On the syntheses, NMR spectroscopic and structural characterisations of $[CuL(C_2H_4)]\cdot PF_6$ and $[Cu_2L_2(\mu\text{-}C_4H_6)]\cdot 2PF_6$: L = (±)-*N,N′*-*bis*(2,4,6-trimethylbenzylidene)-1,2-diaminocyclohexane†

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Copper(I) (±)-*N,N′*-*bis*(2,4,6-trimethylbenzylidene)-1,2-diaminocyclohexane reacts with either ethene or butadiene to give the corresponding alkene complexes. In each case crystallographic studies show that the alkene coordinates in an η^2 fashion. In the butadiene complex a dimer is formed where the butadiene bridges two copper complexes. Variable temperature NMR spectroscopy of the ethene adduct demonstrates fluxional behaviour, which is attributed to the rotation of the coordinated ethene relative to the complex, $\Delta G^{\ddagger}_{255} = 50 \pm 2$ kJ mol^{-1}.

Introduction

Catalytic conversion of alkenes by copper complexes is an important class of reactions. For example, copper-catalysed epoxidations, aziridinations, haloalkylations, cyclopropanations, oxidations, aminations and halogenations of alkenes are all valuable in synthesis.[1,2] Accordingly, research effort is directed towards understanding the structural and electronic aspects of the copper–alkene interaction. In this context, copper(I) complexes with the ligand (±)-*N,N′*-*bis*(2,4,6-trimethylbenzylidene)-1,2-diaminocyclohexane attract interest. For example, Jacobsen and co-workers investigated ligands of this type in copper-catalysed cyclopropanation and aziridination reactions.[2] Additionally, they showed that aromatic alkenes bind directly to the copper ion in its complex with the mesityl-salen version of the basic ligand, **L**, shown in Scheme 1.[3] An attractive feature of complexes of **L** is that the benzylidene groups offer a binding pocket around the alkene coordination site, thus providing a potential means of controlling the chemo- and stereo-selectivity of the catalytic reaction.

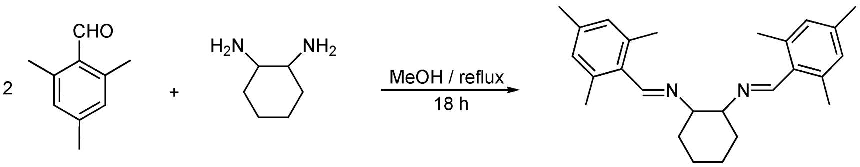
Of further importance in this regard is the catalytic functionalisation of simple feedstock alkenes, such as ethene and butadiene. These alkenes are of industrial significance and are generally less reactive than more functionalised alkenes. It is of some note, therefore, that a gap exists in the literature of the interaction of these molecules with potential copper catalysts. For instance, there is no previous report of the structural determination of a copper-butadiene complex where the butadiene is unsubstituted.[4] We decided to investigate, therefore, the copper-ethene and copper-butadiene complexes of the Cu-**L** system. Our objective was to open up the potential for the catalytic conversion of these important feedstock chemicals using this class of copper complexes as catalysts.

We describe herein the ethene and butadiene complexes of Cu-**L**. Ethene binding is reversible at room temperature where the ethene exhibits elongation of the C=C bond upon binding to the copper. We also demonstrate that butadiene binds to the complex and that the binding is accompanied by the formation of a $[Cu_2\mathbf{L}_2(\mu\text{-}C_4H_6)]^{2+}$ dimer. We have determined the structure of this dimer by X-ray diffraction; the first crystallographic characterisation of a copper-butadiene complex.

Experimental

Instrumentation

All standard ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 (^{1}H at 270.17 MHz, ^{13}C at 67.94 MHz) spectrometer. For samples requiring low temperature VT-NMR analysis, spectra were recorded on a BRUKER AMX-300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz) instrument. 2D spectra were acquired on a BRUKER AMX-500 (^{1}H at 500.13 MHz, ^{13}C at 125.76 MHz) spectrometer. A BRUKER DMX-400 (400 MHz) NMR spectrometer was used to record CP-MAS solid-state spectra. ^{13}C NMR spectra were calibrated using adamantane as an external standard. Peak assignments were based on standard chemical shifts and splitting patterns.



Scheme 1 Synthesis of **L** *via* Schiff-base condensation of 2,4,6-trimethylbenzaldehyde and (±)-1,2-diaminocyclohexane.

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Electron impact and chemical ionisation mass spectra were acquired on a VG Analytical Autospec instrument. GC-MS analyses were carried out using the same instrument linked to a Hewlett Packard 5890 Series 2 gas chromatograph. Electrospray mass spectra were recorded on a Finnigan LCQ MAT standard edition spectrometer. UV/vis spectra were acquired on a Hewlett Packard 8453 diode-array spectrometer attached to a PC with UV/vis Chemstation data processing. A modified cell (1 cm path length) to enable connection to a Schlenk line was used in the analysis of $[Cu(C_2H_4)\mathbf{L}]\cdot PF_6$. FTIR spectra were acquired using a Mattson Research series spectrometer with data processing using Winfirst software. KBr discs were pressed under 6.0 tonnes pressure. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser by the Chemicals and Materials Analysis Unit at the University of Newcastle. Melting points were determined using an Electrothermal 9100 melting point apparatus.

For both complexes, crystals suitable for X-ray diffraction were mounted on a goniometer head and frozen in a liquid nitrogen cryostream. Data were collected at 150(2) K with Mo-Kα radiation (λ = 0.71073 Å) on a Rigaku AFC6S diffractometer. Unit cell parameters and their esd values were determined from a least squares fitting of the setting angles of twenty automatically centered reflections. Three standard reflections, monitored every 150 reflections, showed no significant variation of intensity during data collection. Intensities were corrected for Lorentz and polarisation effects. Transmission coefficients were determined from azimuthal scans of ten reflections. Data collection and cell refinement was performed using a 'MSC/AFC' diffractometer control and the computing data reduction was carried out using 'teXsan (MSC, 1992–1997)'. Structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 with SHELXL-97.[23] All non-hydrogen atoms were refined anisotropically. A riding model was applied to H atoms, which were placed at calculated positions, with the equivalent isotopic thermal parameters of their parent C or N atoms. For $[Cu(C_2H_4)\mathbf{L}]\cdot PF_6$ the data quality was relatively poor, due to the weakly scattering nature of the crystal. This is reflected in the high standard deviations in the structural parameters. The refinement converged satisfactorily, however, and molecular connectivity of the complex and its overall geometry are clear.

Standard Schlenk techniques were employed throughout the handling and characterisation of all copper(I) complexes. All solvents used in reactions (Fisher Chemicals) were either Analytical or HPLC grade and were dried using standard laboratory procedures and stored in sealed ampoules under argon–nitrogen. All dry solvents were degassed prior to use by stirring under vacuum (0.1 mmHg) in an acetone–dry ice slush bath for at least 20 min. Solvents employed for making GC standards were used as received. Deionised water was used throughout. Deuterated NMR solvents (Goss Scientific Instruments Ltd.) were degassed using freeze-thaw techniques (cycle repeated three times). Degassed NMR solvents were stored in sealed ampoules over 3 Å molecular sieves (previously dried under vacuum at 80 °C for 5 h). Racemic (±)-*trans* 1,2-diaminocyclohexane (Aldrich) was used in the preparation of diimine ligands. All other reagents were supplied by Aldrich, Avocado or Lancaster and were used as received unless otherwise stated. Aluminium plates coated with 60 F_{254} silica gel (0.2 mm, Merck) were used during TLC analysis and a UV lamp or a permanganate dip was used in the visualisation of spots.

