

Synthesis, spectral, thermal, and a crystalline structure of complexes containing [MeC(CH₂PPh₂)₃Cu(I)]

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Abstract The preparation of new [MeC(CH₂PPh₂)₃CuCl] **1** and its derivatives was carried out directly by mixing of CuCl and MeC(CH₂PPh₂)₃ ligand in dry THF, the neutral precursor **1** served to prepare [MeC(CH₂PPh₂)₃Cu(NCCH₃)]BF₄ **2** and [MeC(CH₂PPh₂)₃Cu(PCH₂Ph)₃]BF₄ **3**. These complexes are characterized on the basis of elemental analysis, IR, EDS, ¹H, ¹³C and ³¹P{¹H}NMR, FAB-MS, TG/DTA and single-crystal X-ray diffraction studies. Complex **1** crystallizes in the Orthorhombic unit cells with the space group Pna2(1). The structural behavior of MeC(CH₂PPh₂)₃ ligand in the formed complexes during the coordination reaction was monitored by ³¹P{¹H}NMR in CDCl₃ at room temperature for the first time.

Keywords Cu(I) complexes · Tripodal phosphine ligands · Crystal structure · NMR

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Introduction

Over the years, tripodal phosphine ligands have played a very important role in the design and development of metal complexes-mediated catalysis [1–10]. Bidentate and tridentate phosphine ligands provide an important advantage over monodentate phosphine ligands with respect to high control of the coordination number and stereochemistry of their complexes [11]. Moreover, polyphosphine complexes have two or more chelate rings usually minimized the unwanted isomers numbers, and therefore, expected to reveal better stability and catalytic activities [3–11]. Among these ligands, the high C₃-symmetric {3-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-2-methylpropyl}(diphenyl)phosphine, MeC(CH₂PPh₂)₃ and its derivatives are the most extensively investigated ligands to form a large variety of transition metal complexes, which are found to have applications in several fields of catalysis [7–11]. The way in which a given polyphosphine coordinates to transition metal centers depends on the metal type, the counter ions, the ligand arrangement, and the other ligands surrounding the metal center [12]. Due to the presence of phosphine atoms in the backbone of the coordinated ligands, structural and fluxional behavior of such complexes during reaction processes can be easily monitored by ³¹P{¹H}-NMR [13].

In continuation to our ongoing interest in synthesis and characterization of a variety of novel phosphine transition metal complexes [14–18], herein, we synthesized and characterized three new neutral and cationic Copper(I) complexes using MeC(CH₂PPh₂)₃ ligand. The structure of the MeC(CH₂PPh₂)₃CuCl complex was characterized by X-ray single crystal measurement.

Experimental

General remarks, materials, and physical measurements

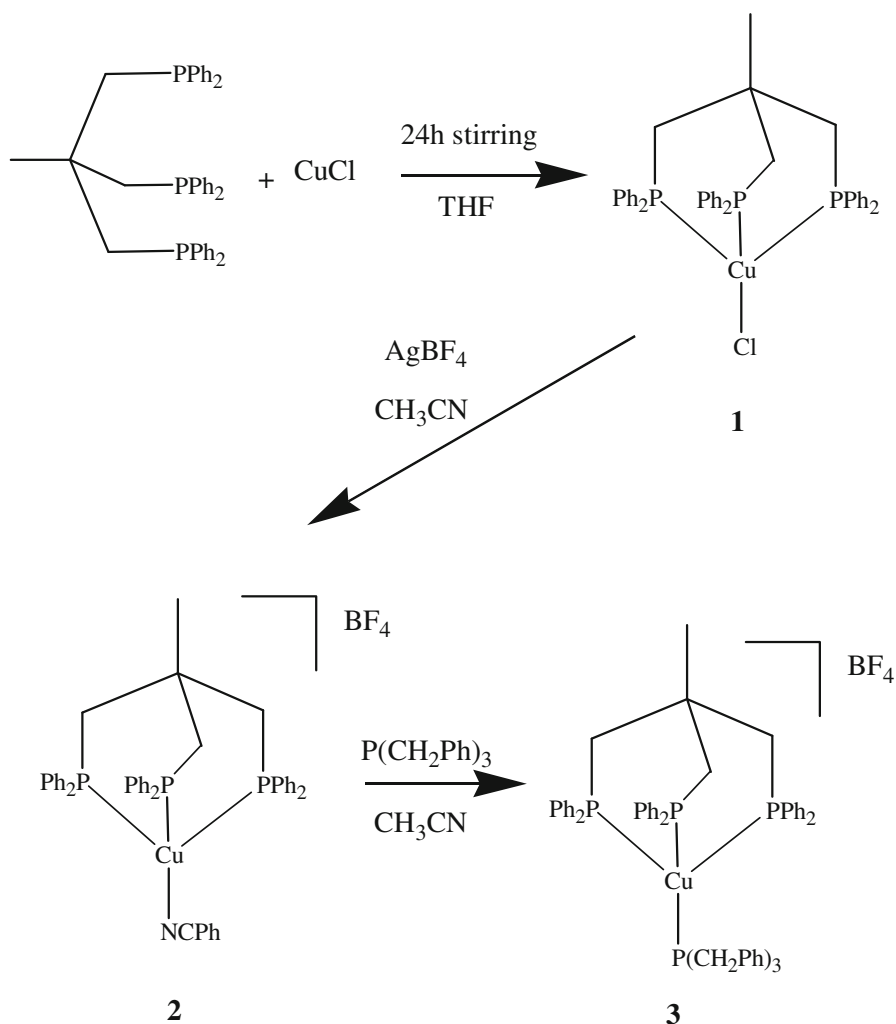
All reactions were carried out in an inert atmosphere (argon) by using standard high vacuum and Schlenk-line techniques. MeC(CH₂PPh₂)₃, CuCl, and AgBF₄ were available from Merck and used as received. Elemental analyses were carried out on an Elementar Vario EL analyzer. High-resolution ¹H, ¹³C{¹H}, DEPT 135, and ³¹P{¹H} NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. FT-IR and FAB-MS data were obtained on a Bruker IFS 48 FT-IR spectrometer and Finnigan 711A (8 kV), modified by AMD, and reported as mass/charge (*m/z*), respectively.

