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Synthesis and reactivity of copper(I) phosphine–alkene complexes: X-ray crystal structure of $CuCl(Ph_2PCPh{=}CH_2)_2$

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Abstract

Copper(I) chloride complexes containing bifunctional phosphine/alkene ligands of the form $CuCl(Ph_2PCH{=}CH_2)_n$ ($n=1$, 3) and $CuCl(Ph_2PCPh{=}CH_2)_2$ have been synthesized, with the latter being characterized by single crystal X-ray diffraction. Complexes decompose rapidly on reaction with hydroborating agents $NaBH_4$ and $Na[B(OMe)_3H]$, although the thermally unstable $Cu(BH_4)(Ph_2PCPh{=}CH_2)_2$ may be observed by NMR spectroscopy. The complexes show considerable resistance to thermally initiated alkene polymerization, the only significant reactivity for diphenylvinylphosphine complexes being trace ligand dissociation and subsequent aerobic oxidation to $Ph_2P(O)CH{=}CH_2$. Similar dissociation/oxidation is not observed for $CuCl(Ph_2PCPh{=}CH_2)_2$. Lewis acid initiated polymerization, using $Et_2O \cdot BF_3$, results in the facile formation of copper(I) coordinated polymeric phosphine ligands for diphenylvinylphosphine complexes, but again no reactivity is induced in the more sterically hindered α-styrenyl analogue.

Keywords: Phosphine; Alkene; Polymerization; Hydroboration; Copper(I) complexes

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1. Introduction

The coordination chemistry of copper has been the subject of extensive research over several decades [1]. Despite such thorough activity, the structure and reactivity of copper complexes remains the focus of considerable research effort [2,3]; copper biochemistry and the stoichiometric use of organocopper reagents in synthesis are particularly significant [4,5]. The stabilization of copper(I) by tertiary phosphines forms some of the earliest studies of coordination chemistry [6,7]. Subsequent work has demonstrated a diversity of structure and stoichiometry derived from the absence of electronic factors in the d^{10} electronic configuration. Thus, whilst monophosphine complexes commonly adopt cubane or stepped tetrameric solid state structures [8,9], more sterically demanding phosphines can favour the formation of dimeric and even monomeric complexes [10,11]. The bridging halide ligands which occur in monophosphine complexes may be cleaved by the use of greater phosphine:copper(I) stoichiometries; once again the absence of ligand field control leads to the isolation of numerous products in which the copper salt, phosphine, reaction solvent and experimental conditions are all influential. The reactivity of copper chloride systems with triphenylphosphine is illustrative of this reagent and condition-based diversity. In addition to $[CuCl(PPh_3)]_4$ formed directly from CuCl or by the phosphine reduction of $CuCl_2 \cdot 2H_2O$ [12], $CuCl(PPh_3)_2$ or $(Ph_3P)_2CuCl_2Cu(PPh_3)/CuCl(PPh_3)_3$ may be isolated from 1:2 metal:ligand reactions in chloroform and thf, respectively [13,14]. $CuCl(PPh_3)_3$ can also be formed from 1:3 reactions in a variety of solvents or molten PPh_3 [14,15]. Whilst numerous tertiary phosphine complexes of copper(I) are reported, the present work focuses on structure and reactivity in the presence of ancillary alkene functionalities. Thus, as part of recent investigations of the phosphine/alkene complexes [16,17] we report the synthesis of diphenylvinyl- and diphenyl-α-styrenyl-phosphine complexes of copper(I), their potential for thermal and catalysed alkene polymerization, and reactivity towards hydroborating agents.

2. Results and discussion

2.1. Synthesis of complexes

The reaction of copper(I) chloride with 1 equiv. of $Ph_2PCH{=}CH_2$ in CH_2Cl_2 affords the monophosphine com-

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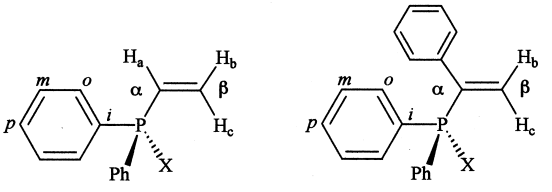
plex $CuCl(Ph_2PCH{=}CH_2)$ (**1**), Table 1. Whilst reports exist of bidentate diphenylvinylphosphine complexes of silver(I) [18], IR spectroscopic evidence is indicative of non-bonded alkene functions in **1**. Thus, although **1** has not been structurally characterized, analogy with known complexes suggests the formation of tetrameric solid state species [8]. ^1H NMR spectroscopy is in accord with the presence of pendant alkene moieties. However, whilst vinylic proton resonances occur at broadly similar chemical shifts and with similar couplings to those of free ligand and metal complexed systems [19], it is notable that the chemical shifts of the terminal vinyl protons H_b and H_c, Scheme 1, are less separated than in comparable systems. These resonances are in fact overlaid and lie at chemical shifts which are reversed relative to their normal field positions, Table 2. Whilst the assignment of these overlaid and coupled resonances is readily elucidated by ^1H 2D COSY NMR spectroscopy, Fig. 1, the origin of this anomalous behaviour is less clear. Since the overlying of H_b and H_c principally originates from the larger than normal downfield shift of H_c, it must be speculated that additional deshielding interactions occur through this moiety. However, as this effect is not reflected in additional ^1H NMR spectroscopic coupling or shifted $^{13}C\{^1H\}$ chemicals shifts for the associated β-carbon, Table 3, it must be considered as a minor effect.