Synthesis of (±)-*N*,*N′*-*bis*(2,4,6-trimethylbenzylidene)-1,2-diaminocyclohexane (L)[2]

2,4,6-Trimethylbenzaldehyde (0.82 g, 5.53 mmol) and (±)-1,2-diaminocylohexane (0.31 g, 2.74 mmol) were dissolved in 30 cm^3 methanol in a 100 cm^3 round bottomed flask equipped with a magnetic stirrer bar. The solution was stirred and heated to reflux for 18 h. After leaving to cool, the solvent was removed *in vacuo* and a white–yellow solid remained. The yellow starting material was removed with diethyl ether (10 cm^3) and the remaining white solid was filtered and recrystallised from methanol to give white needles of **L** (0.88 g, 86%), m.p. 136–137 °C (literature value 122–123 °C).

^{1}H NMR ($CDCl_3$): δ_H (ppm); 1.48-1.56 (m, 2H, cyclohexyl CH_2), 1.79-1.85 (m, 6H, cyclohexyl CH_2), 2.18 (s, 12H, *o*-mesityl CH_3), 2.23 (s, 6H, *p*-mesityl CH_3), 3.35-3.404 (2H, cyclohexyl CH), 6.76 (s, 4H, aryl CH), 8.53 (s, 2H, CH=N) ^{13}C NMR ($CDCl_3$): δ_C (ppm); 20.1 (C_7), 20.6 (C_{10}), 24.1 ($C_{1/2}$), 33.1 ($C_{1/2}$), 76.0 (C_3), 128.7 (C_8), 130.8 (C_{6+9}), 136.9 (C_5), 159.8 (C_4). HR-MS (CI): Calc. for $C_{26}H_{35}N_2$: 375.2799; Found: 375.2800 (MH^+). IR (KBr disc) υ_{max} (cm^{-1}): 2926 s (CH), 2855 m (CH), 1650 s (C=N), 1611 m (C=C), 1361 w, 845 m.

Anal: Calc for $C_{26}H_{34}N_2$: C, 83.35; H, 9.15; N, 7.50; Found: C, 83.15; H, 9.50; N, 7.40.

Copper(I)-ethene complex: $[Cu(C_2H_4)\mathbf{L}]\cdot PF_6$

L (0.05 g, 0.13 mmol) was dried under vacuum for 15 min in a Schlenk tube containing a magnetic stirrer bar. $[Cu(NCCH_3)_4]\cdot PF_6$ (0.05 g, 0.13 mmol) was added to the tube and the contents stirred whilst adding dichloromethane (20 cm^3) *via* cannula. The tube was placed in an ice bath and ethene bubbled through the resulting pale yellow solution for 15 min. The solution became colourless during ethene addition. Ethene was bubbled through cyclohexane (30 cm^3) in a separate Schlenk tube for 15 min and the solution carefully layered over the colourless copper solution. The counter solvent was transferred under a positive pressure of ethene and the tube sealed immediately prior to storage in a refrigerator to promote crystallisation.

After 1 week, a sufficient crop of colourless crystals of $[Cu(C_2H_4)\mathbf{L}]\cdot PF_6$ was available for analysis. A few were taken for X-ray diffraction, and the remainder were filtered under argon, washed with diethyl ether (~2 cm^3) and dried under vacuum for 30 min (0.03 g, 38%), m.p. 179 °C (dec.). Whilst in solution the complex is air sensitive but this sensitivity is much reduced when dried in the crystalline state.

Crystal data. $C_{28}H_{32}CuF_6N_2P$, M = 605.07, monoclinic, a = 17.957(6), b = 18.013(9), c = 9.057(5) Å, α = 90.00, β = 94.86(4), χ = 90.00°, U = 2919(2) Å^3, T= 150(2) K, space group $P2_1/c$ (no. 14), Z = 4, 4047 reflections measured, 1259 unique, (R_{int} = 0.3076) which were used in all calculations. The final $wR(F^2)$ was 0.3454 (all data).

^{1}H NMR (300 K, CD_2Cl_2): δ_H (ppm); 1.5 (m, 4H, cyclohexyl CH_2), 2.0 (d J = 9.6 Hz, 2H, cyclohexyl CH_2), 2.2 (s, 12H, *o*-mesityl CH_3), 2.3 (s, 6H, *p*-mesityl CH_3), 2.6 (d J = 10.3 Hz, 2H, cyclohexyl

CH_2), 3.1 (sbr, 4H, ethene CH_2) 3.7 (2H, cyclohexyl CH), 6.9 (s, 4H, aryl CH), 8.8 (s, 2H, CH=N). ^{1}H NMR (−80 °C, CD_2Cl_2): δ_H (ppm); 1.4 (m, 4H, cyclohexyl CH_2), 2.0 (d J = 5.31 Hz, 2H, cyclohexyl CH_2), 2.1 (s, 12H, *o*-mesityl CH_3), 2.2 (s, 6H, *p*-mesityl CH_3), 2.5 (d J = 10.1 Hz, 2H, cyclohexyl CH_2), 2.6 (d J = 9.7 Hz, 2H, ethene CH_2), 3.1 (d J = 9.7 Hz, 2H, ethene CH_2), 3.5 (2H, cyclohexyl CH), 6.8 (s, 4H, aryl CH), 8.7 (s, 2H, CH=N). ^{13}C NMR (CD_2Cl_2): δ_C (ppm); 20.0, 21.5, 30.3, 69.7, 84.5, 129.4, 133.1, 135.6, 141.1, 170.9. ^{1}H NMR (400 MHz, silica matrix): Unresolved spectrum; assignment of signals impossible. CP-MAS ^{13}C NMR (100 MHz, silica matrix): δ_C (ppm); 17.0, 17.9, 18.4, 20.5, 24.1, 26.7, 31.1, 67.2, 79.3, 85.0, 127.8, 128.9, 133.2, 134.8, 139.1, 162.6, 169.7.

MS (ES +ve ion): *m*/*z* 439 (^{65}Cu^I**L**), 375 (**L**). IR (KBr disc) ν_{max} (cm^{-1}): 2943 s (CH) 2868 m (CH), 1647 s (C=N), 1611 m (C=C aromatic), 1523 w (C=C ethene), 1450 m, 1385 w, 1258 m, 943 m, 842 s (PF), 557 s (PF). Anal: Calc. for $C_{28}H_{38}N_2CuPF_6$: C, 55.05; H, 6.30; N, 4.60; Found: C, 54.45; H, 6.30; N, 4.55.

