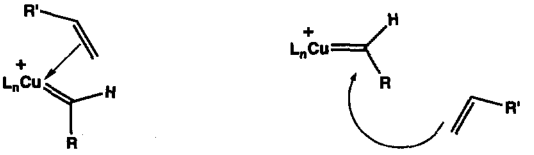
[d] Prepared *in situ*.

[e] *Exo*/*endo* value.

However, for high yields of cyclopropanes the effective concentration of the alkene must be above 1.0 molar. Terminal alkenes, especially styrene, are the most reactive. Although various enantioselective routes to the styrene derived product **12** are available, catalyst control of the relative *trans/cis* stereochemistry by a family of complexes is rarely demonstrated. Selective formation of cyclopropanes related to *trans*-**12** using sterically hindered diazoacetates is known,[16] but catalyst-based *trans/cis* control is rare.

In the PPh_3 substituted catalysts the *trans/cis*-**12** selectivity and rate is influenced by the number of phosphine ligands coordinated to the catalyst, maximizing for $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (**2**). Different PPh_3 : Cu ratios result in inferior selectivity and rates, the 3 : 1 ratio of **3** gives a *trans/cis* value of 2.38 after 16 h, while the complex $[Cu(PPh_3)_4]BF_4$ shows only feeble catalytic activity. Complex **5** catalyses the reaction rather slowly, but in this case with high *trans/cis*-**12** selectivity (4.00). Crystallographic studies show that $M(PCy_3)_2$ (M = Cu, Ag) based complexes often attain a maximum coordination number of only three.[17] The above results indicate although only one free coordination site is required for these catalysts, significant rate enhancements are attained where at least two are present. In support of this notion is the observation that the rate of $N_2{=}CH(CO_2Et)$ decomposition by **2** is faster in the presence of styrene than in its absence. The *trans/cis*-**12** selectivity of the nitrogen–phosphorus chelate complex **7** is also relatively high (2.75), but the reaction proceeds much faster than that catalysed by **5**. Attempts at chiral catalysis using the *in situ* complex $[Cu(MeCN)_2(\mathbf{13})]BF_4$ results in a modest yield of essentially racemic **12**. Similarly, racemic **12** is isolated from very low activity catalysts prepared by (*S*)-BINAP (**14**) addition to $[Cu(MeCN)_4]BF_4$ (**1**) in a 1 : 1 ratio. The low cyclopropane yields obtained from **11** are due to steric factors. Attempts at intramolecular cyclopropanation using **15** are unsuccessful due to the high stability of the diazo-species.

Mechanistically the two most probable transition states for copper-catalysed cyclopropanation involve alkene coordination (**16**) or attack on the coordinated carbene ligand by an outer-sphere alkene (**17**) (Scheme 3). As kinetic regimes often cannot distinguish between these two possibilities[5] we sought for alternative evidence for alkene and carbene coordination. No MeCN exchange with styrene in **2** could be detected by ^{31}P NMR spectroscopy at room temperature or −30°C. Further, no MeCN liberation from **2** is detected by IR or ^{31}P NMR spectroscopy for the related π-acid CO. These results suggest rather small equilibrium constants for MeCN dissociation. In the catalytic systems MeCN is removed by degradation with ethyl diazoacetate during the short induction period, thus preventing equilibrium back reactions. Supporting this idea reactions in acetonitrile alone give small variable yields of $\mathrm{Me\overline{C{=}NC}H(CO_2Et)}$, together with *E/Z* alkene and polymeric material. The catalytic species *do* coordinate π-acids, admission of CO totally inhibits the catalysis but the activity returns once a nitrogen atmosphere is readmitted. The lowest temperature at which our catalysts are active is *ca* 4°C, precluding NMR investigations by low-temperature mixing. However, prompt cooling of the active reaction mixtures using a $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (**2**) pre-catalyst allows the catalytic rest state to be interrogated by ^{31}P NMR spectroscopy. Under these conditions the signal for the starting material [δ_P (109.25 MHz, $CDCl_3$, −30°C) −0.3 ($W_{1/2} = 48$ Hz)] is replaced by a broad resonance at δ_P −0.8 ($W_{1/2} = 180$ Hz) and a smaller sharp signal at δ_P 20.7. This signal is identified as $Ph_3P{-}N_2{=}CHCO_2Et$ by comparison with an authentic sample.[18] However, attempts to probe the structure of the active copper species are thwarted by the quadrupolar nature of copper ($I = 3/2$ for both ^{63}Cu and ^{65}Cu).



16 **17**

Scheme 3.

Crystallographic studies

In order to gain some further insights into the origins of the higher *trans/cis* selectivity shown by complexes **5** and **7** the crystal structures of these molecules were investigated.* ORTEP views of the molecules are shown in Figs 1 and 2, while selected bond length and angle data are presented in Tables 2 and 3. Details of the crystal and structure refinement data for both compounds are summarized in Table 4.