X = CuCl **(1)**
X = CuCl($Ph_2CH{=}CH_2)_2$ **(2)**
X = O **(4)**

X = CuCl($Ph_2PCPh{=}CH_2$) **(3)**
X = O **(5)**

Scheme 1. Atom numbering in **1**–**5**.

The reaction of CuCl and three molar equivalents of $Ph_2PCH{=}CH_2$ generates the tris-phosphine complex $CuCl(Ph_2PCH{=}CH_2)_3$ (**2**). ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectroscopy confirms the conventional P-bound nature of the phosphine ligands which are spectroscopically equivalent in solution. $^1H/^{13}C\{^1H\}$ 2D COSY NMR spectroscopy, Fig. 2, confirms the assignment of $^{13}C\{^1H\}$ NMR resonances. **2** precipitates from solution as microcrystalline material cor-

Table 1
Physical and analytical data for complexes **1**–**4**

Complex	Colour	Melting point (°C)	$\nu(C{=}C)$ [a] (cm^{-1})	Elemental analysis [b]	
				C (%)	H (%)
$CuCl(Ph_2PCH{=}CH_2)$ (**1**)	white	146	1633	54.0 (54.2)	4.3 (4.1)
$CuCl(Ph_2PCH{=}CH_2)_3$ [c] (**2**)	white	88	1635	67.3 (66.6)	6.0 (6.3)
$CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**)	white	145	1683	71.3 (71.1)	5.3 (5.0)
$Ph_2P(O)CH{=}CH_2$ (**4**)	white	104	1627	64.7 (64.5)	6.0 (5.7)

[a] IR, KBr DRIFT reflectance.
[b] Expected values in parentheses.
[c] **2**·0.5thf.

Table 2
^1H NMR ($CDCl_3$) spectroscopic data for complexes **1**–**5**

Complex	Position	Shift (δ)	Multiplicity	$^3J_{ab}$ (Hz)	$^3J_{ac}$ (Hz)	$^2J_{bc}$ (Hz)	$^nJ_{PH}$ (Hz)
$CuCl(Ph_2PCH{=}CH_2)$ (**1**)	Ph	7.34–7.56	m				
	H_a	6.49	ddd	11.4	12.5		18.0
	H_b	5.96	dd	11.4		0.0	40.7
	H_c	6.01	dd		12.5	0.0	26.0
$CuCl(Ph_2PCH{=}CH_2)_3$ (**2**)	Ph	7.14–7.52	m				
	H_a	6.33	ddd	11.7	17.8		20.3
	H_b	5.84	dd	11.7		0.0	34.4
	H_c	5.60	dd		17.8	0.0	17.8
$CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**)	Ph	7.12–7.73	m				
	H_b	6.09	d			0.0	24.9
	H_c	5.32	d			0.0	11.7
$Ph_2P(O)CH{=}CH_2$ (**4**)	Ph	7.20–7.55	m				
	H_a	6.68	ddd	12.5	18.7		24.5
	H_b	6.31	ddd	12.5		1.8	41.0
	H_c	6.27	ddd		18.7	1.8	22.3
$Ph_2P(O)CPh{=}CH_2$ (**5**)	Ph	7.18–7.84	m				
	H_b	6.25	dd			1.1	40.3
	H_c	5.76	dd			1.1	19.4