UV/vis Studies on [Cu(C_2H_4)L]·PF_6

[Cu($NCCH_3$)$_4$]·PF_6 (0.07 g, 0.19 mmol) and diimine ligand **L** (0.07 g, 0.19 mmol) were placed in a Schlenk tube and dissolved in dichloromethane (~10 cm^3) added *via* cannula. The resulting yellow solution was transferred *via* cannula to a specially adapted UV/vis cell fitted with a Young's tap. A spectrum was then recorded between 200 and 800 nm at 298 K, which contained a broad absorbance at ~360 nm. Ethene was then bubbled through the cell (*ca.* 5 min), and a spectrum was recorded of the resulting colourless solution. The absorbance at 360 nm was observed to disappear. The cell was then purged with argon (bubbled through the solution, *ca.* 45 min) to remove all traces of dissolved ethene, which resulted in a yellow solution of the original acetonitrile adduct. A UV/vis spectrum was recorded which showed the band at 360 nm. The process of ethene addition was repeated once more to confirm that the process was fully reversible (Fig. 1).

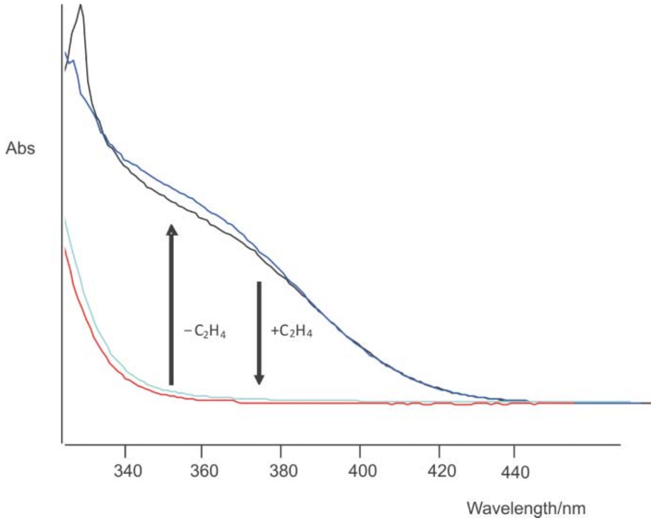


Fig. 1 UV/visible spectra of [Cu**L**($NCCH_3$)]·PF_6 in CH_3CN, upon repeated addition/removal of ethene (298 K).

Copper(I)-butadiene complex: [(Cu_2L_2(μ-1,3-C_4H_6)]·2PF_6

L (0.03 g, 0.08 mmol) was dried under vacuum for 15 min in a 'two-arm' crystallisation chamber. [Cu($NCCH_3$)$_4$]·PF_6 (0.03 g, 0.08 mmol) was added to the tube and the contents shaken whilst adding dichloromethane (5 cm^3) *via* cannula. Diethyl ether (10 cm^3) was transferred to the other side of the chamber *via* cannula, and this side was immersed in an acetone/ice bath. Butadiene (CAUTION) was introduced *via* a needle through a septum in a side arm of the tube, and was condensed into the diethyl ether until a total volume of ~20 cm^3 was obtained (10 cm^3 liquid butadiene). The system was then sealed, wrapped in plastic netting and removed from the acetone/ice bath. After ~3 d the solutions had equilibrated and a crop of crystals of [Cu_2**L**$_2$(μ-1,3-C_4H_6)]·2PF_6 had formed.

A few crystals were taken for X-ray analysis and the remaining solutions were removed using cannula filtration. The crystals were washed with diethyl ether (~2 cm^3) and dried *in vacuo* for 30 min. Whilst in solution the complex is very air sensitive, but it demonstrates remarkable stability in the solid state when dried. No yield data were recorded for [Cu_2**L**$_2$(μ-1,3-C_4H_6)]·2PF_6 when synthesised by this method.

Crystal data. $C_{56}H_{74}Cu_2F_{12}N_4P_2$, M = 1220.23, triclinic, a = 9.234(10), b = 11.342(13), c = 13.985(7) Å, α = 82.61(6), β = 93.35(7), χ = 98.11(10)°, U = 1437(2) Å^3, T = 150(2) K, space group $P\bar{1}$, Z = 1, 5067 reflections measured, 3258 unique (R_{int} = 0.1310) which were used in all calculations. The final $wR(F^2)$ was 0.2678 (all data).

^{1}H NMR (400 MHz, silica matrix): Second order spectrum; no assignment of signals was possible. CP-MAS ^{13}C NMR (100 MHz, silica matrix): δ_C (ppm); 17.3, 18.0, 19.5, 20.9, 23.3, 24.2, 27.4, 30.9, 67.9, 117.5, 127.7, 129.2, 130.3, 131.8, 133.7, 134.8, 139.6, 140.5, 161.8, 171.0, 173.1. MS (ES +ve ion): *m*/*z* 439 (^{65}Cu^I-**L**), 375 (**L**). IR (KBr disc) ν_{max} (cm^{-1}): 2940 m (CH), 2859 w (CH), 1646 s (C=N), 1611 m (C=C aromatic), 1559 w (C=C butadiene), 1506 w (C=C butadiene), 1456 m, 1382 w, 1018 w, 839 vs (PF), 557 s (PF) Anal: Calc for $C_{56}H_{74}N_4Cu_2P_2F_{12}$: C, 55.15; H, 6.10; N, 4.60; Found: C, 54.55; H, 6.15; N, 4.65.

Limited solubility in CD_2Cl_2 or $CDCl_3$ restricted NMR studies of [Cu_2**L**$_2$(μ-1,3-C_4H_6)]·2PF_6. Addition of CD_3CN to a suspension of crystals in CD_2Cl_2 (1:9 *v*/*v* CD_3CN:CD_2Cl_2) resulted in the formation of a yellow solution, believed to be due to the formation of the monomeric acetonitrile adduct [Cu**L**($NCCH_3$)]·PF_6. ^{1}H NMR data quoted below are of poor quality, but when coupled with ^{13}C DEPT NMR information there is sufficient evidence to imply that the decomposition of [Cu_2**L**$_2$(μ-1,3-C_4H_6)]·2PF_6 to the acetonitrile adduct occurs in acetonitrile solution at room temperature.

^{1}H NMR [(CD_2Cl_2:CD_3CN (9:1 v/v))]: δ_H (ppm); 1.4-1.6 (m, 4H, cyclohexyl CH_2), 1.8 (m, 2H, cyclohexyl CH_2), 2.0-2.2 (envelope containing *o*/*p*-mesityl CH_3 and cyclohexyl CH_2), 3.4 (2H, cyclohexyl CH), 6.8 (s, 4H, *aryl* CH), 8.5 (s, 2H, CH=N) [evidence of free C_4H_6: 5.1-5.2 (m, CH_2), 6.3-6.4 (m, CH)] ^{13}C NMR [(CD_2Cl_2:CD_3CN (9:1 v/v))]: δ_C (ppm); 18.9, 20.0, 24.0, 31.0, 70.8, 128.1, 131.9, 135.7, 137.2, 138.3, 162.9.