The $[Cu(F{-}BF_3)(PCy_3)_2]$ (**5**) molecule exhibits positional disorder in one of the cyclohexyl groups (designated "6") and in the three BF_4 fluorine atoms

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* Full details for **5** and **7** are deposited at the Cambridge Crystallographic database.

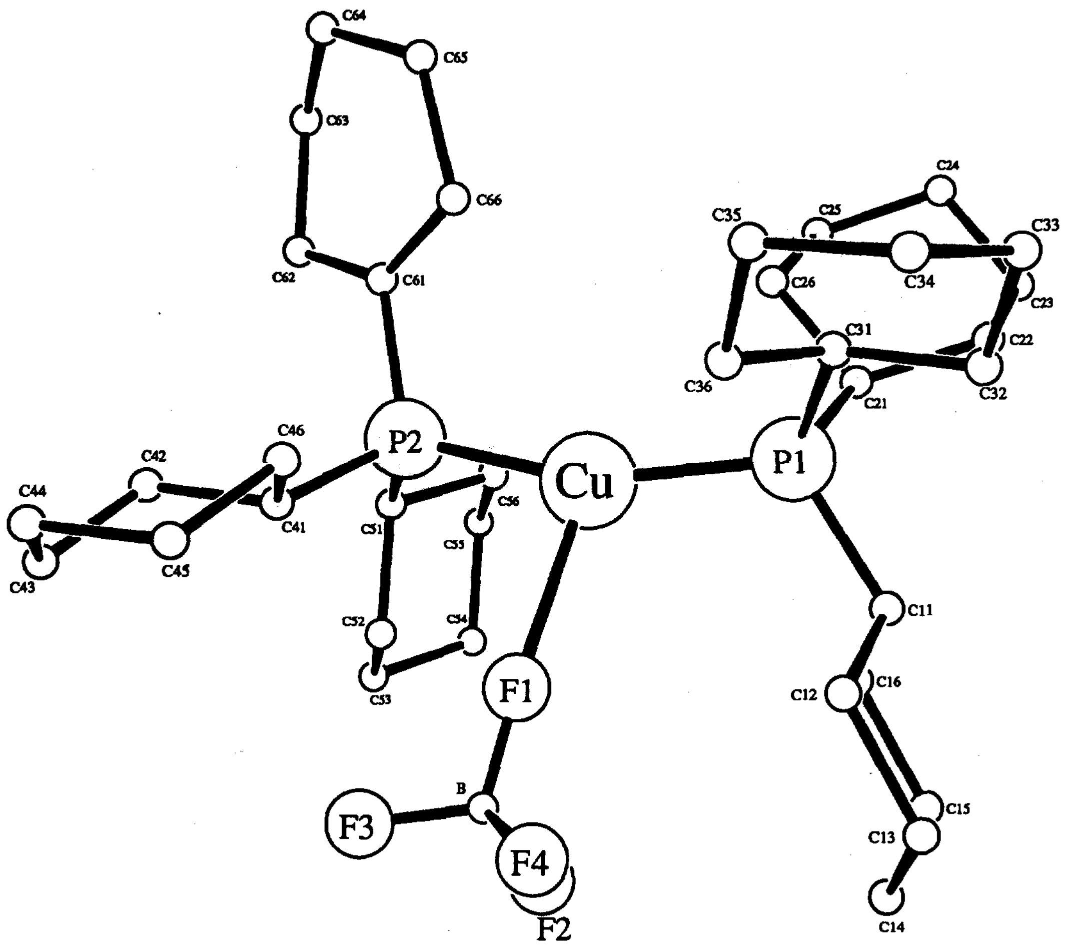

Fig. 1. An ORTEP view of Cu(F—BF$_3$)(PCy$_3$)$_2$ (5); hydrogen atoms are omitted for clarity.

which are not coordinated to the metal. However, the disorder is not of great consequence to the discussion and for this reason and to eliminate clutter the multiple occupancy positions are not shown; the figure shows the primary fluorine atom positions. The semi-coordinated BF$_4$ group is anchored at the coordinated fluorine atom, which is uniquely positioned and shows no disorder. Overall three-coordinate copper is observed in **5** with a Cu—F contact distance of 2.420(6) Å. The second nearest fluorine of the coordinated BF$_4$ group [F(2), 70% occupancy] at *ca* 4.2 Å is effectively non-bonded. Coordination of the anion results in a slight shortening of the coordinated B—F bond B—F(1) to 1.29(2) Å, while the uncoordinated B—F bonds are in the range expected [1.33(2)–1.39(2) Å]. Similar features are seen in the structure of Cu(F—BF$_3$)(PPh$_3$)$_3$ (**6**), where the principal Cu—F contact is 2.306 Å,[19] but in this case no B—F contraction is observed. Commensurate with the high steric bulk of PCy$_3$, a large P—Cu—P angle of 159.98(8)° is observed. This is the largest angle observed in M(PR$_3$)$_2$ (M = Cu, Ag) systems, some 13–15° greater than those in M(X)(PCy$_3$)$_2$ (M = Cu, Ag; X = NO$_3$, ClO$_4$)[17] at 139.0–147.3° and considerably greater than those at 127.6(1)° and 127.1(1)° in the structures [Cu(MeCN)$_2$(PPh$_3$)$_2$]X (X = ClO$_4$, BF$_4$).[20] The bulky phosphines offer considerable steric protection to the metal, however, due to disorder in one of the cyclohexyl rings extensive discussion of the ring geometries is not profitable.

