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PAPER

Cu^{I} complexes containing a multidentate and conformationally flexible dibenzylidene acetone ligand (dbathiophos): Application in catalytic alkene cyclopropanation†

Amanda G. Jarvis, Adrian C. Whitwood and Ian J. S. Fairlamb*

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The synthesis and characterisation of a multidentate conformationally flexible ligand based on the dibenzylidene acetone core structure, dbathiophos (**1**), is described. Ligand **1** has a high affinity for cationic and neutral Cu^{I} species. Three unique Cu^{I} complexes (**4–6**) are reported showing that the ligand backbone of dbathiophos is hemilabile, and able to adopt different 1,4-dien-3-one conformational geometries around Cu^{I}. Complexes **4** and **6** both effectively catalyse the cyclopropanation of styrene with ethyl diazoacetate at low catalyst loadings (1 mol% Cu).

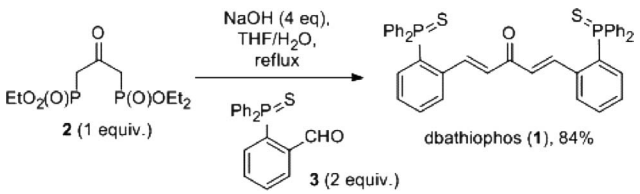
Introduction

The coordination of *E*,*E*-dibenzylidene acetone (dba-H) to transition metals has attracted significant attention over the last 30 years.[1] Electron-deficient dba-H acts as a 1,4-diene ligand in $[Rh(\eta^5\text{-}C_5Me_5)(\eta^2,\eta^2\text{-dba-H})]^2$ and $[Fe(CO)_3[\eta^4\text{-}\{(CO)(CH{=}CHPh)_2\}]$;[3] a range of coordination modes are seen in other Fe,[4] Ru[5] and U[6] complexes. Arguably the most well known metal complexes possessing dba-type ligands are $Pd^0{}_2(dba\text{-}H)_3$ and $Pd^0{}_2(dba\text{-}Z)_3$, which are widely used Pd^0 precursors in synthetic chemistry, catalysis and organometallic coordination chemistry (dba-Z = *E*,*E*-dibenzylidene acetone with different Z-substituents).[7] Intramolecular dba-H 'alkene' (olefin) exchange at Pd^0, *via* C═O coordination, occurs freely in solution, for which several 1,4-dien-3-one conformations are readily accessible.[8] We hypothesised that one could control and enhance 'dba-metal' interactions if suitable 2-electron donor groups could be incorporated into the dba sub-structure. Recent catalytic applications exploiting related chalcone-phosphino ligands[9] reported by Lei and co-workers, and dba effects with Cu^{I} reported by Buchwald,[10] have encouraged us to study more elaborate dba structures. Moreover, Cu^{I} complexes of dienes/polyenes are relatively rare,[11] and hence the synthesis of a novel phosphine sulfide dba ligand **1**, which we refer to as 'dbathiophos', and its Cu^{I} coordination chemistry, is the main subject of this paper. Two Cu^{I} complexes of **1** have been evaluated as catalysts in alkene cyclopropanation reactions.

Ligand **1** was identified as a target which could be accessed quickly and efficiently from readily available starting materials. On a general note, the coordination of phosphine sulfide ligands to metals has been, in our view, fairly neglected when compared to their phosphine counterparts. Specifically, it was anticipated that the combination of a soft phosphine sulfide donor group with an alkene component would provide a unique coordination environment for the soft Cu^{I} centre.[12]

Results and Discussion

Ligand **1** was prepared in 84% yield by Horner–Wadsworth–Emmons reaction of bisphosphonate **2** (see ESI† for the preparation of this compound) with phosphine sulfide benzaldehyde **3** in the presence of NaOH at reflux for 48 h (Scheme 1). Gram-scale quantities of **1** can be produced using this efficient transformation, and single crystals could be grown from CH_2Cl_2 solutions of **1** layered with diethyl ether which were analysed by X-ray diffraction (Fig. 1).



Scheme 1 Synthesis of dbathiophos **1**.

The Cu^{I} coordination chemistry of ligand **1** is intriguing. For example, reaction of **1** with $Cu(CH_3CN)_4PF_6$ in CH_2Cl_2 at ambient temperature gave a new product which shows broad proton signals by ^1H NMR spectroscopy (in CD_2Cl_2) *vide infra* (Scheme 2). Mass spectrometry (ESI-MS and LIFIDI) showed the presence of one ion (*m*/*z* 729) which is $[Cu^{I}(\mathbf{1})]^+$. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 solutions of this material carefully layered with diethyl ether. Microscopic inspection of these crystals showed that both pale yellow (the majority) and

Department of Chemistry, University of York, Heslington, York, UK, YO10 5DD. E-mail: ijsf1@york.ac.uk

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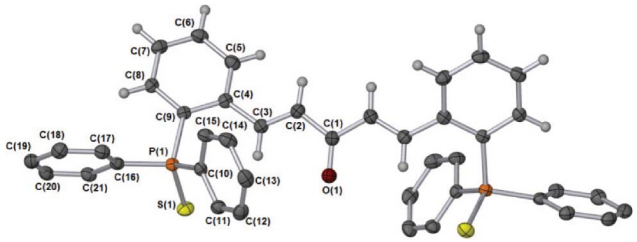
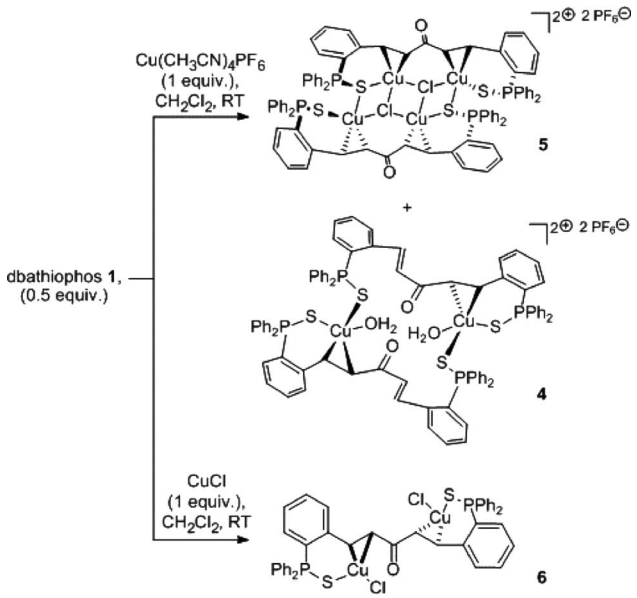


Fig. 1 X-ray structure of dbathiophos **1**. Thermal ellipsoids at 50% probability; (disordered CH_2Cl_2 molecules and selected hydrogens omitted for clarity). Selected bond angles (°): O(1)–C(1)–C(2) 122.2(2), C(9)–P(1)–S(1) 112.80(10), C(10)–P(1)–S(1) 113.18(11), C(16)–P(1)–S(1) 111.36(11). See Table 1 for selected bond lengths. The complex has crystallographically imposed two-fold symmetry with the central C═O bond on the two-fold axis.



Scheme 2 Synthesis of novel Cu^{I} complexes (**2**–**4**) of dbathiophos **1**.

bright yellow types were present. A pale yellow crystal was identified as dinuclear Cu^{I} complex **4**, whereas a bright yellow crystal was found to be tetranuclear Cu^{I} complex **5** (see Fig. 2 and 3). The source of the chloride in **5** is unclear.[13] On other occasions **4** was the only isolatable complex (~65% yield).