A procedure similar to that used in the synthesis of the corresponding ethene complex was followed, substituting butadiene in place of ethene, although the ice bath was removed to avoid condensation of butadiene. This resulted in the instantaneous formation of a white solid upon addition of butadiene to the yellow copper(I) solution. Reducing the concentration of [Cu**L**(NCCH$_3$)]·PF$_6$ (generated *in situ*) by increasing the volume of dichloromethane to 40 cm^3 prevented instantaneous precipitation. Upon layering the solution with butadiene-saturated cyclohexane and transferring the Schlenk tube to the refrigerator, a non-crystalline white solid precipitated after ~2 weeks (0.04 g, 50%). Solid state NMR spectroscopy revealed this solid to be identical to the crystalline product obtained from the vapour-liquid diffusion technique.

Results and discussion

L is prepared from the Schiff-base condensation of 2,4,6-trimethylbenzaldehyde and (±)-1,2-diaminocyclohexane (Scheme 1) in 86% yield following reported procedures.[2] Complexation of **L** with [Cu(NCCH$_3$)$_4$]·PF$_6$ in dichloromethane gives a yellow solution, believed to be due to the formation of an acetonitrile adduct [Cu**L**(NCCH$_3$)]$^+$ (Scheme 2).

The solution of [Cu**L**(NCCH$_3$)]·PF$_6$ is stable under inert atmosphere, but changes colour rapidly on exposure to air, presumably due to aerobic oxidation of the complex. In acetonitrile solution [Cu**L**(NCCH$_3$)]$^+$ exhibits a broad absorption at *ca.* 360 nm (Fig. 1). Upon addition of excess ethene (*ca.* 5 min), this band disappears and the solution decolourises. Bubbling a large excess of argon (*ca.* 45 min) through the ethenylated solution sees the recovery of the original yellow coloured solution and the reappearance of the band at 360 nm. Re-addition of ethene (*ca.* 5 min) results in the disappearance of the band at 360 nm. The cycling of ethene addition and removal can be carried out many times without apparent decomposition of the complex. These spectral changes are consistent with reversible substitution of the coordinated acetonitrile by ethene to give a copper-ethene complex (Scheme 2).

The ethene complex, [Cu**L**(C$_2$H$_4$)]·PF$_6$, could be isolated in solid crystalline form in ~40% yield by layering an ethene-saturated cyclohexane solution onto a solution of [Cu**L**(C$_2$H$_4$)]·PF$_6$ in dichloromethane. X-Ray crystallographic analysis of [Cu**L**(C$_2$H$_4$)]$^+$ was completed with weakly scattering crystals. The data, therefore, carry relatively high errors, which—as Rasika Dias and Wu observe in their recent review of copper(I)-alkene complexes—is something which bedevils this area of chemistry.[4] Nevertheless, despite the high errors, the connectivity of the complex is clear and it is possible to compare this structure broadly with other known copper-ethene complexes. The structure of [Cu**L**(C$_2$H$_4$)]$^+$ is very similar to that of other reported copper(I)-ethene complexes with bidentate ligands, displaying side-on ethene coordination to a copper(I) ion in a pseudo-trigonal planar geometry (Fig. 2).[5–17] The disorder of the diaminocyclohexane backbone precludes a more detailed analysis of the coordination sphere. The dimensions and geometry of the complex closely resemble that of [Cu**L**(styrene)]$^+$ reported by Jacobsen and co-workers.[3] The copper–carbon bond lengths [Cu–C(27) 1.999(19) Å and Cu–C(28) 2.030(15) Å] are typical for such complexes, and

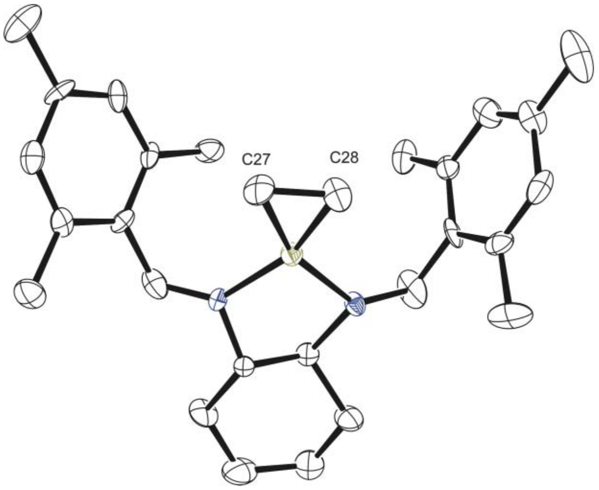
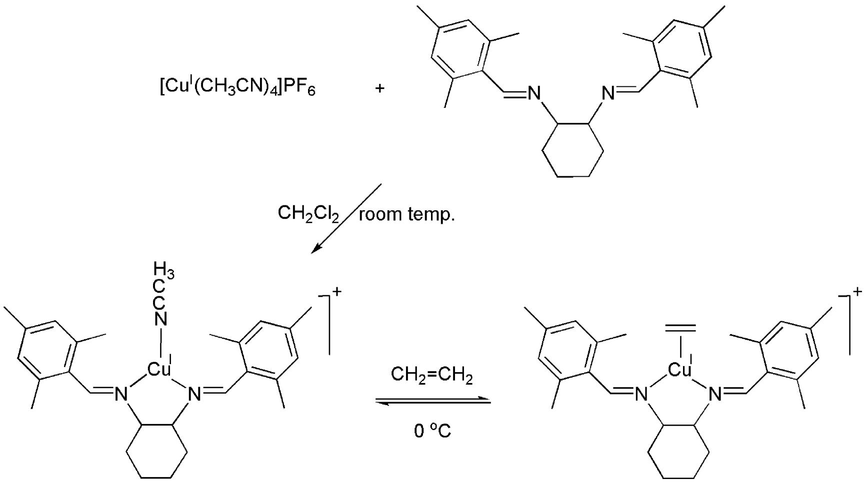


Fig. 2 ORTEP (30% probability ellipsoids) of the X-ray crystal structure of the copper(I)-ethene complex [Cu**L**(C$_2$H$_4$)]·PF$_6$ (hydrogen atoms, disordered cyclohexyl carbon atoms and hexafluorophosphate counterions are omitted for clarity). Some disorder in the cyclohexane backbone is modelled with split atoms. Selected distances/Å Cu(1)–N(1) 1.976(15), Cu(1)–N(2) 1.993(14), Cu(1)–C(28) 2.004(18), Cu(1)–C(27) 2.023(18), C(27)–C(28) 1.42(3).



Scheme 2 Synthesis of copper(I)-ethene complex [Cu**L**(C$_2$H$_4$)]PF$_6$.

indicate an essentially symmetric coordination of ethene to the copper(I) ion. N–Cu–C bond angles [N(1)–Cu–C(27) 116.7(7)° and N(2)–Cu–C(28) 117.8(7)°] further demonstrate the symmetrical coordination mode of the ethene.