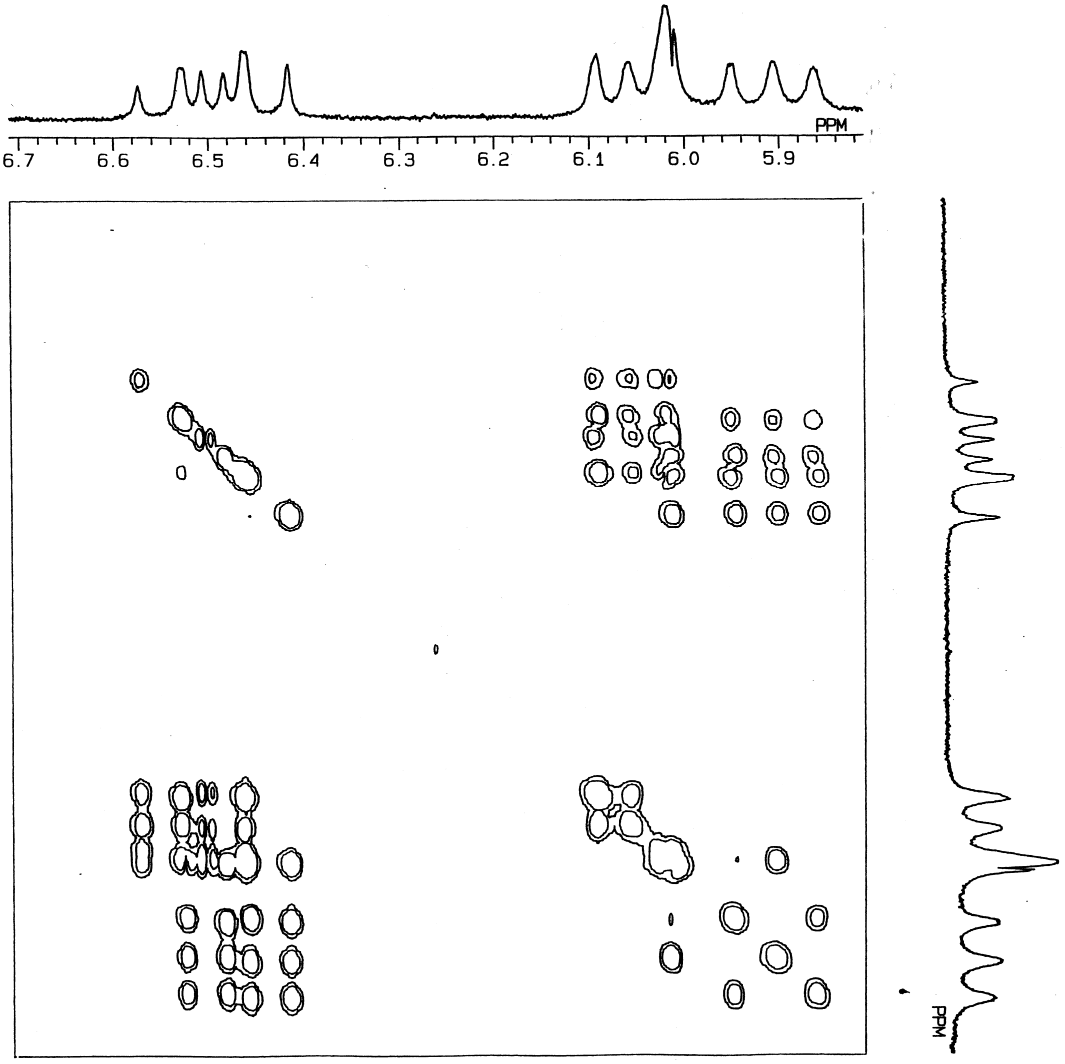


Fig. 1. ^1H 2D COSY NMR spectrum of $CuCl(Ph_2PCH{=}CH_2)$ (**1**) in $CDCl_3$ showing coupling of vinylic protons.

Table 3
$^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data for complexes **1**–**5**

Complex	$^{31}P\{^1H\}$ [a] (δ)	$^{13}C\{^1H\}$ [b] (δ)						
		α	β		*i*	*o*	*m*	*p*
$CuCl(Ph_2PCH{=}CH_2)$ (**1**)	−5.6 [c]	132.29	131.70		133.24	128.96	133.62	130.29
	−8.6 [d]	(18.3)	(8.6)		(38.0)	(9.7)	(14.8)	(s)
$CuCl(Ph_2PCH{=}CH_2)_3$ (**2**)	−9.8 [c]	131.97	130.40		132.80	127.71	132.94	129.99
	−11.3 [d]	(20.7)	(8.5)		(27.3)	(8.5)	(13.5)	(s)
$CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**)	0.0 [c]	139.98	132.04	P*Ph*$_2$	130.76	128.57	134.38	130.08
	−1.2 [d]	(14.7)	(9.8)		(31.8)	(9.8)	(14.6)	(s)
				PC*Ph*	130.85	128.34	127.84	127.67
					(6.1)	(s)	(10.9)	(s)
$Ph_2P(O)CH{=}CH_2$ (**4**)	23.3 [c]	131.65	135.04		132.80	131.75	128.97	132.26
	18.7 [d]	(96.5)	(s)		(106.2)	(9.7)	(12.2)	(2.5)
$Ph_2P(O)CPh{=}CH_2$ (**5**)	19.4 [c]							
	16.0 [d]							

[a] $Ph_2PCH{=}CH_2$, $^{31}P\{^1H\}$, $CDCl_3$, $\delta = -11.4$; $Ph_2PCPh{=}CH_2$, $^{31}P\{^1H\}$, $CDCl_3$, $\delta = -6.8$.

[b] $^nJ(CP)$ (Hz) in parentheses, $CDCl_3$.

[c] $CDCl_3$.

[d] C_7D_8.