The reaction of CuCl with **1** in CH_2Cl_2 at ambient temperature gave complex **6** in 73% yield. Complex **6** was crystallised from CH_2Cl_2 solutions layered with pentane, which allowed a single crystal X-ray structure to be determined (Fig. 4).

The Cu^{I} centre in complex **4** exhibits a distorted tetrahedral arrangement; the sulfur atoms and the alkene form an almost planar triangle with the water arranged perpendicularly to the others. On comparison with the bond lengths for **1** the C═C (s-*cis*) and P═S bonds lengthen on coordination to Cu^{I} (Table 1), whereas the non-coordinated C═C bonds (s-*trans*) share similar bond lengths with **1** (note that the C═C bonds in **1** adopt a s-*cis* conformation relative to the carbonyl moiety due to steric reasons). The P–S bonds, which are in similar environments, have bond lengths which are identical (within error). The 1,4-dien-3-one backbones in both bridging 'dba' ligands adopts a s-*cis*,s-*trans* conformation, which is identical to $Pd_2(dba\text{-}H)_3$ (where both C═C bonds are coordinated to Pd^{0}).[14]

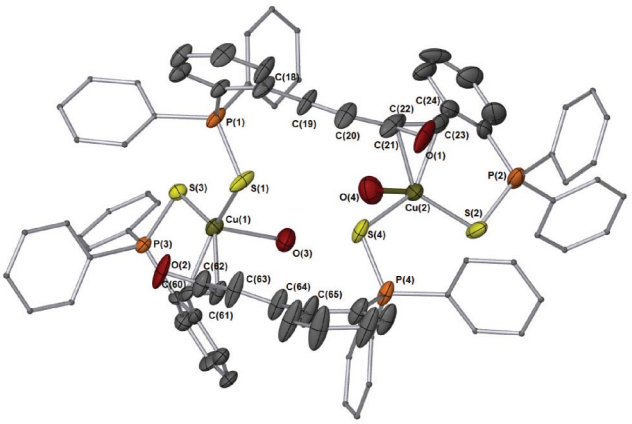


Fig. 2 X-ray structure of dinuclear Cu^{I} complex **4**. Thermal elipsoids shown at 50% probability; 2 × PF_6 molecules and hydrogens (except H_2O) omitted for clarity. Selected bond angles (°): S(3)–Cu(1)–S(1) = 117.91(6), C(60)–Cu(1)–O(3) = 99.84(19), C(61)–Cu(1)–O(3) = 92.1(2), S(3)–Cu(1)–O(3) = 96.22(13), S(1)–Cu(1)–O(3) = 98.62(13), S(4)–Cu(2)–S(2) = 119.84(7), C(23)–Cu(2)–O(4) = 98.5(2), C(22)–Cu(2)–O(4) = 94.1(2), S(4)–Cu(2)–O(4) = 96.42(13), S(2)–Cu(2)–O(4) = 95.52(14).

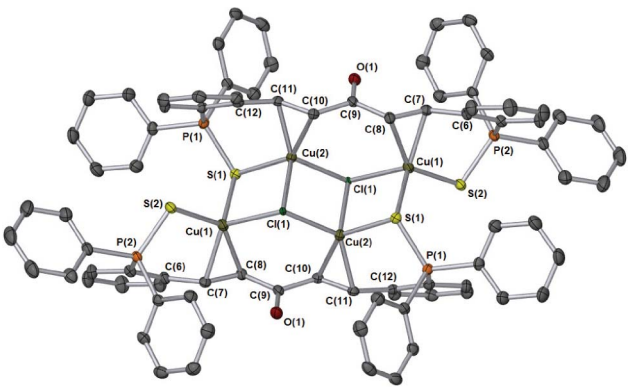


Fig. 3 X-ray structure of tetrameric Cu^{I} complex **5**. Thermal elipsoids shown at 50% probability; 2 × PF_6, hydrogens and disordered ether and CH_2Cl_2 solvent molecules are omitted for clarity. Selected bond angles (°): C(7)–Cu(1)–S(2) = 102.24(8), C(8)–Cu(1)–S(2) = 139.68(8), C(7)–Cu(1)–Cl(1) = 125.06(8), C(8)–Cu(1)–Cl(1) = 102.56(8), S(2)–Cu(1)–Cl(1) = 104.95(3), C(7)–Cu(1)–S(1) = 115.78(8), C(8)–Cu(1)–S(1) = 93.14(8), S(2)–Cu(1)–S(1) = 112.26(3), Cl(1)–Cu(1)–S(1) = 96.37(2). The complex lies about an inversion centre.

Each ligand in complex **5** bridges two Cu^{I} centres, which are capped by the phosphine sulfide moieties. Two chloride ligands are found embedded within the structure, forming a 'pleated ladder'; the inner step is a rhombus whereas the two outside steps possess different bond angles and are twisted as a consequence. As this exact structure is only supported by X-ray diffraction data we were keen to check that the bridging ligands were chloride and not hydroxide. First of all the Cu–Cl bond distances are similar to recently reported Cu–Cl ladder complexes.[15] Furthermore, the bond lengths in related Cu–OH complexes are *ca.* 1.9–2.3 Å.[16] In Cu–Cl complexes the bond lengths are typically 2.3–2.8 Å,[14] which matches our data (*ca.* 2.3–2.6 Å) more closely.

Table 1 Comparison of key bond lengths (Å) in compounds **1–4**

	Key bonds and lengths (Å)					
Cpd.	C═C	C═O	P═S	Cu–S	Cu–C	Cu–Cl
1	C(2)–C(3) 1.324(5)	C(1)–O(1) 1.221(6)	P(1)–S(1) 1.9619(11)	—	—	—
4	C(22)–C(23) 1.360(9) C(19)–C(20) 1.346(8) C(60)–C(61) 1.384(8) C(63)–C(64) 1.319(8)	C(21)–O(1) 1.224(7) C(62)–O(2) 1.225(7)	P(1)–S(1) 1.993(2) P(2)–S(2) 1.987(3) P(3)–S(3) 2.002(2) P(4)–S(4) 1.995(2)	Cu(1)–S(1) 2.2826(18) Cu(1)–S(3) 2.2488(16) Cu(2)–S(2) 2.2619(18) Cu(2)–S(4) 2.2585(18)	Cu(1)–C(60) 2.091(6) Cu(1)–C(61) 2.125(6) Cu(2)–C(22) 2.089(6) Cu(2)–C(23) 2.087(7)	—
5	C(8)–C(7) 1.373(4) C(10)–C(11) 1.373(4)	C(9)–O(1) 1.224(4)	P(1)–S(1) 2.0221(10) P(2)–S(2) 1.9936(10)	Cu(1)–S(1) 2.4872(8) Cu(1)–S(2) 2.2767(8) Cu(2)–S(1) 2.2948(8)	C(7)–Cu(1) 2.112(3) C(8)–Cu(1) 2.164(3) C(10)–Cu(2) 2.108(3) C(11)–Cu(2) 2.089(3)	Cu(1)–Cl(1) 2.4155(7) Cu(2)–Cl(1) 2.3330(7) Cu(2)#1–Cl(1) 2.5906(7) Cu(2)–Cl(1)#1 2.5907(7)
6	C(2)–C(3) 1.375(4)	C(1)–O(1) 1.228(5)	P(1)–S(1) 2.0072(12)	Cu(1)–S(1) 2.2546(9)	C(2)–Cu(1) 2.060(3) C(3)–Cu(1) 2.053(3)	Cu(1)–Cl(1) 2.1908(9)