From the point of view of alkene activation, the most notable feature is the C=C distance of the coordinated ethene [C(27)–C(28) 1.42(3) Å]. This represents an elongation *vs.* free ethene [1.337(2) Å], consistent with a loss in bonding character in the C=C bond. The value of 1.42(3) Å is longer than that in any copper(I)-ethene complex previously reported, see Table 1 and Scheme 3. Due to the high error associated with the measurement it is not possible to comment definitively on the significance of the differences in the bond lengths between the coordinated and free ethene. However, further inspection of Table 1 reveals that the chemical shift of the ethylenic protons in [Cu**L**(C_2H_4)]$^+$ is very large compared to the shifts in other structurally characterised copper(I)-ethene complexes. The size of the shift may be due in part to the ligand geometry (see below) but it may also be indicative of a significantly weakened ethene bond commensurate with the large C=C bond length. Further evidence for the weakening of the ethene bond upon complexation to the copper in [Cu**L**(C_2H_4)]$^+$ comes from the IR spectrum of [Cu**L**(C_2H_4)]·PF_6 which exhibits a band at 1523 cm^{-1} and can be tentatively assigned to the C=C stretching frequency of the ethene, a shift of ~100 cm^{-1} compare to free ethene.

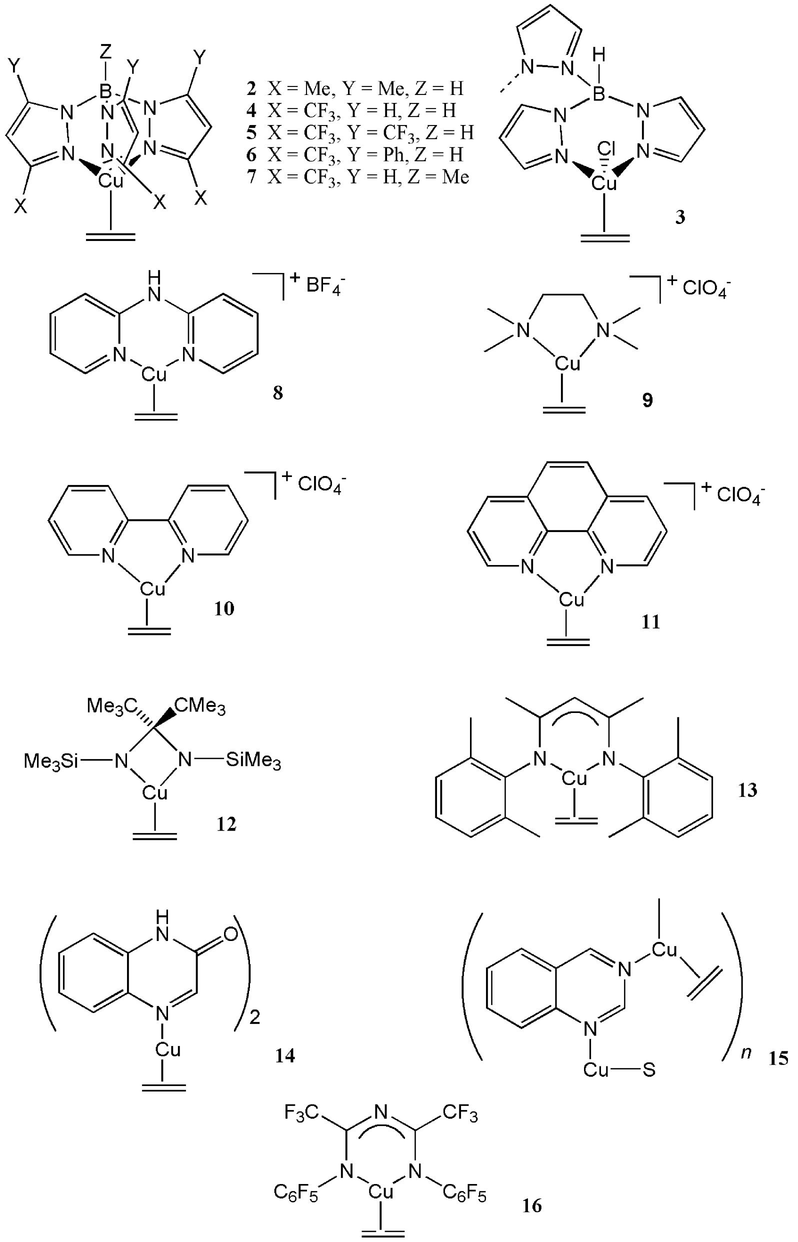
The ^{1}H NMR spectrum of [Cu**L**(C_2H_4)]$^+$ at 300 K in CD_2Cl_2 is very similar to that of the free diimine ligand **L**, except for an extra broad resonance at *ca.* 3.1 ppm. This resonance integrates to four protons and is assigned to the protons of the coordinated ethene (Fig. 3). The position of this signal is shifted significantly upfield from uncoordinated ethene (δ_H 5.42 ppm, upfield shift $\Delta\delta_H$ 2.32 ppm). Such upfield shifts are observed with other copper(I)-ethene complexes.[5–17] The magnitude of the shift in [Cu**L**(C_2H_4)]$^+$, however, is considerably larger than that recorded for most other complexes with neutral bidentate ligands such as bipyridine and phenanthroline (Table 1).[9–11]

The reasons for this large shift in [Cu**L**(C_2H_4)]$^+$ are difficult to explain, but may be related to efficient donor properties of **L**, which, due to its electron-donating mesityl groups, may enhance the electron back donating ability of the copper(I) ion, which in turn leads to the unusually high shift. An alternative explanation may be the constrained environment of the ethene binding site. The ethene is sandwiched between the two mesityl groups [average C(ethene)–C(nearest mesityl) distances are 3.94 and 3.87 Å]. At such short distances the effects of the ring currents of the mesityl groups on the chemical shifts of the ethene protons cannot

Table 1 Selected structural and NMR spectroscopic parameters for structurally characterised copper(I)-ethene complexes with nitrogen-donating ligands (Scheme 3)

Molecule	C=C distance/Å	Cu–C distances/Å	δ(H)/ppm	δ(C)/ppm	Reference
[Cu(C_2H_4)**L**]$^+$	1.42(3)	2.004(18) 2.023(18)	3.1[a]	85.0[a]	This work
2	1.329(9)	2.023(5) 2.004(6)	4.41[a]	—	5
3	1.347(5)	2.003(3) 1.995(3)	4.43[a]	—	5
4	1.34(2)	2.009(9) av.	4.98[b] 4.80[c]	85.8[b]	6
5	1.325(9)	2.022(6) av.	4.94[b] 4.96[c] 4.98[d]	89.5[d]	6
6	1.30(1)	2.012(11) av.	5.20[b] 4.91[c]	85.7[b],[c]	6
7	1.334(4)	2.033(3) 2.043(3)	4.80[c]	85.4	7
8	1.359(7)	2.019(3)	4.70[e]	—	8
9	1.36(1)	1.95(1) 1.969(9)	4.16[e],[h] 4.31[e]	—	9, 12
10	1.360(13) 1.346(18)[f]	2.028(11) 2.019(9) 1.979(13)[f] 1.943(14)	4.92[e]	—	9, 10 , 11
11	1.361(22)	1.998(13) 2.022(12)	5.00[e]	—	9, 10 , 11
12	1.362(6)	1.987(3)	3.48[b] 3.35[g] 3.63[c]	73.0	13
13	1.365(3)	1.986(2) 1.992(2)	2.91[b]	74.7	14
14	1.32(1)	2.046(6)			15
15	1.30(1)	2.022(6)			16
16	1.364(4)	2.010(3) 2.018(3)	3.27[b]	86.1[c]	17
Ethene	1.3369(16)		5.44[h] 5.38	123.5	18

[a] CD_2Cl_2. [b] C_6D_6. [c] $CDCl_3$. [d] C_6D_{12}. [e] $(CD_3)_2CO$. [f] Two independent molecules in the asymmetric unit. [g] $CD_3C_6D_5$. [h] Low temperature NMR spectroscopy.