The coordination geometry about copper in **7** is approximately tetrahedral. The most significant deviation is the P—Cu—N angle of 98.3(1)° due to the chelate ligand. Direct comparison with related phosphorus nitrogen chelates on copper(I) is difficult as apparently no other is crystallographically characterized. The Cu—P distance at 2.195(2) Å is in the range expected by comparison with the structures of Cu(MeCN)$_n$(PPh$_3$)$_{4-n}$ (n = 0–2).[13] The Cu—NMe$_2$ distance at 2.179 Å is somewhat longer than Cu^I—N bond distances observed in coordinated acetonitrile complexes,

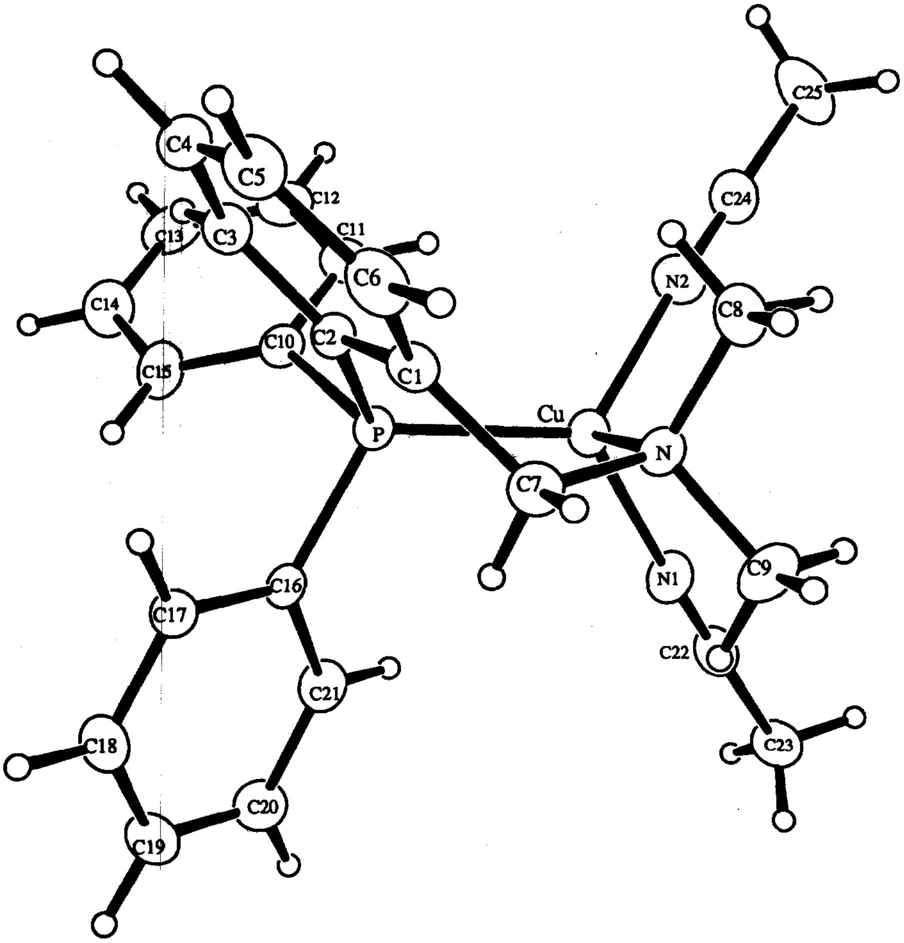

Fig. 2. An ORTEP view of $[Cu(MeCN)_2\{1,2-(Me_2NCH_2)(PPh_2)C_6H_4\}]BF_4$ (7).

2.02–2.12 Å.[13] Solution ^1H NMR studies suggest that the chelate ring is flat, but in the solid state the ring is kinked about the methylene linkage of the chelate ligand. This is most clearly seen in the N—C(7)—C(1) and Cu—P—C(2) angles, which are 114.9(5)° and 105.7(2)°, respectively. Rapid ring deformation must occur in solution rendering the CH_2 and NMe_2 groups equivalent in the ^1H NMR spectra. The $[BF_4]^-$ counter-anion in $[Cu(MeCN)_2\{1,2-(Me_2NCH_2)(PPh_2)C_6H_4\}]BF_4$ (7) exhibits positional disorder, hence, additional positions are tabulated with the other data.