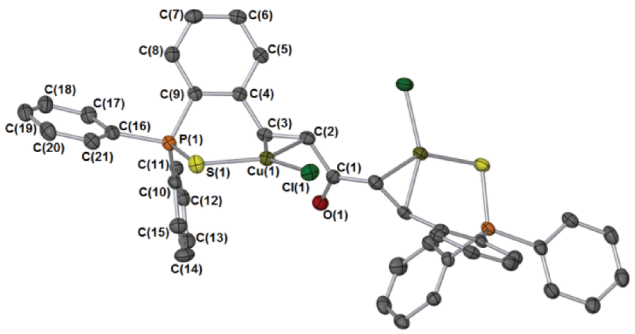


Fig. 4 X-ray structure of dinuclear Cu^{I} complex **6**. Thermal elipsoids shown at 50% probability; Selected bond angles (°): C(3)–C(2)–Cu(1) 70.22(18), C(1)–C(2)–Cu(1) 105.11(17), P(1)–S(1)–Cu(1) 98.81(4), C(3)–Cu(1)–S(1) 104.51(9), C(2)–Cu(1)–S(1) 143.46(10), Cl(1)–Cu(1)–S(1), 111.34(4). The complex has crystallographically imposed two-fold symmetry with the central C═O bond on the two-fold axis.

The Cu^{I} environment in **5** is closer to a classic tetrahedral arrangement than in **4**, but it can still be considered as distorted. The 1,4-dien-3-one backbone in both bridging 'dba' ligands adopts a s-*cis*,s-*cis* conformation. The Cu–C bond lengths are longer than those found in **4**, with the Cu–C bonds α to the carbonyl group longer than the β Cu–C bonds (see Table 1).

The P–S bonds in **5** also exhibit marked differences in their bond lengths. For example, P(1)–S(1) is 2.0221(10), which forms part of the outer step, whereas P(2)–S(2) is only 1.9936(10), being located on the outside edge of the pleated ladder. The Cu–Cl bond which forms part of the inner step is significantly shorter {Cu(2)–Cl(1) = 2.3330(7)} than the Cu–Cl bond located in the outer step {Cu(1)–Cl(1) = 2.4155(7)}. Complex **6** exhibits a trigonal planar geometry around Cu^{I}. The C–Cu bond lengths are much shorter than those found in **4** and **5**, but both the C–Cu and Cu–Cl bond lengths in **6** are consistent with a reported neutral Cu^{I} complex possessing a phosphine sulfide ligand.[17]

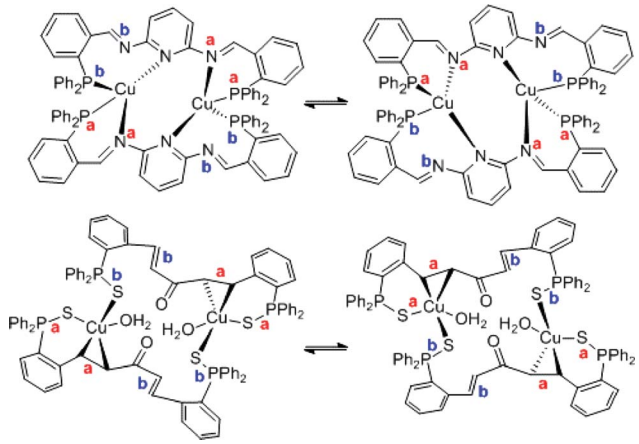
NMR spectroscopic analysis

The ^{1}H NMR spectrum of **4** exhibits fluxional behaviour at 300 K. We suspected that the free and coordinated alkenes were undergoing exchange on the NMR timescale. A variable temperature ^{1}H NMR experiment[18] confirmed that the very broad signals recorded at 300 K were indeed those of the free and coordinated alkenyl protons. The proton chemical shifts of the coordinated alkene (δ 5.94 and 5.99) possess a $^{3}J_{HH}$ coupling constant of 13.3 Hz, whereas the non-coordinated alkene (δ 6.60 and 7.82), has a $^{3}J_{HH}$ coupling constant of 16.4 Hz (confirmed by a low temperature 2D ^{1}H-^{1}H COSY experiment, see ESI†). The larger coupling constant and chemical shift difference is consistent with a free alkene moiety.

The ^{31}P NMR spectrum of **4** exhibits two broad singlets, indicating two phosphine sulfide chemical environments (δ 46.4 and 40.6, and one septet at −143.80 ($^{1}J_{PF}$ = 711 Hz), which is attributed to the PF_6 anion). The two singlets sharpen on lowering the temperature to 230 K. A 2D ^{1}H–^{31}P HMQC experiment shows that the ^{31}P signal at δ 40.6 couples with the proton at δ 5.94, whereas the ^{31}P signal at δ 46.4 couples with δ 7.82. Unfortunately, we were unable to get complete ^{13}C NMR spectroscopic data for complex **4** (see ESI†).

Interestingly, a related cationic Cu^{I} complex, [(2,6-(Ph_2P(*o*-C_6H_4)CH═N)$_2C_5H_3N$)$_2Cu_2$](BF_4)$_2$ (**7**) was reported by Yeh and Chen[19] very recently (Scheme 3). They noted dynamic exchange between the coordinated and the non-coordinated imine groups in solution {$\Delta G^{\ddagger}$ = 8.8 kcal mol^{-1} (36.8 kJ mol^{-1}), estimated}.

Using *gNMR* software,[20] we were able to simulate the line shape of the experimentally observed spectra to gain the rate constants for the exchange process at a number of temperatures. An Arrhenius plot of $1/T$ against ln k gives a straight line with



Scheme 3 Dynamic exchange in dinuclear cationic Cu^{I} complex **4** (bottom) and a related reported dinuclear cationic Cu^{I} complex **7** (top).[19] The two anions for each complex are omitted for clarity.

slope $-E_a/R$, allowing the activation energy to be estimated (58.23 kJ mol^{-1}). In addition, an Eyring plot of $\ln(k/T)$ against $1/T$ afforded a straight line plot ($R^2 = 0.9995$) from which the enthalpy ($\Delta H^{\ddagger} = 56.0 \pm 6.4$ kJ mol^{-1}) and entropy ($\Delta S^{\ddagger} = 0.43 \pm 6.9$ J mol^{-1} K^{-1}) of activation were determined. The small $\Delta S^{\ddagger}$ value is in keeping with the exchange being intramolecularly independent of water dissociation. The $\Delta H^{\ddagger}$ value indicates that the barrier to rotation is primarily enthalpic. The free energy of activation ($\Delta G^{\ddagger}$) at 300 K is 55.9 ±9.7 kJ mol^{-1} (13.4 ±2.3 kcal mol^{-1}).