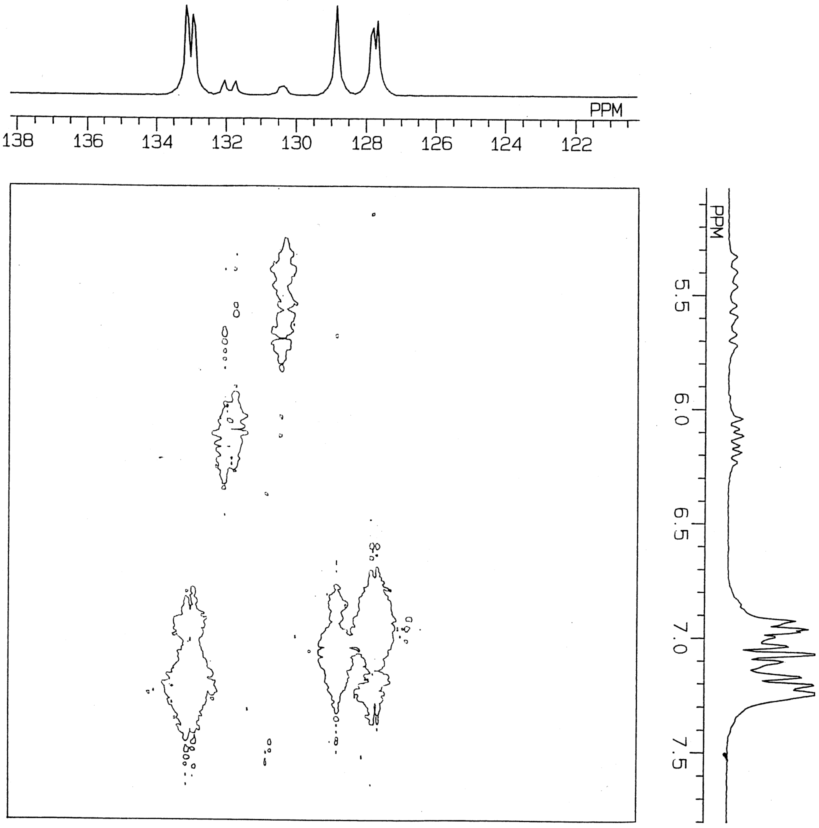


Fig. 2. $^1H/^{13}C\{^1H\}$ 2D COSY NMR spectrum of $CuCl(Ph_2PCH{=}CH_2)_3$ (**2**) in $CDCl_3$.

responding to the solvate **2**·0.5thf. Evidence for this formulation is provided by ^1H NMR spectroscopy which identifies non-bonded thf at $\delta = 1.82$ (t) and 3.70 (t) in $CDCl_3$, and thermogravimetric analysis which yields a mass loss of 4.5% (4.7%) in the temperature range 50–60°C.

In contrast to the formation of **2**, the reaction of CuCl and 3 equiv. of $Ph_2PCPh{=}CH_2$ results in the isolation of $CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**) on recrystallization from CH_2Cl_2/Et_2O. The increased cone angle of the α-styrenyl ligand evidently favours bis-complex formation on steric grounds. Such changes in stoichiometry from reactant to product are not unusual, the facile modification of metal:ligand stoichiometry has been observed in other copper(I) phosphines, for example the shift from $Cu(NO_3)(PPh_3)_3$ to $Cu(NO_3)(PPh_3)_2$ on recrystallization [20]. Phenyl substitution in **3** relative to the vinyl complexes **1** and **2** results in a significant simplification of the ^1H NMR features associated with the alkene moiety, with protons centred at the β-carbon being reduced to phosphorus-coupled doublets, Table 2.

Since phosphine oxidation forms a facile deactivation pathway for both phosphine ligands and complexes at ambient or elevated temperatures [21,22], the phosphine oxides $Ph_2P(O)CH{=}CH_2$ (**4**) and $Ph_2P(O)CPh{=}CH_2$ (**5**) have been prepared by peroxydisulfate oxidation of the corresponding phosphines. Analytical and spectroscopic data again confirm the integrity of these products, Tables 1–3. Attempts to assign the $^{13}C\{^1H\}$ NMR resonances of **4** using proton-coupled ^{13}C NMR spectroscopy result in complex spectra as a consequence of extensive $^2J(CH)$ and $^3J(CH)$ coupling. $^1H/^{13}C\{^1H\}$ 2D COSY NMR spectroscopy provides in simpler route to such interpretation, Fig. 3, from which $^{13}C\{^1H\}$ and ^{13}C NMR resonances, as well as $^nJ(CP)$ and $^nJ(CH)$ couplings, can be assigned. The latter couplings are typical of phosphorus(V) interaction with aromatic and alkene sp^2 carbons.