CONCLUSIONS

The observed rate differences and selectivities shown by these complexes indicate that alkene coordination and a transition state similar to **16** is important in cyclopropanation catalysis by **2**, **7** and related sterically unencumbering ligands. For the species **3** and **5** no alkene coordination is proposed to occur due to steric blocking of the fourth coordination site at the copper. In these cases direct attack on the coordinated carbene $[L_nCu{=}CH(CO_2Et)]$ (viz. **17**) is likely.

EXPERIMENTAL

General

All manipulations involving nitrogen ligated copper complexes, together with catalytic reactions, were performed under nitrogen atmospheres using standard Schlenk techniques. All alkenes and ethyl diazoacetate were commercial products (Aldrich), used after drying over 4 Å molecular sieves. Commercial PCy_3 was used as supplied. Carbon disulphide and dichloromethane were distilled from CaH_2 immediately prior to use; hexane, light petroleum (b.p. 40–60°C) and Et_2O were dried

Table 2. Selected bond length and angle data for $Cu(F—BF_3)(PCy_3)_2$ (**5**)

(a) Distances (Å)

Cu—P(1)	2.235(2)	P(2)—C(51)	1.857(6)
Cu—P(2)	2.237(2)	P(2)—C(61)	1.843(8)
Cu—F(1)	2.420(6)	B—F(1)	1.29(2)
P(1)—C(11)	1.841(8)	B—F(2)	1.39(2)
P(1)—C(21)	1.859(7)	B—F(3)	1.33(2)
P(1)—C(31)	1.851(6)	B—F(4)	1.38(2)
P(2)—C(41)	1.854(7)		

Nearest interionic distances

C(33)—F(7)	3.22(2) (a)	C(65)—F(6)	3.25(3) (a)
C(41)—F(1)	3.27(1) (b)		

Symmetry operators: (a) $x, y, z-1$; (b) x, y, z

(b) Angles (°)

P(1)—Cu—P(2)	159.98(8)	C(11)—P(1)—C(31)	108.4(3)
P(1)—Cu—F(1)	108.5(2)	C(21)—P(1)—C(31)	105.1(3)
P(2)—Cu—F(1)	91.5(2)	Cu—P(2)—C(41)	110.3(2)
Cu—F(1)—B	176(1)	Cu—P(2)—C(51)	111.7(2)
Cu—P(1)—C(11)	115.7(2)	Cu—P(2)—C(61)	113.1(3)
Cu—P(1)—C(21)	109.3(2)	C(41)—P(2)—C(51)	106.1(3)
Cu—P(1)—C(31)	111.3(2)	C(41)—P(2)—C(61)	110.5(4)
C(11)—P(1)—C(21)	106.4(3)	C(51)—P(2)—C(61)	104.6(3)

over sodium wire. Column chromatography and preparative TLC were run on activated silica gel; Fisons S/0780/60 and Merck Kieselgel 60 $HF_{254+366}$, respectively. IR spectra were recorded using a Perkin–Elmer 983G instrument. Proton NMR spectra were recorded on Jeol-270 (270 MHz) or Bruker WH-400 (400 MHz) spectrometers. ^{13}C NMR (67.8 MHz), ^{31}P NMR (109.3 MHz) and ^{19}F NMR (254.1 MHz) spectra were recorded on the Jeol-270. Mass spectra were obtained on Finnigan 1020 (electron impact ionization, EI) or VG–ZAB (fast atom bombardment ionization, FAB) machines. Optical activities were assayed by polarimetry on a Optical Activity Ltd AA-10 instrument. Catalytic reaction mixtures were investigated with a Sigma-3 GC using a Carbowax-20M column, a carrier gas flow of 30 cm^3 min^{-1} (N_2) and either a temperature program (8 min at

Table 3. Selected bond length and angle data for $[Cu(MeCN)_2\{1,2\text{-}(Me_2NCH_2)(PPh_2)C_6H_4\}]BF_4$(**7**)

(a) Distances (Å)

Cu—P	2.195(2)	Cu—N(1)	2.020(7)
Cu—N	2.179(5)	Cu—N(2)	1.974(7)

Nearest interionic distances

F(2)—C(22)	3.13(1) (a)	F(6)—C(23)	3.09(2) (b)

Symmetry operators: (a) $1+x, y, z$; (b) $1/2+x, 1/2-y, z-1/2$

(b) Angles (°)

P—Cu—N	98.3(1)	Cu—P—C(2)	105.7(2)
N—Cu—N(1)	105.9(3)	Cu—P—C(10)	120.5(2)
N—Cu—N(2)	103.1(2)	Cu—P—C(16)	117.9(2)
N(1)—Cu—N(2)	105.7(3)	C(2)—C(1)—C(7)	123.0(6)
P—Cu—N(1)	120.8(2)	P—C(2)—C(1)	119.1(5)
P—Cu—N(2)	120.2(2)	N—C(7)—C(1)	114.9(5)