Scheme 3 Copper(I)-ethene complexes with N-coordinating ligands.

be discounted. Similar shifts were reported by Vitagliano and co-workers for a copper(I)-ethene complex using the diamine analogue of **L**.[19]

A reduction in temperature leads to sharpening and splitting of the broad resonance at 3.1 ppm strongly indicating that the broadness of the peak is due to a dynamic process of the ethene group on the NMR time scale, likely to be an intramolecular fluxional process. The ^{1}H NMR spectrum in CD_2Cl_2 at 193 K displays two sharpened doublets at 3.09 and 2.64 ppm. All other signals remain unshifted, other than slight changes due to the effects of reducing the temperature.

Using the crystal structure as a basis on which to make the assignment, we assign one of the doublets to a pair of vicinal *cis* protons, and the other doublet to the other pair. This assignment stems from the unusual pseudo trigonal planar coordination geometry around the copper(I) ion, where two vicinal *cis* protons lie below the plane and the other two protons lie above. The assignment of the two ethene doublets was aided by the ^{1}H–^{1}H COSY spectrum recorded at 193 K (Fig. 4). The twisted conformation of **L** breaks the mirror symmetry of the plane thus generating two inequivalent chemical environments for each hydrogen atom in the geminal pairs. The two doublets do not split about the mean resonance of 3.1 ppm observed at 300 K (average resonance of doublet of doublets at 193 K = 2.9 ppm). This slight shift could be due to the effects of reducing temperature on the geometry of **L** which is in close proximity to the ethene. In the low temperature spectrum of $[Cu\mathbf{L}(C_2H_4)]^+$ there is no evidence for uncoordinated ethene (which would appear at ~δ_H 5.42 ppm), which suggests that

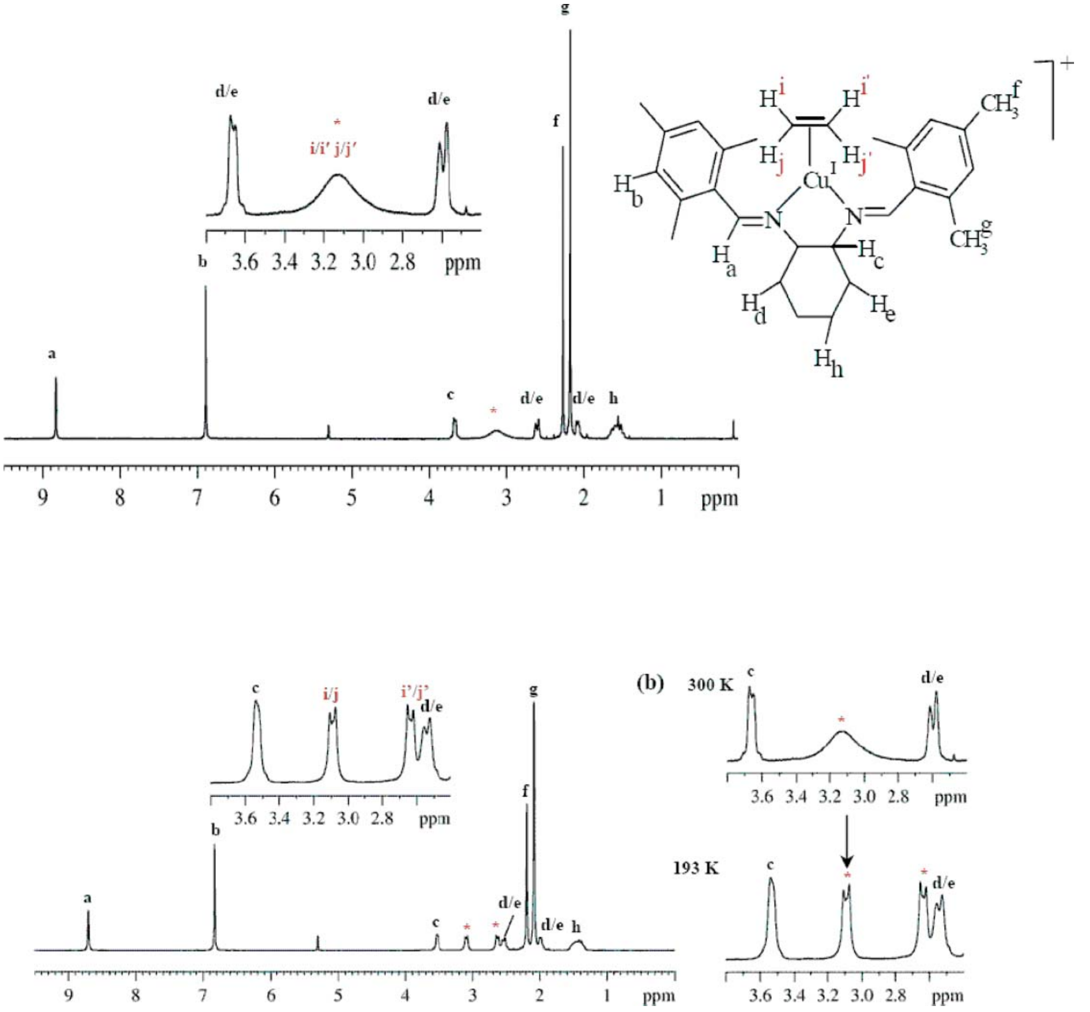


Fig. 3 (top) ^{1}H-NMR spectrum and assignment of [Cu**L**(C_2H_4)]·PF_6 in CD_2Cl_2 at 300 K and (bottom) ^{1}H NMR spectrum of [Cu**L**(C_2H_4)]·PF_6 in CD_2Cl_2 at 193 K; (b) influence of temperature on the coordinated C_2H_4 signals.

the ethene remains coordinated to copper and is not sufficiently labile to undergo any intermolecular exchange processes on the NMR timescale.

[Cu**L**(C_2H_4)]$^+$ was studied by VT-NMR spectroscopy. A series of ^{1}H NMR spectra was recorded at 10 K intervals between 305 K and 195 K. During these investigations, the broad resonance at 3.1 ppm exhibited classical coalescence behaviour, passing through a coalescence point at 255 K before sharpening up to two doublets. The rate constant for the environmental exchange is calculated as 136 ± 4 Hz, giving a value of the exchange rate constant $k = 302 \pm 10\ s^{-1}$ and an activation barrier of $\Delta G^{\ddagger} = 50 \pm 2$ kJ mol^{-1} at 255 K. A lack of similar studies reported in the literature makes it difficult to comment comparatively on this value. However, Hoffman and co-workers published a copper(I)-norbornene complex containing an iminophosphanamide ligand, with the alkene rotation barrier calculated as $\Delta G^{\ddagger} = 41 \pm 2$ kJ mol^{-1}.[13] A styrene analogue of complex **13** reported by Dai and Warren was shown to have a value of $\Delta G^{\ddagger} = 45 \pm 3$ kJ mol^{-1}.[14] Both of these values are similar to that calculated for [Cu**L**(C_2H_4)]$^+$.