2.2. Thermal and Lewis acid catalysed polymerization studies

The thermal effects of heating complexes **1–3** to 100°C in deuterated toluene have been followed using $^{31}P\{^1H\}$ NMR spectroscopy. In inert atmospheres no evidence for chemical change can be observed for **1–3** over 8 h. Under similar conditions in air, **1** and **2** show trace oxidation ($<5\%$) to free **4** ($^{31}P\{^1H\}$ C_7D_8 $\delta = 18.7$), although no loss of integrity is recorded for the more sterically hindered α-styrenyl complex **3**. Since vinyl and α-styrenyl substituted phosphine ligands are readily distinguish from their saturated or polymerized analogues in $^{31}P\{^1H\}$ NMR spectroscopy by the respective presence and absence of diamagnetic deshielding [16], it is evident that these complexes display no propensity for thermally initiated alkene polymerization.

Early reports have demonstrated that both free $Ph_2PCH{=}CH_2$ [23] and its silver(I) complexes [18] undergo Lewis acid catalysed alkene polymerization. Thus,

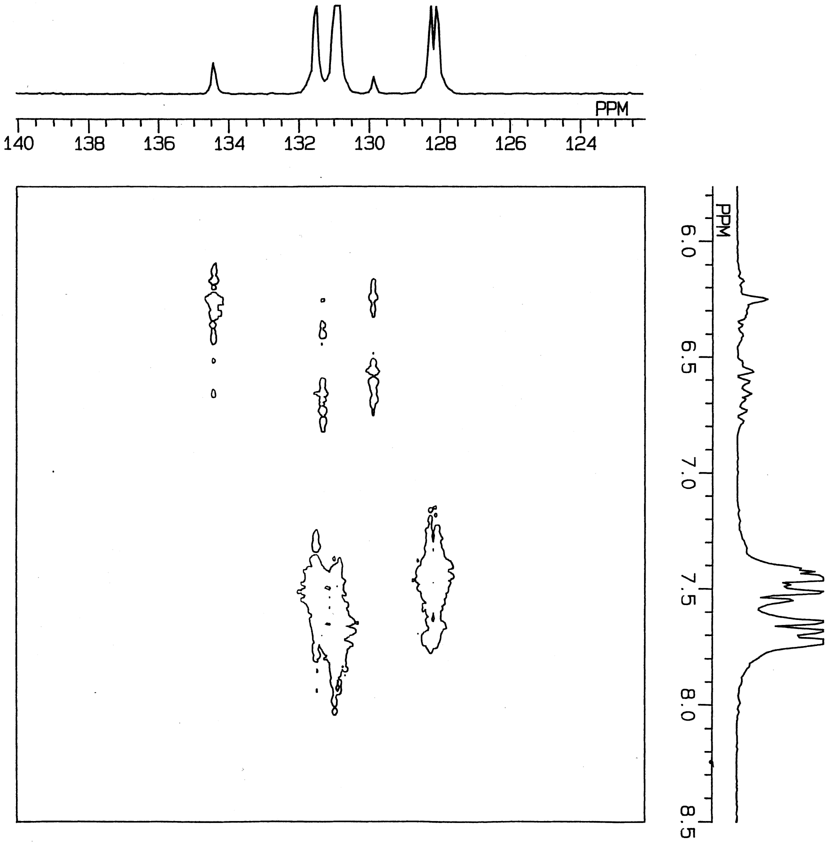


Fig. 3. $^1H/^{13}C\{^1H\}$ 2D COSY NMR spectrum of $Ph_2P(O)CH{=}CH_2$ (**4**) in $CDCl_3$.

$Et_2O \cdot BF_3$ catalysed polymerization studies have been performed in $CDCl_3$ and followed using NMR spectroscopy. The exposure of **1** to $Et_2O \cdot BF_3$ over ca. 1 h results in the precipitation of $[CuCl(Ph_2PCH–CH_2–)_n]$ (**6**) (C 54.0 (54.3); H 4.2 (4.2)) in ca. 80% yield. The corresponding reaction of **2** affords precipitates of variable hydrocarbon content consistent with concomitant ligand polymerization and dissociation. Since $[CuCl(Ph_2PCH–CH_2–)_n]$ (**6**) (and its corresponding product obtained from **2**) are insoluble in common NMR solvents, spectroscopic evidence to support polymerization is limited. No IR band corresponding to $\nu(C{=}C)$ can be located, however, such absorbances are often weak and difficult to assign even in authentic diphenylvinylphosphines. Thus interpretation is limited to elemental analysis consistent with the formation of **6**. Whilst it is obvious that **2** would provide identical elemental analysis, the considerable solubility of **2**, $Et_2O \cdot BF_3$ and the common decomposition product **4**, in $CDCl_3$ preclude the presence of these materials. The composition of the remaining reaction solution material is complex and dynamic. $^{31}P\{^1H\}$ NMR spectroscopy identifies five principal components, although their relative proportions vary with time and decrease overall relative to numerous other species. After 1 day a copper(I) phosphine complex ($\delta = -5.4$ and 2.5 ppm), the $[Ph_2PCH{=}CH_2 \cdot BF_3]$ adduct ($\delta = 1.7$ ppm) and additional products $\delta = 17.1$ ppm (dd $J = 62.5$ and 1187.6 Hz) and $\delta = 22.3$ ppm (dd $J = 58.9$ and 183.9 Hz) are all observed. The propensity for rapid phosphine exchange, plus the complex vinylic and ethylene resonances present in ^1H NMR spectra, make detailed interpretation impossible. However, further BF_3 reactivity beyond simple Lewis acid behaviour is certainly possible. Fluoride and tetrafluoroborate complexes of copper(I) phosphines are known [24], whilst the formation of BF_4^- complexes from the reaction of $Et_2O \cdot BF_3$ and $PdCl_2P_2$ complexes is well established [25].

$CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**) is inert under the conditions which produce reactivity in **1** and **2**; **3** is recovered unchanged from exposure to $Et_2O \cdot BF_3$. In view of the ease with which styrene undergoes thermal and catalysed polymerization relative to ethene, the greater stability of **3** is notable. Since neither structural nor spectroscopic characterization of **3** suggests anomalous behaviour compared to **1**, **2** or $CuCl(PPh_3)_n$, it must be suggested that coordination to the relatively crowded $CuClP_2$ centre and the presence of the α-phenyl moiety are sufficient to inhibit reactivity.

2.3. Reactivity of copper complexes towards hydroborating agents

Although $Cu(BH_4)$ decomposes below ambient temperature, in the presence of tertiary phosphine and/or phenanthroline ligands, $NaBH_4$ reacts with copper(I) salts to form stabilized complexes. The system is particularly sensitive to the nature of the phosphine employed with only triarylphosphines, PPh_2Me and various chelating phosphines containing PPh_2 fragments affording products with extended lifetimes at, or above, ambient temperature [26]. Since initial reports in this area, several strands of activity have been pursued, focusing on both structure and reactivity. Interest centres on the relationship between stoichiometry and tetrahydroborate bonding [27], and on the application of transition metal tetrahydroborates to regioselective reduction [28]. Substituted tetrahydroborates have allowed further modification of reduction reactivity, and have afforded the stable hexameric hydride $[CuH(PPh_3)]_6$ from the reaction of $Na[B(OMe)_3H]$ and $CuCl(PPh_3)$ [29], although the latter reaction is again critically dependent on the phosphine present.

Since the range of tertiary phosphines which stabilize copper(I) tetrahydroborates and hydrides is limited, it is inevitable that the isolation of $Ph_2PCH{=}CH_2$ and $Ph_2PCPh{=}CH_2$ complexes will be, at best, difficult. Indeed the reaction of **1**–**3** and $Na[B(OMe)_3H]$ at −10°C proceeds through a transient red intermediate to afford metallic copper and free $Ph_2PCH{=}CH_2$ or $Ph_2PCPh{=}CH_2$; the coloration of the intermediate is consistent with that of $[CuH(PPh_3)]_6$. At lower temperatures reaction and decomposition progress more slowly, but there is no evidence for the formation of a kinetically stable hydride. **1** and **2** also form unstable products on reaction with $NaBH_4$, metallic copper and free $Ph_2PCH{=}CH_2$ being identified. Once again the reactivity of **3** contrasts with that of **1** and **2**. Reaction of **3** with a slight excess of finely ground $NaBH_4$ in $CDCl_3$ at −10°C affords complete conversion to $Cu(BH_4)(Ph_2PCPh{=}CH_2)_2$ (**7**). The long-term instability of **7** has prevented elemental analysis; however, NMR is consistent with the formulation presented. ^1H NMR data are clearly indicative of a change of $Ph_2PCPh{=}CH_2$ environment with modifications in both chemical shift and $^3J(PH)$ couplings for H_b and H_c (^1H ($CDCl_3$) $\delta = 6.16$ (d, $^3J(PH) = 25.7$ Hz), 5.38 (d, $^3J(PH) = 12.6$ Hz)), and since there is no evidence for free phosphine, it is reasonable to assume the 1:2 copper:phosphine stoichiometry is maintained. The BH_4^- moiety is observed in ^1H and $^{11}B\{^1H\}$ NMR (^1H ($CDCl_3$) $\delta = 1.59$ (q, $^1J(^{11}BH) = 24.3$ Hz), $^{11}B\{^1H\}$ ($CDCl_3$) $\delta = -36.5$). $^{31}P\{^1H\}$ NMR spectroscopy is less informative owing to the facility of copper(I) complexes to undergo rapid ligand exchange, a feature which is typified by the observation of a single resonance for $Cu(BH_4)(PPh_2Me)_3$ and PPh_2Me mixtures [28]. In **7** a single new $^{31}P\{^1H\}$ NMR spectroscopic resonance is recorded at 1.0 ppm. Supporting evidence for the presence of coordinated BH_4^- is provided by solid state IR spectroscopy, from which bands at 2381 and 2011 cm^{-1} are identified. These are less separated than the terminal and bridging $\nu(Cu\text{–}H_t)$ and $\nu(Cu\text{–}H_b)$ bands of most pseudo-tetrahedral $Cu(\eta^2\text{-}BH_4)P_2$ systems, but are certainly indicative of BH_4^- coordination [30].