Table 4. Crystal and structure refinement data

Compound	$[Cu(c\text{-}hex_3P)_2F—BF_3]$	$[Cu(Ph_2PC_6H_4CH_2NMe_2)MeCN_2]BF_4$
Mol. wt	711.2	551.8
a (Å)	16.102(3)	13.772(3)
b (Å)	24.931(9)	14.468(3)
c (Å)	9.563(2)	15.067(5)
β (°)	93.61(3)	115.70(2)
V (Å^3)	3831(3)	2705(2)
Space group	$P21/n$ (No. 14)	Cc (No. 9)
Z	4	4
D_{calc} (g cm^{-3})	1.233	1.355
μ (cm^{-1})	6.94	9.10
Crystal dimensions (mm)	$0.65 \times 0.40 \times 0.22$	$0.40 \times 0.30 \times 0.22$
Transmission coefficients	0.607, 0.403	0.922, 0.650
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Scan width (°)	$(0.7 + 0.35 \tan \theta)$	$(0.6 + 0.35 \tan \theta)$
2θ range (°)	3.0–50.0	3.0–50.0
Unique data measured	6970	2576
Unique data used	3545 ($> 3\sigma$)	2043 ($> 3\sigma$)
No. of variables	381	315
R $(\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$ (%)	6.5	4.3
R_w $([(\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w F_o{}^2)]^{1/2}$ (%)	7.3	4.8
Shift/error	0.02	0.02
$\Delta\rho_{max}$ (e Å^{-3})	0.62	0.44

145°C/ramp to 185°C over 5 min/12 min at 185°C) or an isothermal run at 100°C. The complex $[Cu(MeCN)_4]BF_4$ (**1**) was prepared in an identical manner to $[Cu(MeCN)_4]PF_6$ using HBF_4 (48%wt in water) and recrystallized from MeCN before use.[12] The species $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (**2**)[13] and the ligand **4**[21] are literature compounds.

Preparations and catalysis

Preparation of $Cu(F—BF_3)(PCy_3)_2$ (**5**). Solid PCy_3 (0.60 g, 2.14 mmol) was added to a suspension of $[Cu(MeCN)_4]BF_4$ (**1**) (0.33 g, 1.07 mmol) in CH_2Cl_2 (30 cm^3) at room temperature. The reaction was stirred for 1 h, during which time the mixture became homogeneous. The colourless solution was filtered, concentrated to a minimal volume and crystallized by addition of Et_2O and cooling, resulting in two crops of colourless plates; 0.57 g (75%); m.p. 218–219°C. Found: C, 60.5; H, 9.1; M(cation)$^+$, 623. Calc. for $C_{36}H_{66}BCuF_4P_2$: C, 60.8; H, 9.35%; M(cation), 623. ν_{max} (cm^{-1}) (KBr disc): 2919s, 2842s (CH) and 1080s (BF). δ_H (400 MHz, $CDCl_3$): 1.13–1.46 (30 H, m, axial H), 1.68–1.95 (30 H, m, equatorial H) and 1.95–2.06 [6 H, m, H—C(1)]; δ_C (67.8 MHz, $CDCl_3$): 25.9 [6 C, s, C(4)], 27.0 [12 C, t, J(PC) = 6 Hz, C(2)], 31.0 [12 C, s, C(3)] and 31.6 [6 C, t, J(PC) = 11 Hz, C(1)]; δ_P (109.3 MHz, $CDCl_3$): 21.3 (PCy_3); δ_F (254.1 MHz, C_6D_6): 148.96, 149.00; δ_F (254.1 MHz, acetone-d$_6$): 149.47, 149.51; δ_F (254.1 MHz, DMSO-d$_6$): 146.80, 146.85.

Preparation of $[Cu(F—BF_3)(PPh_3)_3]$ (**6**). Addition of PPh_3 (0.62 g, 2.40 mmol) to $[Cu(MeCN)_4]BF_4$ (**1**) (0.25 g, 0.80 mmol) in CH_2Cl_2 (50 cm^3), followed by crystallization from CH_2Cl_2–Et_2O afforded colourless cubes of $[Cu(MeCN)(PPh_3)_3]BF_4$ (**3**); 0.72 g (92%). The complex had properties closely related to the known ClO_4 salts;[13] m.p. 225–226°C. Found: C, 68.3; H, 4.8; N, 1.7; M(cation-MeCN)$^+$, 849. Calc. for $C_{56}H_{48}BCuF_4NP_3$: C, 68.8; H, 4.95; N, 1.4%; M(cation), 890. ν_{max} (cm^{-1}) (KBr disc): 3062m (CH), 2282w, 2244w (CN), 1485s, 1434s (CC) and 1050s br (BF). δ_H (270 MHz, $CDCl_3$): 2.03 (3 H, s, Me), 7.00–7.12 (18 H, m, Ph-*o*), 7.12–7.23 (18 H, m, Ph-*m*) and 7.32–7.41 [9 H, m, Ph-*p*]; δ_P (109.3 MHz, $CDCl_3$): 1.4 (PPh_3). Heating the solid under vacuum (0.05 mm Hg) at 90°C (2 h) followed by recrystallization from CH_2Cl_2–Et_2O yielded colourless needles of $[Cu(F—BF_3)(PPh_3)_3]$, 0.57 g (82%), with literature properties;[19] m.p. 219–220°C. Found: C, 68.9; H, 4.75. Calc. for $C_{54}H_{45}BCuF_4P_3$: C, 69.2; H, 4.8. ν_{max} (cm^{-1}) (KBr disc): 3062m (CH), 1482s, 1437s (CC) and 1060s br (BF). δ_H (270 MHz, $CDCl_3$): 6.95–7.10 (18 H, m, Ph-*o*), 7.10–7.23 (18 H, m, Ph-*m*) and 7.32–7.42 [9 H, m, Ph-*p*]; δ_P (109.3 MHz, $CDCl_3$): 1.8 (PPh_3).