The ^{1}H NMR spectrum of complex **6** shows all of the expected proton signals (Fig. 6). The ^{31}P NMR spectrum shows one phosphorus singlet (δ 40.8). Whilst the alkenyl protons {δ 6.07 ($\Delta\delta = 2.1$) and 5.83 ($\Delta\delta = 0.65$)} become shielded on coordination to Cu^{I}, unusually the signal at δ 5.83 (α-proton) appears broad at 293 K, whereas the neighbouring β-proton appears as a doublet signal (13.9 Hz). A variable temperature ^{1}H NMR experiment showed that the broad signal sharpens to give a doublet with a matching $^{3}J_{HH}$ coupling constant (13.9 Hz), confirming that both proton environments are associated with the alkene moiety. Cu coordination also causes a small decrease in the $^{3}J_{HH}$ coupling

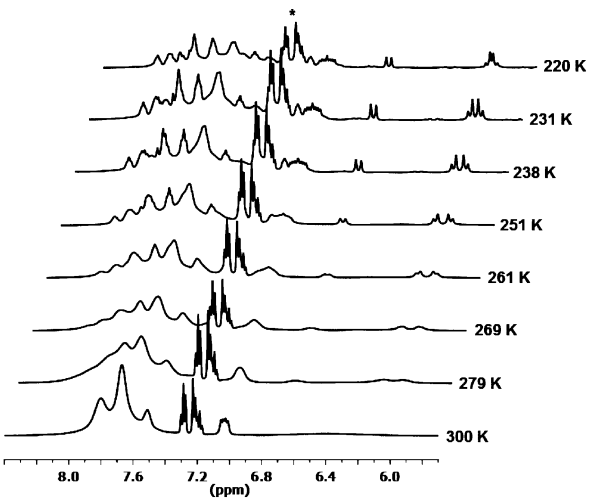


Fig. 5 Variable temperature ^{1}H NMR spectra of complex **4** in CD_2Cl_2 at 500 Hz (* trace toluene).

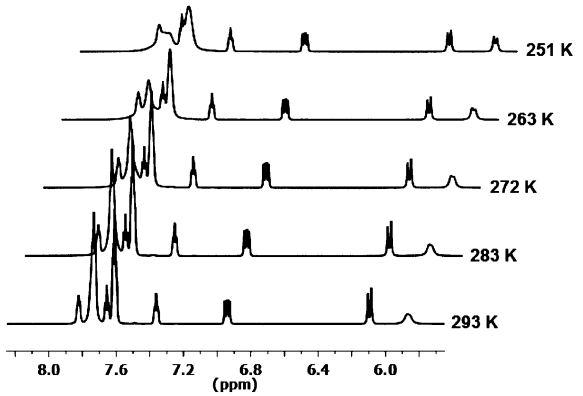


Fig. 6 Variable temperature ^{1}H NMR spectra of complex **6** in CD_2Cl_2 at 700 Hz.

constant relative to the free ligand **1** (15.8 Hz). The broadness of the α-proton is attributed to a partial restricted rotation about the C–C bonds connecting the C═O moiety. ^{13}C NMR spectroscopic analysis (in CD_2Cl_2) confirmed coordinated C═C bonds with broad signals observed at δ 95.3 and 94.4.

On the interconversion of 4↔5↔6

We hypothesised that it ought to be possible to interconvert complexes **4**↔**5**↔**6**, by either chloride addition, or chloride metathesis by the PF_6 anion. This was assessed by the addition of a soluble chloride source (n-Bu_4NCl). Thus, to a CD_2Cl_2 solution of complex **4** (15 mg, 0.01 mmol, 0.015 M) was added aliquots of a CD_2Cl_2 solution containing n-Bu_4NCl (see Fig. 7).

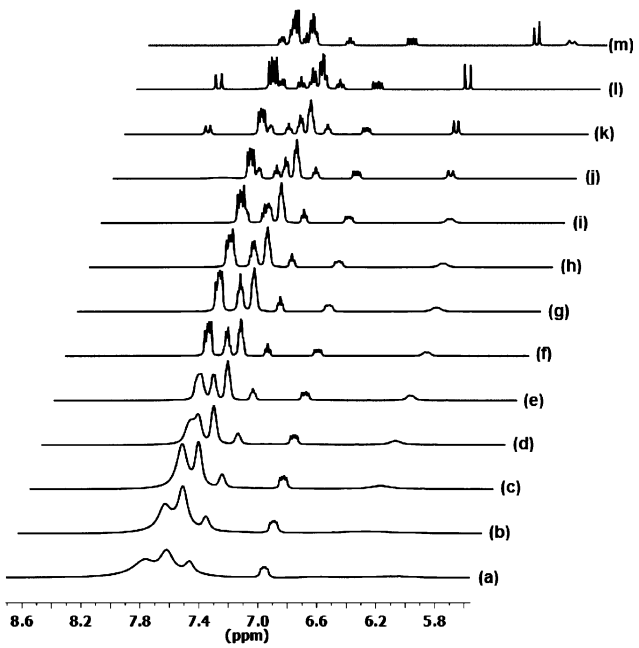


Fig. 7 Addition of chloride (n-Bu_4NCl) to complex **4** in CD_2Cl_2 monitored by ^{1}H NMR spectroscopy at 500 MHz (at 298 K). (a) Complex **4**; (b) 0.3 eq. n-Bu_4NCl; (c) 0.6 eq.; (d) 0.9 eq.; (e) 1.2 eq.; (f) 1.5 eq.; (g) 1.8 eq.; (h) 2.1 eq.; (i) 2.4 eq.; (j) 3 eq.; (k) 3.6 eq.; (l) ligand **1**; (m) Complex **6**.

Both ^{1}H and ^{31}P NMR spectra were recorded after each aliquot was added (see ESI† for ^{31}P NMR spectra). Spectroscopic analysis shows that no observable 'intermediate' complex (*e.g.* **5**) is formed in this reaction upon the addition of 0.5 equiv. of chloride per Cu. Increasing the chloride concentration leads to a new proton signal (broad) at δ 6.2–6.4. Following the addition of over 3 equiv. of chloride per Cu, only the free ligand **1** is observed and not complex **6**. Ligand **1** was identified by comparison {spectra (k) and (l) in Fig. 7} of the proton signals at δ 6.48 appearing as a doublet (15.6 Hz). A similar experiment by UV-Vis spectroscopic analysis revealed the presence of several Cu species in solution, for which further deductions could not be made.

The reaction of complex **6** with $AgPF_6$ (varying equivalents, see Fig. 8) in CD_2Cl_2 shares a similar ^{1}H NMR spectrum with complex **4**. On cooling, solutions of complex **6** with $AgPF_6$ (*ca.* 2.5 equiv.), the broad signals at δ 5.85–6.15 do not sharpen up akin to complex **4** (Fig. 5). Ag^{I} complexation to **1** is likely competing with Cu^{I} coordination, which could account for the incomplete conversion to **4** from **6**.