The ^{13}C NMR spectrum of [Cu**L**(C_2H_4)]$^+$ has a signal at 85 ppm which correlates to an alkene group (*c.f.* free ethene δ_C 123 ppm, upfield shift $\Delta\delta_C$ 38 ppm). DEPT analysis was consistent with this resonance being due to the CH_2 groups of ethene.

Synthesis of [$Cu_2$$L_2$($C_4H_6$)]·2$PF_6$

An analogous procedure to that used in the preparation of [Cu**L**(C_2H_4)]·PF_6 was initially followed. The addition of butadiene to a solution of [Cu**L**($NCCH_3$)]·PF_6 resulted in the instantaneous formation of a white precipitate of the butadiene adduct in 50% yield. The precipitate was insoluble in either $CDCl_3$ or CD_2Cl_2. Infrared spectroscopic studies suggested that the precipitate contained an imine, ν(C=N) at 1644 cm^{-1}, but it was unclear whether or not butadiene was present. ES-MS analysis of the compound confirmed the presence of a Cu**L** fragment ([Cu**L**]$^+$ *m/z* 437), but provided no evidence of butadiene coordination. This observation is not surprising since complexes with weakly coordinated alkene/diene molecules are not generally observable by mass spectrometry. Microanalysis is consistent with a [Cu_2**L**$_2$(C_4H_6)]·2PF_6 formulation.

Crystals of the butadiene adduct of [Cu_2**L**$_2$]$^+$ were obtained using a two-arm crystallisation chamber which enabled the slow

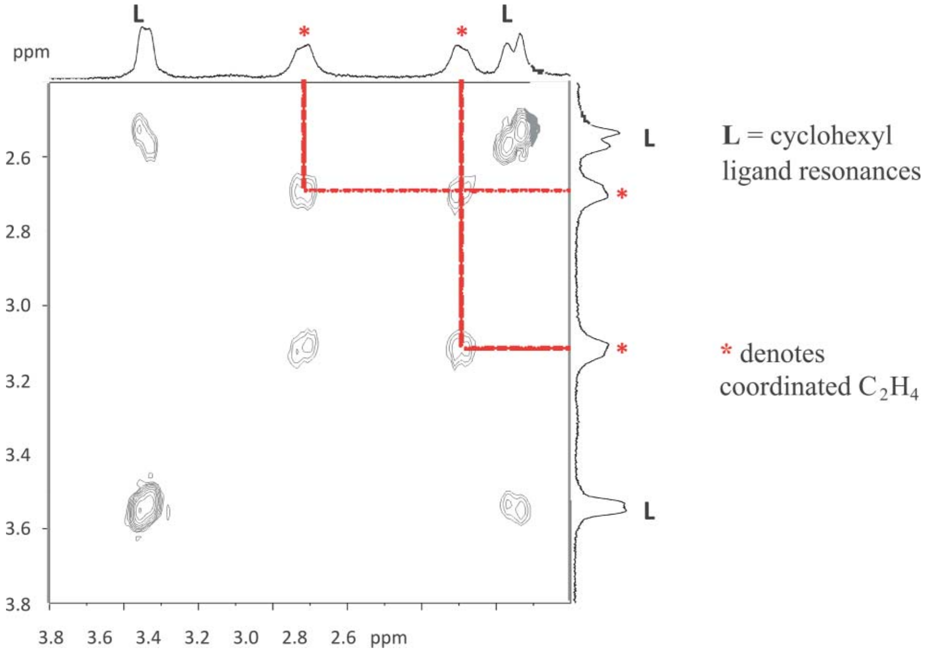


Fig. 4 Selected region of ^{1}H-COSY of $[Cu\mathbf{L}(C_2H_4)]\cdot PF_6$ in CD_2Cl_2 at 193 K.

vapour diffusion of butadiene and diethyl ether into a solution of $[Cu\mathbf{L}(NCCH_3)]\cdot PF_6$ in dichloromethane. After 3 d at room temperature, the system reached equilibrium and small yellow crystals formed. The molecular structure of the butadiene complex is shown in Fig. 5. The compound is a dicationic dimer with a bridging butadiene group between two Cu**L** units: $[Cu_2\mathbf{L}_2(C_4H_6)]^{2+}$. The doubly charged nature of the cation presumably explains its insolubility in non-polar solvents.

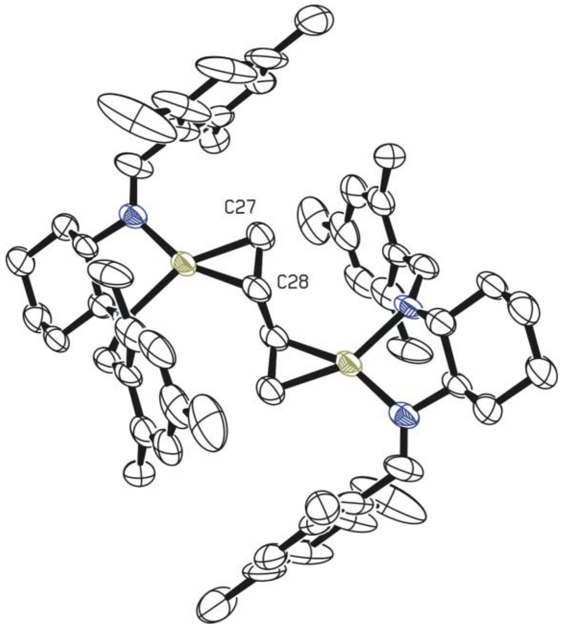


Fig. 5 ORTEP (30% probability ellipsoids) of the X-ray crystal structure of the copper(I)-butadiene complex $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ (hydrogen atoms and hexafluorophosphate counterions omitted for clarity). Selected distances/Å Cu(1)–C(27) 2.028(8), Cu(1)–C(28) 2.059(8), Cu(1)–N(1) 1.990(7), Cu(1)–N(2) 2.000(6), C(27)–C(28) 1.388(10), C(28)–C(28′) 1.475(14).

Both copper(I) ions are coordinated in an η^2-fashion by the alkene groups of the *transoid* butadiene. The bond lengths and angles of each copper(I) centre are almost identical to those in $[Cu\mathbf{L}(C_2H_4)]^+$ (Table 2). The bond lengths in the coordinated butadiene molecule reflect localised η^2-bonding on the two terminal alkene groups [C(27)–C(28) 1.388(10) Å, C(28)–C(28′) 1.475(14) Å]. Comparison of these values with those of uncoordinated butadiene [(C–C) 1.45 Å, (C=C) 1.36 Å] reveals a small increase in the alkene bond lengths upon complexation to copper(I). The bond lengths for coordinated butadiene in $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ are not significantly different to those in copper(I) complexes with other conjugated dienes (Table 2).