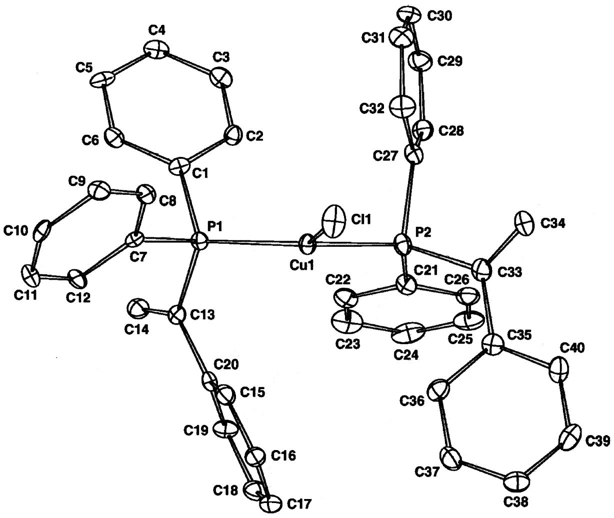


Fig. 4. Single crystal X-ray diffraction structure of $CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**).

2.4. Single crystal X-ray diffraction characterization of $CuCl(Ph_2PCPh{=}CH_2)_2$ (3)

Whilst numerous copper(I) phosphine complexes have been crystallographically characterized, the majority of studies have focused on elucidating the relationship between complex structure and phosphine steric/electronic parameters in $[CuClP]_n$ complexes [1]. Structural determinations of $CuClP_2$ donor sets are less common; only $CuCl[P(o\text{-}tolyl)_3]_2$ [31] and two forms of solvated $CuCl(PPh_3)_2$ [9,14] have been reported. Thus, suitable crystals of **3**, formed by recrystallization from CH_2Cl_2/Et_2O, were studied by X-ray diffraction. Structural characterization, Fig. 4, indicates a three coordinate copper(I) structure with P-bound ligands and pendant styrene moieties. No local symmetry is observed at the metal centre; however, NMR spectroscopic evidence consistently demonstrates the equivalence of phosphine ligands in solution. Thus, in the absence of ligand field influences, solid state asymmetry is clearly dependent on steric and packing factors.

Bond lengths in **3** are broadly similar to those of $CuCl(PPh_3)_2$, Table 4. Bond angles indicate an almost planar arrangement around the copper centre. The steric repulsion of the phosphine ligands is demonstrated by the large P–Cu–P angle, with considerable asymmetry being apparent from the two P–Cu–Cl angles. Once again similar features have been observed in $CuCl(PPh_3)_2$, although the deviations from an idealized trigonal planar geometry are more pronounced in **3**.

3. Conclusions

Copper(I) forms complexes with diphenylvinyl- and diphenyl-α-styrenyl-phosphine in which phosphine ligands adopt P-bound coordination. Pendant alkene moieties are thermally stable, but vinyl functions polymerize in the pres-

Table 4
Selected bond lengths (Å) and angles (°) for $CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**)

	$CuCl(Ph_2PCPh{=}CH_2)_2$ (**3**)	$CuCl(PPh_3)_2\cdot0.5thf$ [a]	$CuCl(PPh_3)_2\cdot0.5C_6H_6$ [b]
Cu–Cl	2.214(2)	2.214(1)	2.208(2)
Cu–P(1)	2.224(2)	2.2564(9)	2.260(2)
Cu–P(2)	2.242(2)	2.2676(9)	2.272(2)
C(13)–C(14)	1.319(7)		
C(33)–C(34)	1.344(8)		
Cl(1)–Cu–P(1)	120.95(6)	120.58(4)	120.74(6)
Cl(1)–Cu–P(2)	109.61(6)	113.86(4)	113.76(7)
P(1)–Cu–P(2)	127.93(6)	125.55(4)	125.48(7)

[a] Ref. [14].
[b] Ref. [9].

ence of boron trifluoride. Phenyl substitution of the α-carbon renders the alkene less susceptible to polymerization, but also affords a tetrahydroborate complex that is sufficiently stable to allow NMR characterization.