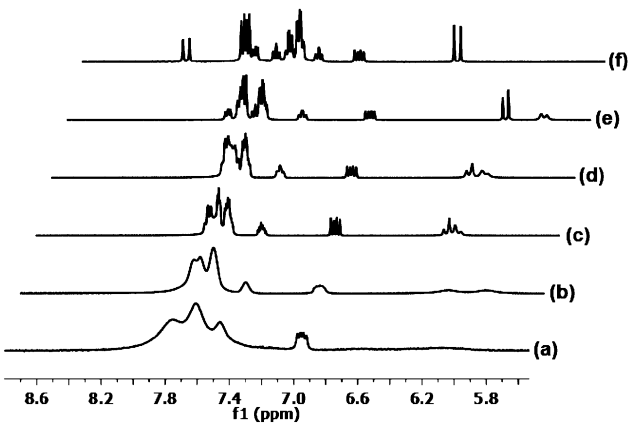
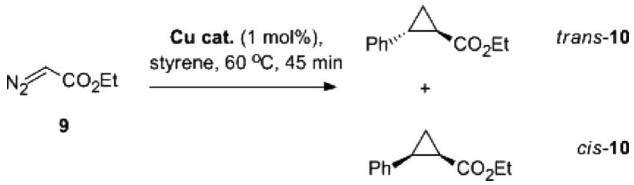


Fig. 8 Addition of $AgPF_6$ to complex **4** in CD_2Cl_2 monitored by ^{1}H NMR spectroscopy at 500 MHz (at 298 K). a) Complex **4**; b) 2 eq. $AgPF_6$; c) 1 eq. $AgPF_6$; d) 0.5 eq. $AgPF_6$; e) Complex **6**; f) ligand **1**.

Catalytic alkene cyclopropanation

The reactivity of complex **4** as a catalyst was investigated in a benchmark alkene cyclopropanation reaction, where Cu^{I}/Cu^{III} species are believed to play an important role.[21] With adequate controls in place (entries 1 and 2, Table 2), heating ethyl diazoacetate **9** in styrene (reagent and solvent) in the presence of 1 mol% of **4** at 60 °C for 45 min afforded the cyclopropane **10** in a diastereomeric ratio of 32 : 68 and 85% overall conversion (entry 3). This compares well with a recently reported Cu^{I}/Cu^{III} catalyst system for this cyclopropanation reaction.[22] Complex **6** is a marginally superior catalyst to **4** for this reaction (entry 4). The minor by-products of the alkene cyclopropanation reaction, diethyl fumarate and diethyl maleate, are formed by a well established competing reaction pathway.[22] A stoichiometric reaction of **4** with **9** (**9** : Cu, 1 : 1) in CD_2Cl_2 at ambient temperature showed no observable formation of either diethyl maleate or diethyl fumarate after 1 h (by ^{1}H NMR spectroscopy). After 24 h a small amount of these products was observable. However, under 'catalytic' conditions (**4** : **9**, 1 : 100), in the absence of styrene, an 80% conversion to diethyl fumarate and diethyl maleate (ratio: 60 : 40) was recorded by ^{1}H NMR spectroscopic analysis.

Table 2 Cu^{I}-catalysed alkene cyclopropanation



Catalyst (1 mol%)	Conversion (%)[a]	Diastereomeric ratio (*cis*-**10**/*trans*-**10**)
No catalyst	0	—
CuBr	24	40 : 60
4	85	32 : 68
6	91	30 : 70

[a] % Conversion to diastereomeric cyclopropane products by ^{1}H NMR spectroscopy (by-products include diethyl maleate and diethyl fumarate (see ESI† for details).

Conclusion

In summary, the synthesis and characterisation of dbathiophos **1**, and cationic and neutral Cu^{I} complexes derived thereof, have been reported. In three structurally unique Cu^{I} complexes (**4–6**) it was shown that the ligand backbone of **1** is hemilabile, multidentate and able to adopt different 1,4-dien-3-one conformations around Cu^{I}. We have further established that complexes **4** and **6** effectively catalyse the cyclopropanation of styrene using ethyl diazoacetate **9** at low catalyst loadings (1 mol% Cu). Indeed, catalytic efficacy was commensurate with a recently reported catalyst system.[22a]

It is interesting to note that complex **7** acts as a Cu model for the catalytic conversion of nitrite to nitrate.[19] The similar dynamic behaviour and coordination chemistry implies that **4** could also act as a Cu model. Our findings concerning further applications of **1**, and the Cu^{I} complexes thereof, will be reported in due course.

Experimental section

General details

NMR spectra were obtained in the solvent indicated, using a JEOL ECX400 or JEOL ECS400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C and 162 MHz for ^{31}P, respectively), a Bruker 500 (500 MHz, 126 MHz and 202 MHz for ^{1}H, ^{13}C and ^{31}P, respectively) and low temperature NMR studies were carried out on a Bruker AV700 (700 MHz and 283 MHz for ^{1}H and ^{31}P respectively). Chemical shifts were referenced to the residual undeuterated solvent of the deuterated solvent used ($CHCl_3$ δ = 7.26 and 77.16, $CDHCl_2$ δ = 5.31 and 53.80, ^{1}H and ^{13}C respectively). NMR spectra were processed using MestrNova software. We estimate that the error on the variable temperature NMR measurements is ±1.5 °C (determined by a methanol calibration at 500 MHz). Melting points were recorded using a Stuart digital SMP3 machine. TLC analysis was carried out on Merck TLC aluminium sheets (silica gel 60 F254) and flash chromatography run on silica gel 60. IR spectroscopy was undertaken using a Jasco/MIRacle FT/IR-4100typeA spectrometer on the neat

Table 3 Single crystal XRD data

Compound reference	ijf0821m (**1**)	ijf0829a (**4**)[29]	ijf0825m (**5**)[30]	ijf1015m (**6**)[31]
Chemical formula	$C_{41}H_{32}OP_2S_2{\cdot}2(CH_2Cl_2)$	$C_{82}H_{64}Cu_2O_4P_4S_4{\cdot}2(PF_6)$	$C_{82}H_{64}Cl_2Cu_4O_2P_4S_4{\cdot}2(PF_6){\cdot}1.58(C_4H_{10}O){\cdot}0.41(CH_2Cl_2)$	$C_{41}H_{32}Cl_2Cu_2OP_2S_2$
Formula Mass	836.58	1782.47	2117.11	864.71
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
a/Å	24.539(3)	25.838(3)	12.0204(7)	29.431(3)
b/Å	9.8002(10)	25.365(3)	14.5437(9)	8.9496(10)
c/Å	17.1991(17)	14.7220(15)	15.1233(9)	16.2751(18)
α/°	90.00	90.00	71.942(1)	90.00
β/°	90.768(2)	97.563(2)	71.271(1)	115.307(2)
γ/°	90.00	90.00	66.585(1)	90.00
Unit cell volume/Å^3	4135.8(8)	9564.7(17)	2246.5(2)	3875.4(7)
Temperature/K	110(2)	110(2)	110(2)	110(2)
Space group	$C2/c$	$P2(1)/c$	$P\bar{1}$	$C2/c$
No. of formula units per unit cell, Z	4	4	1	4
No. of reflections measured	15724	16818	23138	18084
No. of independent reflections	3666	16818	11056	4810
R_{int}	0.0302	0.0000	0.0218	0.0640
Final R_1 values ($I > 2\sigma(I)$)	0.0569	0.0828	0.0452	0.0423
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1612	0.1993	0.1207	0.0954
Final R_1 values (all data)	0.0679	0.1422	0.0614	0.0880
Final $wR(F^2)$ values (all data)	0.1732	0.2117	0.1305	0.1134

compounds, or solution IR spectra were obtained on a Nicolet Avatar 370 FT-IR spectrometer in the solvent stated. MS spectra were measured using a Bruker Daltronics micrOTOF machine with electrospray ionisation (ESI) or on a Thermo LCQ using electrospray ionisation. UV-visible spectra were recorded using a JASCO V-560. Elemental analysis was carried out on an Exeter Analytical CE-440 Elemental Analyser. Dry and degassed toluene, DCM and hexane were obtained from a Pure Solv MD-7 solvent purification system. THF and ether were either obtained from a Pure Solv MD-7 solvent purification system and degassed by the freeze–pump–thaw method, or dried over sodium-benzophenone ketyl and collected by distillation. Benzene was dried over sodium-benzophenone ketyl, and ethanol was dried and distilled from magnesium-iodine. Nitrogen gas was oxygen free and was dried immediately prior to use by passage through a column containing sodium hydroxide pellets and silica. Commercial chemicals were purchased from Sigma–Aldrich or Alfa Aesar.

Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo-Kα radiation (λ = 0.71073 Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using "SMART".[23] Frame integration and unit-cell refinement software was carried out with "SAINT+".[24] Absorption corrections were applied by SADABS (v2.10, Sheldrick). Structures were solved by direct methods using SHELXS-97[25] and refined by full-matrix least squares using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions, except for the alkene hydrogens in **5** and **6** which were located by difference map. Important X-ray details are collated in Table 3.

(1*E*,4*E*)-1,5-bis(2-(diphenylphosphorothioyl)phenyl)pent-an-1,4-dien-3-one (1)

[3-(Diethoxy-phosphoryl)-2-oxo-propyl]-phosphonic acid diethyl ester[26] (256 mg, 1 eq., 0.776 mmol) was added to a stirring solution of 2-(diphenylthiophosphino)benzaldehyde,[27] (500 mg, 2 eq., 1.56 mmol) in THF (3 mL). To this NaOH (124 mg, 4 eq., 3.11 mmol) dissolved in H_2O (0.5 mL) and THF (1 mL) was added dropwise. The mixture was refluxed for 48 h. After cooling, the solution was washed with saturated $NH_4Cl_{(aq)}$ (5 mL), extracted with ethyl acetate (5 × 5 mL), dried over Na_2SO_3 and filtered. After removing the solvent *in vacuo* the product was recrystallised from DCM/Hexane (1 : 3 *v*/*v*) to afford the title compound as a yellow solid (435 mg, 84%). M.p. 133–138 °C$_{(dec)}$; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.17 (d, J = 16.0 Hz, 2H, H$_c$), 7.84–7.69 (m, 10H, H$_e$ and *o*-Ar), 7.64–7.57 (m, 2H, H$_f$), 7.56–7.49 (m, 4H, *p*-Ar), 7.49–7.41 (m, 8H, *m*-Ar), 7.34 (tdd, J = 7.5, 2.3, 1.3 Hz, 2H, H$_g$), 7.09 (ddd, J = 14.5, 8.0, 1.0 Hz, 2H, H$_h$), 6.48 (d, J = 16.0 Hz, 2H, H$_b$); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 188.6 (C═O), 141.5 (d, J = 8 Hz, C$_c$), 138.9 (d, J = 7 Hz, C$_d$), 133.9 (d, J = 83 Hz, *ipso*-C), 133.4 (d, J = 11 Hz, C$_h$), 132.7 (d, J = 11 Hz, *o*-Ar), 132.5 (d, J = 85, *ipso*-C), 132.4 (d, J = 3 Hz, C$_f$), 132.2 (d, J = 3 Hz, *p*-Ar), 129.6 (d, J = 12 Hz, C$_g$), 129.0 (d, J = 13 Hz, *m*-Ar), 128.8 (d, J = 10 Hz, C$_e$), 126.8 (C$_b$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.07 (s); HRMS (ESI) m/z [MNa]$^+$ 689.1266 (calculated for $C_{41}H_{32}NaOP_2S_2$: 689.1262); LRMS (ESI) m/z (rel.%) 689.1 [MNa]$^+$ (100), 667.1 [MH]$^+$ (3); IR (solid, ν cm^{-1}): 3053 (w), 1656 (w), 1619 (w), 1602 (w), 1460 (w), 1436 (m), 1184 (w), 1098 (m), 753 (m), 711 (s), 692 (s), 636 (s), 614 (m), 575 (m); UV-vis (CH_2Cl_2) λ_{max} nm: 318 (ε = 19513 mol^{-1} dm^3 cm^{-1}); Anal. Calcd. for $C_{41}H_{32}OP_2S_2.1/10CH_2Cl_2$ (675) C 73.10, H 4.81; Observed C 73.32, H 4.83. Elemental analysis was conducted on crystals used for the XRD analysis.

Cu(1)PF$_6$ (solvent) (4)

A solution of $Cu(MeCN)_4PF_6$,[28] (168 mg, 1 eq., 0.45 mmol) in dry, degassed CH_2Cl_2 (5 mL) was added by cannula to a solution of ligand **1** (300 mg, 1 eq., 0.45 mmol) in dry, degassed CH_2Cl_2 (10 mL).‡ The resulting solution was stirred for 2 h at 20 °C.

‡ The reaction was also carried out in THF. The product precipitated overnight and the resulting yellow crystals were collected by filtration (48%).

CH_2Cl_2 was removed *in vacuo* to give a concentrated solution (4 mL) and layered with dry, degassed toluene (5 mL) to afford yellow crystals (270 mg, 69%) separated by filtration. M.p. 200 °$C_{(dec)}$; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.20–7.26 (br m, ~56H), 6.98 (dd, J = 15.0, 7.5 Hz, 4H), 6.52 (br s, 2H), 6.21 (br s, 2H); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 46.43 (br s), 40.59 (br s), −143.80 (hept, J_{PF} = 711 Hz); ^{13}C NMR (126 MHz, CD_2Cl_2) observed signals – C═O not observed δ 137.8 (d, J = 8 Hz), 136.4, 136.1, 134.8–134.3 (m), 134.0–132.1 (m), 131.1 (d, J = 14 Hz), 131.0–130.8 (m), 130.6–129.9 (m); HRMS (ESI) m/z 729.0708 (calculated for $C_{41}H_{32}OP_2S_2Cu$: 729.0660); IR (solid, ν cm^{-1}): 1652 (m), 1457 (m), 1438 (m), 1312 (w), 1170 (w), 1103 (m), 836 (s), 691 (s); UV-vis (CH_2Cl_2) λ_{max} nm: 320 (ε = 18345 mol^{-1} dm^3 cm^{-1}); Anal. Calcd. for $C_{82}H_{64}Cu_4F_{12}P_6$ (Cu_2(**1**)$_2PF_6$) C 56.26, H 3.69, N 0.00; Observed C 56.61, H 4.02, N 0.20.