Synthesis of the complex [MeC(CH₂PPh₂)₃CuCl] **1**

A mixture of MeC(CH₂PPh₂)₃ (100 mg, 0.16 mmol) in 20 mL of dry dichloromethane and CuCl (16 mg, 0.16 mmol) in 40 mL of dry THF was placed in a round-bottom flask and stirred at room temperature until the tepidity disappeared (1 day). The solution was concentrated to about 4 mL under reduced pressure. The addition of 50 mL of dry diethyl ether caused the precipitation of white powder,

which was filtered and then dried under vacuum to 105.3 mg (yield 90 % based on Cu). (Scheme 1).

Cu(I)Cl (0.16 mmol) was treated with MeC(CH₂PPh₂)₃ ligand (0.16 mmol), to produce **1** as white crystal, m.p. = 253 °C. ¹H-NMR (CDCl₃): δ (ppm) 1.57 (s, 3H, CH₃), 2.16 (m, 6H, PCH₂), 7.10–7.80 (3 m, 30H, C₆H₅), ³¹P{¹H}(CDCl₃): δ (ppm) –30.2 ppm. ¹³C{¹H}NMR (CDCl₃): δ (ppm) 35.78 (s, CH₃), 43.63 (s, C), 49.19 (m, CH₂), 128.23–141.22 (4 m, C₆H₅). MS *m/z* 722.67 [M⁺] for C₄₁H₃₉ClCuP₃. Calculated: C, 68.05; H, 5.43; Cl, 4.90 %. Found C, 68.35; H, 5.32; Cl, 4.78 %.



Scheme 1 Synthesis of new Cu(I) complexes 1–3

Synthesis of the $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuNCCH}_3]\text{BF}_4$ **2**

A solution of $\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuCl}$ (50 mg, 0.07 mmol) in dry 20 mL of CH_3CN was treated with solid AgBF_4 (14 mg, 0.08 mmol) directly. The reaction mixture was stirred for 10 min at RT during which the white precipitate of AgCl was formed, which was filtrated off (P4), the solution was concentrated to about ~ 2 mL under reduced pressure. The addition of 50 mL of dry *n*-hexane caused the precipitation of white powder, which was filtered and then dried under vacuum to 43 mg (yield 72 % based on Cu). An equivalent amount of $\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuCl}$ and AgBF_4 was mixed together, to give **2** as light yellow crystal, m.p. = 270 °C. ^1H NMR (CDCl_3): δ (ppm) 1.67 (s, 3H, CH_3), 1.92 (s, 3H, CH_3CN), 2.28 (m, 6H, PCH_2), 7.00–7.90 (3 m, 30H, C_6H_5), $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3): δ (ppm) -20.2 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) 1.21 (s, CH_3CN), 37.82 (s, CH_3), 43.83 (s, C), 50.96 (m, CH_2), 117.95 (s, CH_3CN), 129.00–142.00 (4 m, C_6H_5). MS m/z 991.2 [M^+] for $[\text{C}_{48}\text{H}_{44}\text{CuP}_3]\text{BF}_4$. Calculated: C, 65.57; H, 5.02; F, 8.67 %. Found C, 65.35; H, 5.12; F, 8.48 %.