Preparation of $[Cu(MeCN)_2\{1,2\text{-}(Me_2NCH_2)$

$(PPh_2)C_6H_4\}]BF_4$ (**7**). A degassed solution of 1,2-$(Me_2NCH_2)(PPh_2)C_6H_4$ (**4**) (0.34 g, 1.05 mmol) in CH_2Cl_2 (5 cm^3) was added by cannula to a suspension of $[Cu(MeCN)_4]BF_4$ (**1**) (0.33 g, 1.03 mmol) in CH_2Cl_2 (10 cm^3) at ambient temperature and stirred (30 min). The resulting deep yellow solution was filtered under nitrogen and concentrated to *ca* 4 cm^3. An equal volume of degassed Et_2O was added and the yellow by-products removed by filtration under nitrogen. Further Et_2O addition and slow cooling afforded two crops of colourless rhomboid crystals; 0.37 g (66%); m.p. 128–130°C (dec.). Found: C, 54.1; H, 5.0; N, 7.2; M(cation)$^+$, 464. Calc. for $C_{25}H_{28}BCuF_4N_3P$: C, 54.1; H, 5.1; N, 7.6%; M(cation), 464. ν_{max} (cm^{-1}) (KBr disc): 3044w, 2999w, 2960w, 2940w, 2875w, 2837w, 2795w (CH), 2300w, 2267w, 2243w (CN), 1478m, 1454m, 1430m (CC), and 1060s br (BF); δ_H (270 MHz, $CDCl_3$): 2.28 (6 H, s, MeCN), 2.44 (6 H, s, NMe_2), 6.84–6.90 (1 H, m, phenylene), 7.26–7.59 (13 H, m, Ph + phenylene); δ_P (109.3 MHz, $CDCl_3$): 1.3 (PPh_2).

Typical procedure for catalytic cyclopropanation. Neat $N_2{=}CH(CO_2Et)$ (0.2 cm^3, 1.90 mmol) was added by microlitre syringe to a solution containing styrene (1.1 cm^3, 9.5 mmol) and $[Cu(MeCN)_4]BF_4$ (**1**) (12 mg, 0.04 mmol, 2 mol%) in CH_2Cl_2 (5 cm^3) and the reaction stirred at room temperature until nitrogen evolution ceased. The cyclopropane *trans*/*cis* and alkene *E*/*Z* ratios were determined by GC; the relevant response factors were checked at regular intervals. Chromatography in 1 : 1 CH_2Cl_2 : light petroleum afforded styrene followed by the cyclopropane *trans*/*cis*-**12**.[10] *Trans*-**12**: TLC (1 : 1 CH_2Cl_2 : hexane), $R_f = 0.57$; GC retention time = 18.7 min (program). δ_H (400 MHz, $CDCl_3$): 1.23 [3 H, t, *J*(HH) = 7.2 Hz, Me], 1.30 [1 H, ddd, *J*(HH) = 8.4, 6.5, 4.5 Hz, H—C(3)], 1.59 [1 H, ddd, *J*(HH) = 9.2, 5.4, 4.5 Hz, H—C(3)], 1.89 [1 H, ddd, *J*(HH) = 8.4, 5.4, 4.2 Hz, H—C(1)], 2.51 [1 H, ddd, *J*(HH) = 9.2, 6.5, 4.2 Hz + unresolved long range couplings to Ph, H—C(2)], 4.16 [2 H, q, *J*(HH) = 7.2 Hz, OCH_2], 7.08–7.10 (2 H, m, Ph-*o*) and 7.10–7.29 (3 H, m, Ph-*m* + *p*). *Cis*-**12**: TLC (1 : 1 CH_2Cl_2 : hexane), $R_f = 0.35$; GC retention time = 16.9 min (program). δ_H (400 MHz, $CDCl_3$): 0.96 [3 H, t, *J*(HH) = 7.2 Hz, Me], 1.32 [1 H, ddd, *J*(HH) = 9.1, 7.8, 5.1 Hz, H—C(3)], 2.07 [1 H, ddd, *J*(HH) = 9.1, 7.8, 5.6 Hz, H—C(1)], 2.57 [1 H, dt, *J*(HH) = 9.1, 9.1, 7.5 Hz + unresolved long range couplings to Ph, H—C(2)], 3.86 [2 H, q, *J*(HH) = 7.2 Hz, OCH_2] and 7.10–7.29 (5 H, m, Ph). The diastereomers could be separated by preparative TLC (10 : 1 light petroleum : EtOAc); complete resolution was only achieved at low plate loadings. Optical activities were assessed by use of literature optical rotations.[22] Continued elution with 1 : 1 CH_2Cl_2 : EtOAc afforded a mixture of diethyl fumarate/maleate. Fumarate (*E*-alkene): TLC (1 : 1 CH_2Cl_2 : hexane), $R_f = 0.11$–0.28; GC retention time = 8.2 min (program). δ_H (270 MHz, $CDCl_3$): 1.30 [3 H, t, *J*(HH) = 7.2 Hz, Me], 4.23 [2 H, q, *J*(HH) = 7.2 Hz, OCH_2] and 6.80 (2 H, s, =CH). Maleate (*Z*-alkene): TLC (1 : 1 CH_2Cl_2 : hexane), $R_f = 0.11$–0.28; GC retention time = 10.3 min (program). δ_H (270 MHz, $CDCl_3$): 1.29 [3 H, t, *J*(HH) = 7.2 Hz, Me], 4.23 [2 H, q, *J*(HH) = 7.2 Hz, OCH_2] and 6.42 (2 H, s, =CH).