The infrared spectrum of $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ shows weak absorptions in the alkene region (1600–1500 cm^{-1}). By comparison with other known copper-butadiene complexes, the bands at 1559 and 1506 cm^{-1} are tentatively assigned to vibrations of the coordinated butadiene molecule.[22] These values reflect a significant shift to lower wavenumber, the corresponding bands for uncoordinated butadiene are 1643 and 1595 cm^{-1}, $\Delta\nu$ 84 and 89 cm^{-1}, and compare well with those in a copper(I)-butadiene complex reported by Jagner and co-workers (Table 2).[21,22]

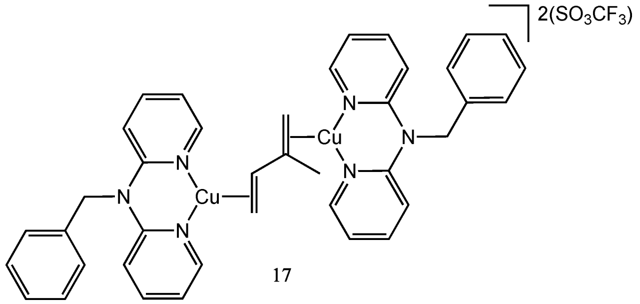
It is assumed that in the synthesis of $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ '$[Cu\mathbf{L}(C_2H_6)]^+$' is formed initially, and $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ is the dominant product of the reaction due to its insolubility. Attempts to synthesise $[Cu\mathbf{L}(C_2H_6)]^+$ by adding a solution of $[Cu\mathbf{L}(C_2H_4)]PF_6$ to liquid butadiene were unsuccessful. The limited solubility of $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ in weakly-coordinating solvents (CD_2Cl_2, $CDCl_3$) made characterisation by NMR spectroscopy difficult. Addition of CD_3CN to $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ results in complete dissolution and the likely formation of the acetonitrile adduct $[Cu\mathbf{L}(NCCH_3)]\cdot PF_6$ The coordinated butadiene appears to be readily displaced by acetonitrile, even in

Table 2 Comparison of spectroscopic and structural data for $[Cu_2\mathbf{L}_2C_4H_6]^{2+}$ with copper(I)- complexes with conjugated dienes

Compound	d(C=C)/Å	d(C–C)/Å	$\Delta\upsilon$/cm^{-1}	Reference
$[Cu_2\mathbf{L}_2(C_4H_6)]^{2+}$	1.388(10)	1.475(14)	−84, −89	This work
$[Cu_2Cl_2(H_2CC(Me)CHCH_2)]$	1.381(21), 1.383(21)	1.442(21)	—	20
	1.358(7), 1.359(7)	1.471(6)	−71, −78	21
	1.360(8), 1.353(8)	1.440(8)	—	22
$[Cu_2Cl_2(H_2CC(Me)C(Me)CH_2)]$	1.35(1)	1.48(1)	−103, −87	22
$[Cu_2Cl_2(C_4H_6)]$	—	—	−89, −89	22

a dilute mixed-solvent system comprising CD_3CN in CD_2Cl_2 (1:9 v/v).

The copper(I)-isoprene complex (**17**) reported by Song and Trogler was characterised by NMR spectroscopy in deuterated methanol,[20] and it was hoped that $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ could be characterised in an analogous manner (Scheme 4). However, it was discovered that the solubility of $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ in methanol is poor, and NMR spectra recorded in CD_3OD were not of sufficient quality to assign the peaks.



17

Scheme 4 Copper isoprene complex (**17**).[20]

The CP-MAS ^{13}C NMR spectrum of $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$, shows that signals in the imine carbon region at 162 and 171 ppm are shifted downfield compared to free **L** (160 ppm, from solution-state NMR spectroscopy), which is indicative of coordination to copper(I). The spectrum is much more complicated than the ^{13}C NMR solution spectrum of $[Cu\mathbf{L}(C_2H_4)]\cdot PF_6$. Consequently, $[Cu\mathbf{L}(C_2H_4)]\cdot PF_6$ was also studied using CP-MAS ^{13}C NMR spectroscopy, to enable an equal comparison. The solid state ^{13}C NMR spectrum of the copper(I)-ethene complex was similar to that recorded in solution. Some extra peaks were observed in the imine, aromatic and alkene regions, reflecting a slight asymmetry in the complex in the solid state. The absence of a peak at 85 ppm, corresponding to coordinated ethene, in the spectrum of $[Cu_2\mathbf{L}_2(C_4H_6)]^{2+}$ is expected; however, an extra broad signal at 117.5 ppm is present, which is not observed in the spectrum of $[Cu\mathbf{L}(C_2H_4)]^+$. This band, therefore, is assigned as arising from the coordinated butadiene. ^{13}C NMR shifts for free butadiene are at 138 and 118 ppm (recorded in $CDCl_3$), therefore assignment of the peak at 117.5 ppm as complexed butadiene is reasonable, although there is a negligible change in chemical shift caused by complexation to copper. Many signals in the aromatic region in $[Cu_2\mathbf{L}_2(C_4H_6)]^{2+}$ between 140 and 128 ppm, dictate that any signal from butadiene in this region cannot be confidently assigned.

A lack of ^{13}C NMR data in the literature for any conjugated diene which is complexed to copper(I) (solution or solid state NMR data) makes it difficult to comment comparatively on the negligible upfield shift observed in the solid state ^{13}C NMR spectrum of $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$.

Reactivity studies

In preliminary studies, both copper(I)-alkene complexes were investigated in a series of reactions with nucleophiles. It was expected that the coordination of copper would enhance the reactivity of the bound alkene groups towards nucleophilic attack by carboxylic acids and alcohols. A series of tests was carried out using $[Cu\mathbf{L}(C_2H_4)]\cdot PF_6$ and $[Cu_2\mathbf{L}_2(C_4H_6)]\cdot 2PF_6$ in attempted reactions with acetic acid, tetrabutylammonium acetate, phenylacetic acid and methanol. In all cases, reaction products corresponding to nucleophilic attack on the coordinated alkene were not observed.

$[Cu\mathbf{L}(NCCH_3)]\cdot PF_6$ was also investigated as a potential catalyst in the addition of nucleophiles to butadiene. The reactions of butadiene with tetrabutylammonium acetate, phenylacetic acid and methanol in the presence of $[Cu\mathbf{L}(NCCH_3)]\cdot PF_6$ were attempted, however, no products were observed from reaction of butadiene with any of the nucleophiles.

Conclusions

A diimine ligand (**L**) has been prepared and used in the synthesis of two novel copper(I)-complexes containing ethene and butadiene. Coordination of ethene to copper(I) leads to a significant decrease in the bonding character of the alkene double bond, as shown by de-shielding of ethene signals in the ^{1}H and ^{13}C NMR spectra, a decrease in the ν(C=C) stretch in the IR spectrum, and an increase in C=C bond length. The ethene binding by copper was shown to be reversible. Coordination of butadiene gives a dimeric complex, with two Cu-**L** units bridged by a butadiene ligand. IR spectroscopy reveals substantial decreases in the ν(C=C) alkene stretches compared to free butadiene, and the crystal structure provides evidence for a loss of conjugation caused by complexation to copper. Despite the spectroscopic and structural evidence that the alkene electronic structure is significantly perturbed upon coordination to copper, the complexes do not exhibit any activity in the enhancement of reaction of ethene or butadiene with nucleophiles.

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