4. Experimental

4.1. Single crystal X-ray diffraction

Crystal data for $[CuCl(Ph_2PCPh{=}CH_2)_2]$ (**3**), $C_{40}H_{34}ClCuP_2$. Crystal dimensions $0.05\times0.05\times0.2$ mm. $M=675.60$, monoclinic, space group $P2_{1/C}$. $a=9.207(2)$, $b=9.894(2)$, $c=36.510(7)$ Å, $\beta=93.80(3)°$, $V=3318.5(12)$ Å^3, $Z=4$, $D_{calc}=1.352$ g cm^{-3}, $T=293(2)$ K, λ(Mo Kα) = 0.71073 nm, μ(Mo Kα) = 0.863 mm^{-1}; observed data 4748, unique no. of observed data 3115 ($I>2\sigma(I)$), $R=0.0566$, $wR=0.1352$. Max./min. final difference $+0.472/-0.390$ e Å^{-3}. Intensity data were recorded on a FAST TV area detector following previously described procedures [32]. The structure was solved by direct methods (SHELXS-86) and refined by full matrix least squares on F^2 (SHELX-92), with all non-hydrogen atoms being refined anisotropically. Hydrogen atoms were assigned fixed positions and thermal parameters defined by their respective carbon atoms.

4.2. Spectroscopy

All reactions were carried out under nitrogen using dry degassed solvents using previously described methods [33]. ^1H, $^{13}C\{^1H\}$, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were obtained at 270.05, 67.8 and 81.1 MHz, respectively, in $CDCl_3$ and/or C_7D_8, on a JEOL GSX-270 instrument. Standard acquisition parameters were used in each case, although 8–10 s pulse delays were found necessary to obtain reasonable $^{13}C\{^1H\}$ and ^{13}C NMR spectra. $^1H/^{13}C\{^1H\}$ 2D COSY NMR spectra were obtained using the pulse sequence $(\pi/2, {}^1H)$–$(t^1/_2)$–Δ_1–$(\pi/2, {}^1H; \pi/2, {}^{13}C)$–$\Delta_2$, where $\Delta_1={}^1/_2J$ and $\Delta_2={}^1/_4J$ and $J=120$ Hz [19].

4.3. Ligand synthesis

$Ph_2PCH{=}CH_2$ was prepared by the Grignard route from commercial $CH_2{=}CHMgBr$ and Ph_2PCl. $Ph_2PCPh{=}CH_2$ was similarly prepared using Grignard formed by the reaction of α-bromostyrene and magnesium turnings. Syntheses followed conventional procedures [34]. In each case the ^1H and $^{31}P\{^1H\}$ NMR data are comparable with literature values [35].

4.4. Complex synthesis

Two synthetic routes were utilized, i.e. the stoichiometric reaction of copper(I) chloride or the reduction of hydrated copper(II) chloride in the presence of excess phosphine. Whilst both routes are acceptable, the former is preferable in terms of yield and control of metal:ligand stoichiometry. Thus the following is typical; 2.00 g copper(I) chloride (2.02 mmol) is slurried in dry dichloromethane (45 cm^3). One equivalent of $Ph_2PCH{=}CH_2$ (ca. 4.5 g, 2.1 mmol) is added and the reactants stirred until the insoluble salt is consumed. The solution is then filtered and **1** precipitated by the addition of hexane. Separation of the resulting solid by filtration and drying in vacuo affords **1** in 95% yield.

4.5. Phosphine oxide synthesis

4.5.1. $Ph_2P(O)CH{=}CH_2$

$Ph_2PCH{=}CH_2$ (1.08 g; 5.1 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and slurried with Oxone® for 1 day, after which the solution was filtered and concentrated to dryness affording $Ph_2P(O)CH{=}CH_2$ in quantitative yield. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR: see Tables 2 and 3. IR (KBr): ν(O=P) 1174 cm^{-1}. MS (EI) *m/e* = 228 (100%). $Ph_2P(O)CPh{=}CH_2$: The compound was similarly prepared and characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see Table 3). IR (KBr): ν(O=P) 1189 cm^{-1}. MS (EI) *m/e* = 305 (100%).

4.6. Thermal polymerization studies

The following is typical: **1** (4.3 mg) was dissolved in dry degassed C_7D_8 (2.0 cm^3) and placed in a sealed 4.0 mm

NMR tube under nitrogen. The solution was heated to 100°C for periods of 1 h for up to 8 h. After each hour the tube was cooled to ambient temperature and the NMR spectrum recorded.

4.7. BF_3 initiated polymerization studies

An NMR sample of **1** (6.3 mg) was prepared in $CDCl_3$ as above and $Et_2O \cdot BF_3$ (10 μl) added under nitrogen. The NMR spectrum was obtained after 1 h, 1 day and 7 days at ambient temperature, precipitated material being removed by filtration and dried in vacuo. Additional $CDCl_3$ was added to the remaining solution to maintain constant volume.

4.8. Reactions with $NaBH_4$ and $NaB(OMe)_3H$

$NaBH_4$ (5.0 mg; 0.13 mmol) was placed in a dry 4.0 mm NMR tube under nitrogen and cooled to −10°C. A solution of **1** (23.3 mg; 0.11 mmol) was prepared in $CDCl_3$ (2.0 cm^3), precooled to −10°C and transferred to the NMR tube under nitrogen. NMR spectra were obtained after 1 h and 1 day.

Supplementary data

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 134113. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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