Cyclopropanation of 1,1-*dimethylethene* (**9**). Application of the above procedure afforded the cyclopropane having literature properties.[8] TLC (1 : 1 CH_2Cl_2 : hexane): $R_f = 0.37$; GC retention time = 4.9 min (100°C). ν_{max} (cm^{-1}) (thin film): 2960s, 2925s, 2858m (CH) and 1732s (CO). δ_H (270 MHz, $CDCl_3$): 0.84 [1 H, dd, *J*(HH) = 8, 4 Hz, H—C(3)], 1.08 [1 H, dd, *J*(HH) = 5, 4 Hz, H—C(3)], 1.15 (3H, s, Me), 1.21 (3 H, s, Me), 1.27 [3 H, t, *J*(HH) = 7 Hz, OCH_2*Me*), 1.48 [1 H, dd, *J*(HH) = 8, 5 Hz, H—C(1)] and 4.07–4.19 (2 H, m, OCH_2). MS (EI): 142 (M$^+$).

Cyclopropanation of cyclohexane (**10**). Using the standard method afforded the cyclopropane having literature properties.[6] TLC (1 : 1 CH_2Cl_2 : hexane), $R_f = 0.44$; GC retention time = 9.3 min (program). ν_{max} (cm^{-1}) (thin film): 2930s, 2861s (CH) and 1725s (CO). δ_H (270 MHz, $CDCl_3$): 1.28 [3 H, t, *J*(HH) = 7 Hz, Me-*exo*], 1.29 [3 H, t, *J*(HH) = 7 Hz, Me-*endo*], 1.20–1.99 (11 H, m, ring protons), 4.10 [2 H, q, *J*(HH) = 7 Hz, OCH_2-*exo*] and 4.12 [2 H, q, *J*(HH) = 7 Hz, OCH_2-*endo*]. MS (EI): 168 (M$^+$).

Cyclopropanation of 1,2,3,4,5,6,7,8-*octahydronaphthylene* (**11**). Using the above protocol yielded the cyclopropane as a clear oil. TLC (1 : 1 CH_2Cl_2 : hexane), $R_f = 0.50$; GC retention time = 17.9 min (program). ν_{max} (cm^{-1}) (thin film): 2920s, 2849s, (CH) and 1725s (CO). δ_H (270 MHz, $CDCl_3$): 1.28 [3 H, t, *J*(HH) = 7 Hz, Me], 1.30–2.28 (17 H, m, ring protons) and 4.13 [2 H, q, *J*(HH) = 7 Hz, OCH_2]. MS (EI): 222 (M$^+$).

Decomposition of $N_2{=}CH(CO_2Et)$ *in* MeCN. A solution of $N_2{=}CH(CO_2Et)$ (0.2 cm^3, 1.90 mmol) in MeCN (1 cm^3) was decomposed by $[Cu(MeCN)_4]BF_4$ (**1**) (12 mg, 0.04 mmol, 2 mol%) over 3 h. Preparative TLC afforded 39 mg (23%) of *E*/*Z*-$(EtO_2C)CH{=}CH(CO_2Et)$, $R_f = 0.20$–0.40, and a slow moving band, $R_f = 0.09$–0.16, containing variable amounts of $Me\overline{C{=}N}CH(CO_2Et)$, *ca* 11 mg (9%) as a yellow oil with literature properties.[23] TLC (3 : 2 hexane : EtOAc), $R_f = 0.35$. ν_{max} (cm^{-1}) (thin film): 1784s (C=N) and 1709s (CO). δ_H (270 MHz, $CDCl_3$): 1.41 [3 H, t, *J*(HH) = 7 Hz,

CH_2Me), 2.34 (3 H, s, CMe), 4.08 [2 H, q, J(HH) = 7 Hz, OCH_2]. MS (EI): 127 (M^+).