Crystals of [Cu_2(**1**)$_2$(μ-OH_2)$_2$]2PF_6 (**4**) suitable for XRD analysis were obtained by layering CH_2Cl_2 with Et_2O, along with crystals of [Cu_4Cl_2(**1**)$_2$]2PF_6 (**5**) presumably formed in the presence of trace HCl or chloride abstraction of CH_2Cl_2.[13]

Cu_2Cl_2(1) (6)

In a glove box, ligand **1** (125 mg, 1 eq., 0.188 mmol) was dissolved in dry, degassed CH_2Cl_2 (7 mL) and CuCl (37 mg, 2 eq., 0.375 mmol) was added. After stirring for 1 h at 23 °C, more CH_2Cl_2 (2 mL) was added to dissolve the last traces of CuCl and the reaction stirred overnight, until no solid remained. Half the solvent was removed *in vacuo*, and the concentrated solution left overnight. The precipitate was filtered, washed with pentane (5 mL) and dried *in vacuo* to give a yellow crystalline product (119 mg, 73%). The solid was stored in a glove-box. M.p. 223 °$C_{(dec)}$; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83–7.79 (m, 2H, H_e), 7.79–7.67 (m, 12H, Ar), 7.66–7.54 (m, 10H, H_f and Ar), 7.37–7.31 (m, 2H, H_g), 6.92 (ddd, J = 14.5, 7.5, 1.0 Hz, 2H, H_h), 6.07 (d, J = 14.0 Hz, 2H, H_c), 5.83 (d (br), J = 14.0 Hz, 2H, H_b); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 184.2 (C═O), 139.8 (d, J = 8 Hz, C_d), 134.4 (d, J = 2 Hz, C_f), 133.9 (d, J = 3 Hz, *p*-Ar), 133.1 (d, J = 11 Hz, Ar), 132.9 (d, J = 11 Hz, C_h), 131.8 (d, J = 85 Hz, *ipso*-C), 131.6 (d, J = 9 Hz, C_e), 129.6 (d, J = 13 Hz, Ar), 128.6 (d, J = 13 Hz, C_g), 127.2 (d, J = 86 Hz, *ipso*-C), 95.3 (br, C═C), 94.4 (br, C═C); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 40.78 (s); LRMS (ESI) m/z (rel.%) 1397.2 [Cu(**1**)$_2$]$^+$ (29), 829.0 [M-Cl]$^+$ (100), 729.1 [M-$CuCl_2$]$^+$ (87), 667.1 [**1**+H]$^+$ (4); HRMS (ESI) m/z 826.9623 (calculated for $C_{41}H_{32}Cl\,Cu_2OP_2S_2$ = 826.9645); IR (solid, ν cm^{-1}): 1653 (w), 1537 (w), 1455 (w), 1433 (m), 1312 (m), 1247 (w), 1103 (m), 1084 (m), 1064 (m), 967 (m), 756 (s), 691 (s); IR (CH_2Cl_2, ν cm^{-1}): 3046 (w), 1653 (w), 1539 (w), 1457 (w), 1439 (m), 1314 (w), 1271 (m), 1265 (m), 1261 (m), 1106 (w); UV-vis (CH_2Cl_2) λ_{max} nm: 396 (ε = 12199 mol^{-1} dm^3 cm^{-1}) shoulders at 326 (ε = 10213 mol^{-1} dm^3 cm^{-1}) and 258 (ε = 34 000 mol^{-1} dm^3 cm^{-1}); Anal. Calcd. for $C_{41}Cl_2Cu_2H_{32}OP_2S_2.CH_2Cl_2$ (949) C 53.12, H 3.61; Observed C 53.17, H 3.58.

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Notes and references

1 For an excellent review detailing various transition metal complexes bearing a dba-H ligand(s), see: A. Z. Rubezhov, *Russ. Chem. Rev.*, 1988, **57**, 1194–1207.
2 (*a*) H. B. Lee and P. M. Maitlis, *J. Organomet. Chem.*, 1973, **57**, C87–C89; (*b*) J. A. Ibers, *J. Organomet. Chem.*, 1974, **73**, 389–400.
3 S. Bernès, R. A. Toscano, A. C. Cano, O. G. Mellado, C. Alvarez-Toledano, H. Rudler and J.-C. Daran, *J. Organomet. Chem.*, 1995, **498**, 15–24.
4 (*a*) C. Alvarez-Toledano, E. Delgado, B. Donnadieu, E. Hernandez, G. Martin and F. Zamora, *Inorg. Chim. Acta*, 2003, **351**, 119–122; (*b*) F. Ortega-Jimenez, M. C. Ortega-Alfaro, J. G. Lopez-Cortes, R. Gutierrez-Perez, R. A. Toscano, L. Velasco-Ibarra, E. Pena-Cabrera and C. Alvarez-Toledano, *Organometallics*, 2000, **19**, 4127–4133; (*c*) S. Rivomanana, C. Mongin and G. Lavigne, *Organometallics*, 1996, **15**, 1195–1207.
5 S. V. Osintseva, F. M. Dolgushin, N. A. Shteĺtser, P. V. Petrovskii, A. Z. Kreindlin, L. V. Rybin and M. Y. Antipin, *Organometallics*, 2005, **24**, 2279–2288.
6 (*a*) N. W. Alcock, N. Herron, T. J. Kemp and C. W. Shoppee, *Chem. Commun.*, 1975, 785–786; (*b*) N. W. Alcock, P. Meester and T. J. Kemp, *J. Chem. Soc., Perkin Trans. 2*, 1979, 921–926; (*c*) N. W. Alcock and P. Meester, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **B35**, 609–611; (*d*) M. Alagar, S. Kannan, K. Rajagopal, V. Venugopal, R. V. Krishnakumar, M. Subha Nandhini and S. Natarajan, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **E60**, m773–m775.
7 (*a*) I. J. S. Fairlamb, *Org. Biomol. Chem.*, 2008, **6**, 3645–3656; (*b*) I. J. S. Fairlamb and A. F. Lee, *Organometallics*, 2007, **26**, 4087–4089; (*c*) I. J. S. Fairlamb, A. R. Kapdi and A. F. Lee, *Org. Lett.*, 2004, **6**, 4435–4438; (*d*) Y. Macé, A. R. Kapdi, I. J. S. Fairlamb and A. Jutand, *Organometallics*, 2006, **25**, 1785–1800; (*e*) I. J. S. Fairlamb, A. R. Kapdi, A. F. Lee, G. P. McGlacken, F. Weissburger, A. H. M. de Vries and L. Schmieder-van de Vondervoort, *Chem.–Eur. J.*, 2006, **12**, 8750–8761; (*f*) P. Sehnal, H. Taghzouti, I. J. S. Fairlamb, A. Jutand, A. F. Lee and A. C. Whitwood, *Organometallics*, 2009, **28**, 824–829.
8 F. A. Jalón, B. R. Manzano, F. Gómez-de, la Torre, A. M. López-Agenjo, A. M. Rodríguez, W. Weissensteiner, T. Sturm, J. Mahía and M. Maestro, *J. Chem. Soc., Dalton Trans.*, 2001, 2417–2424.
9 (*a*) Y. Zhao, H. Wang, X. Hou, Y. Hu, A. Lei, H. Zhang and L. Zhu, *J. Am. Chem. Soc.*, 2006, **128**, 15048–15049; (*b*) For related ligand effects, see: Q. Liu, H. Duan, X. Luo, Y. Tang, G. Li, R. Huang and A. Lei, *Adv. Synth. Catal.*, 2008, **350**, 1349–1354; (*c*) X. Luo, H. Zhang, H. Duan, Q. Liu, L. Zhu, T. Zhang and A. Lei, *Org. Lett.*, 2007, **9**, 4571–4574; (*d*) W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang and A. Lei, *J. Am. Chem. Soc.*, 2008, **130**, 14713–14720; (*e*) H. Zhang, X. Luo, K. Wongkhan, H. Duan, Q. Li, L. Zhu, J. Wang, A. S. Batsanov, J. A. K. Howard, T. B. Marder and A. Lei, *Chem.–Eur. J.*, 2009, **15**, 3823–3829.
10 A. Kiyomori, J.-F. Marcoux and S. L. Buchwald, *Tetrahedron Lett.*, 1999, **40**, 2657–2660.
11 For Cu^I complexes containing η^2-isoprene, other η^2-dienes and η^4-isoprene, see: (*a*) M. J. Bainbridge, J. R. Lindsay Smith and P. H. Walton, *Dalton Trans.*, 2009, 3143–3152; (*b*) M. Hakansson, S. Jagner and D. Walther, *Organometallics*, 1991, **10**, 1317–1319; (*c*) M. Hakansson, K. Brantin and S. Jagner, *J. Organomet. Chem.*, 2000, **602**, 5–14; (*d*) A. Camus, N. Marish, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 1977, **23**, 131–144. There are only a handful of complexes where crystallographic evidence shows a single Cu centre bound to two or more alkenes from the same polyene, see: (*e*) B. J. Bellott and G. S. Girolami, *Organometallics*, 2009, **28**, 2046–2052. Several coordination polymers utilise Cu^I-alkene binding to stabilize large supramolecular networks, see; (*f*) Q. Ye, X.-S. Wang, H. Zhao and R.-G. Xiong, *Chem. Soc. Rev.*, 2005, **34**, 208–225; (*g*) For a series of HPYA (4-pyridylacrylic acid) and 3-HPYA (3-pyridylacrylic acid) of 1D and 2D copper(I)-alkene coordination polymers with high thermal stability, see; (*h*) J. Zhang, R.-G. Xiong, X.-T. Chen, C.-M. Che, Z. Xue and X.-Z. You, *Organometallics*, 2001, **20**, 4118–4121.
12 B. J. Hathaway, In *Comprehensive coordination chemistry* (Eds) G. Wilkinson, R. D. Gillard and J. A. McCleverty, Oxford: Pergamon, 1987, vol. 5, p. 534.