Preparation of $N_2{=}C(CO_2Et)(CS_2CH_2CH{=}CH_2)$ (**15**) *and attempted intramolecular cyclopropanation.* Freshly prepared $LiNPr^i_2$ (LDA) (10.00 mmol) in THF (10 cm^3) was added slowly by cannula to a mixture of $N_2{=}CH(CO_2Et)$ (1.09 g, 9.51 mmol) and CS_2 (0.76 g, 9.98 mmol) in THF (40 cm^3) at −78°C, causing a darkening to orange. Allyl bromide (0.85 cm^3, 1.19 g, 9.82 mmol) was then added by syringe. The solution was allowed to come to room temperature (2 h), during which time its colour darkened to brown. The solution was stirred at ambient temperature, concentrated and quenched (NH_4Cl solution, 20 cm^3). Extraction with CH_2Cl_2 and water afforded on drying (Na_2SO_4) a yellow oil. Chromatography on SiO_2 (115 × 30 mm), eluting with 10 : 1 (light petroleum : CH_2Cl_2), afforded small amounts of an uncharacterized species. TLC (4 : 1 hexane : CH_2Cl_2), $R_f = 0.75$. Continued elution with 4 : 1 (light petroleum : CH_2Cl_2) yielded **15** as a yellow oil, 0.53 g (24%). TLC (4 : 1 hexane : CH_2Cl_2), $R_f = 0.38$. ν_{max} (cm^{-1}) (thin film): 2985m, 2938w, 2910w (CH), 2105w, (NN), 1706s (CO) and 1063s (CS). δ_H (270 MHz, $CDCl_3$): 1.47 [3 H, t, J(HH) = 7.1 Hz, Me], 3.72 [2 H, dt, J(HH) = 6.6, 1.3, 1.3 Hz, CH_2CH], 4.52 [2 H, q, J(HH) = 7.1 Hz, OCH_2], 5.38 [1 H, ddt, J(HH) = 10.0, 1.3, 1.3, 1.0 Hz, $={CH_2}$], 5.50 [1 H, ddt, J(HH) = 16.9, 1.3, 1.3, 1.0 Hz, $={CH_2}$] and 5.90 [1 H, m, J(HH) = 16.9, 10.0, 6.6, 6.6 Hz, =CH]. δ_C (67.8 MHz, $CDCl_3$): 14.1 (Me), 40.3 (OCH_2), 61.9 (SCH_2), 121.4 (=CH), 129.7 ($={CH_2}$), 146.4, 160.5, 164.2 ($C{=}N_2$, C=O, C=S). MS (EI): 230 (M^+). Attempted intramolecular cyclopropanation using **1** in CH_2Cl_2 at ambient temperature or 1,2-dichloroethane at 65°C led only to the recovery of the starting material.

Crystallographic studies

Colourless crystals of $Cu(F{-}BF_3)(PCy_3)_2$ (**5**) were grown from an Et_2O solution containing traces of CH_2Cl_2 at −20°C. Greenish tinged crystals of $[Cu(MeCN)_2\{1,2\text{-}(Me_2NCH_2)(PPh_2)C_6H_4\}]BF_4$ (**7**) were grown from a CH_2Cl_2–Et_2O mixture at 0°C. For each complex a colourless crystal was mounted on a glass fibre with epoxy resin. In each case cell dimensions and space group data were obtained by standard methods on an Enraf–Nonius CAD4 four-circle diffractometer with graphite-monochromated Mo-K_α radiation. The θ–2θ technique was used, as previously described,[24] to record the intensities of all non-equivalent reflections, for which $3° < 2\theta < 50°$. Scan widths were calculated as $A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to $K\alpha_1$–$K\alpha_2$ splitting. Scan speeds were varied depending on the prescan reflection intensity. Data were collected as previously described on the Enraf–Nonius CAD4 diffractometer.[24]

Solution and refinement of the structures. Computations were carried out using the data with $F^2_o > 3\sigma(F^2_o)$, where $\sigma(F^2_o)$ was estimated from counting statistics.[25] Corrections were applied for Lorentz and polarization effects and for absorption.[26] In each case the positions of the metal and one phosphorus atom were determined using a Patterson map. Other atoms were located from Fourier-difference syntheses. The initial calculations were made with the MolEN program set,[27] while the final full-matrix least-squares refinement was performed using the TEXRAY program set.[28] Full-matrix least-squares refinement was based on F. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2\{(C + R^2B) + 0.03F_o^2\}^2]/Lp^2$; S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count and Lp = Lorentz polarization factor. Atomic scattering factors for both non-hydrogen[29] and hydrogen[30] atoms were taken from literature values. The effects of anomalous dispersion were included using literature values for $\Delta f'$ and $\Delta f''$.[31]

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