13 Halide activation of CH_2Cl_2 by Cu^I complexes has been reported. For example, [Cu(dppm-)] reacts with both CH_2Cl_2 and CH_2Br_2, see: (*a*) C. E. Anson, L. Ponikiewski and A. Rothenberger, *Z. Anorg. Allg. Chem.*, 2006, **632**, 2402–2404. Lui reported a series of Cu^I complexes with dithiophosphates and bis(diphenylphosphino) alkane ligands, where Cu clusters were found to react with both CH_2Cl_2 or $CHCl_3$ (dependant on ligand to metal ratio), see; (*b*) B.-J. Liaw, T. S. Lobena, Y.-W. Lin, J.-C. Wang and C. W. Liu, *Inorg. Chem.*, 2005, **44**, 9921–9929. We suspect that the source of chloride is most likely trace HCl in CH_2Cl_2.

14 (*a*) C. G. Pierpont and M. C. Mazza, *J. Chem. Soc. Chem. Commun.*, 1973, 207; (*b*) M. Ogasawara, K. Yoshida, H. Kamei, K. Kato, Y. Uozumi and T. Hayashi, *Tetrahedron: Asymmetry*, 1998, **9**, 1779–1787; (*c*) K. Selvakumar, M. Valentini, M. Wörle and P. S. Pregosin, *Organometallics*, 1999, **18**, 1207–1215.

15 Y. Takemura, T. Nakajima and T. Tanase, *Dalton Trans.*, 2009, 10231–10243.

16 (*a*) G. A. van Albada, I. Mutikainen, O. Roubeau, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta*, 2002, **331**, 208–215; (*b*) S. Balboa, R. Carballo, A. Castiñeiras, J. M. González-Pérez and J. Niclós-Gutiérrez, *Polyhedron*, 2008, **27**, 2921–2930; (*c*) Y.-Q. Zheng and J.-L. Lin, *Z. Anorg. Allg. Chem.*, 2002, **628**, 203–208.

17 E. W. Ainscough, H. A. Bergen, A. M. Brodie and K. A. Brown, *J. Chem. Soc., Dalton Trans.*, 1976, 1649–1656.

18 The variable temperature ^{1}H NMR spectra of complex **4** reveal sharp signals for the alkene protons. However, we suspect that another unidentifiable species is present as the proton integrals are not perfect. Further spectroscopic analysis is also complicated by the phosphorus phenyl groups moving toward inequivalence at lower temperatures (also see ESI†).

19 C.-S. Chen and W.-Y. Yeh, *Chem. Commun.*, 2010, **46**, 3098–3100.

20 *gNMR* software package (version 5.1, P. H. M. Budzelaar, Department of Chemistry, University of Manitoba), see: http://home.cc.umanitoba.ca/~budzelaa/gNMR/gNMR.html (last accessed 19/11/2010).

21 H. Lebel, J.-F. Marcoux, C. Molinaro and A. B. Charette, *Chem. Rev.*, 2003, **103**, 977–1050.

22 (*a*) J. García-López, V. Yañez-Rodríguez, L. Roces, S. García-Granda, A. Martínez, A. Guevara-García, G. R. Castro, F. Jiménez-Villacorta, M. J. Iglesias and F. López Ortiz, *J. Am. Chem. Soc.*, 2010, **132**, 10665–10667; (*b*) Also see: I. V. Shishkov, F. Rominger and P. Hofmann, *Organometallics*, 2009, **28**, 1049–1059; (*c*) J. I. García, G. Jiménez-Osés, V. Martínez-Merino, J. A. Mayoral, E. Pires and I. Villalba, *Chem. Eur. J.*, 2007, **13**, 4064–4073; (*d*) W. Kirmse, *Angew. Chem., Int. Ed.*, 2003, **42**, 1088–1093.

23 *Smart diffractometer control software (v5,625),* Bruker-AXS, Bruker AXS GmbH, Karlsruhe, Germany.

24 *Saint+ (v6.22) Bruker AXS,* Bruker AXS GmbH, Karlsruhr, Germany.

25 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

26 B. Corbel, L. Medinger, J. P. Haelters and G. Strutz, *Synthesis*, 1985, 1048–1051.

27 A. Maraval, G. Magro, V. Maraval, L. Vendier, A. M. Caminde and J. –P. Majoral, *J. Organomet. Chem.*, 2006, **691**, 1333–1340.

28 G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90–92.

29 The crystals contained disordered solvents, presumably a mixture of dichloromethane and diethyl ether which could not be modelled as discrete atoms. Therefore the SQUEEZE algorithm was used to account for the solvent. The solvent void was measured to be 1469 $Å^3$ and 776 electrons were attributed to the solvent. Since this is due to a mixture of solvents, it is not possible to determine the overall formula, formula weight or density for the crystals. It is assumed that the oxygen ligands bound to the copper are water molecules, but suitable locations for the hydrogens could not be determined and so these were omitted.

30 The crystals contained a mixture of disordered solvents. Relative occupancy of each solvent was allowed to refine; overall occupancy was restrained to be 1.0. The solvents were modelled as a diethyl ether (79.4%) [with one terminal carbon disordered over two sites (C42 and C42a)] and a dichloromethane disordered over two sites (7.2% and 13.4%). All solvent atoms were modelled isotropically. Within the solvents, C–C bonds were restrained to be 1.51 Å, C–O bonds to 1.425 Å and C–Cl to 1.728 Å.

31 There is a small void in the model (volume 31 $Å^3$). However, the largest peak in the difference map in the void is only 0.62 e $Å^{-1}$, so the space is assumed to be empty.