Synthesis of the $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuP}(\text{CH}_2\text{Ph})_3]\text{BF}_4$ **3**

A solution of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuNCCH}_3]\text{BF}_4$ (27 mg, 0.03 mmol) in 20 mL of dry CH_3CN was treated with (10 mg, 0.032 mmol) $\text{P}(\text{CH}_2\text{Ph})_3$ dissolved in 10 mL of dry CH_3CN . The reaction mixture was stirred for 2 h at RT, and then the solution was concentrated to about 1 mL under reduced pressure. The addition of 50 mL of dry diethyl ether caused the precipitation of white powder, which was filtered and then dried under vacuum to 20 mg (yield 61 % based on Cu).

Equivalent amount of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuNCCH}_3]\text{BF}_4$ and AgBF_4 was mixed to give **3**.

White crystal. m.p. = 220 °C. ^1H NMR (CDCl_3): δ (ppm) 1.76 (s, 3H, CH_3), 2.17 (m, 6H, PCH_2Ph), 2.38 (m, 6H, PCH_2), 7.00–7.80 (3 m, 45H, C_6H_5), $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3): δ (ppm) -10.4 . $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) 38.42 (s, CH_3), 44.53 (s, C), 49.87 (m, CH_2Ph), 51.88 (m, CH_2), 128.00–142.00 (br, m, C_6H_5). MS (FAB, m/z): 790.2 [M^+] for $[\text{C}_{62}\text{H}_{60}\text{CuP}_4]\text{BF}_4$. Calculated: C, 69.09; H, 5.57; F, 7.06 %. Found C, 68.85; H, 5.45; F, 7.25 %.

X-ray structural analyses for the desired complex **1**

The crystal was grown by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Data were collected at 173(2) Siemens P4 diffractometer operating in the omega scan mode, using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Details of crystal data, data collection, and structure refinement are given in Table 1. The structure was solved by direct methods using the Bruker SHELXS-97 programme and refined by full matrix least-squares on F^2 using the Bruker SHELXL-97 programme [19, 20].

Table 1 Crystal data and structure refinement for complex **1**

Empirical formula	C ₄₁ H ₃₉ ClCuP ₃
Formula weight	723.62
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	a = 20.708(10) Å α = 90° b = 10.273(5) Å β = 90° c = 16.965(8) Å γ = 90°
Volume	3609(3) Å ³
Z	4
Density (calculated)	1.332 mg/m ³
Absorption coefficient	0.841 mm ⁻¹
F(000)	1504
Crystal size	0.34 × 0.22 × 0.20 mm ³
Theta range for data collection	1.97–25.90°
Index ranges	–25 < = h < = 25, –12 < = k < = 12, –20 < = l < = 20
Reflections collected	29,457
Completeness to theta = 25.90°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8499 and 0.7631
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	6,882/1/415
Goodness-of-fit on F ²	0.856
Final R indices [I > 2σ(I)]	R1 = 0.0429, wR2 = 0.0708
Absolute structure parameter	–0.008(11)
Largest diff. peak and hole	0.726 and –0.224 e Å ⁻³
CCDC number:853698	

Results and discussion

Complex synthetic investigation

The reason for choosing the C₃-symmetric MeC(CH₂PPh₂)₃ ligand with the equivalent P atoms was to reduce the number of possible isomeric metal complexes. The reaction scheme for the synthesis of new [MeC(CH₂PPh₂)₃Cu(I)] complexes is depicted in Scheme 1.

The air-stable complex [MeC(CH₂PPh₂)₃Cu(I)Cl] **1** was obtained in a very good yield by mixing CuCl with equivalent of MeC(CH₂PPh₂)₃ in dry THF. Treatment of **1** with equivalent amount of AgBF₄ in CH₃CN leads to monocation air-sensitive [MeC(CH₂PPh₂)₃Cu(I)(NCP)]BF₄ **2** formation, which served to prepare air unstable monocation [MeC(CH₂PPh₂)₃Cu(I)(P(CH₂Ph)₃)]BF₄ **3**. The structure of the desired complexes have been deduced from elemental analysis, FAB-mass

spectrometry, infrared spectroscopy, EDS, UV–visible, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR, spectroscopy TG/DTA, and X-ray single crystal measurement.

Electronic absorption and IR spectral studies

The electronic absorption spectrum of desired complexes was acquired in chloroform at room temperature. The complexes formed colorless solutions (10^{-4} M). The complexes displayed intense transitions in the UV–Vis region. Bands ($\epsilon \sim 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) in the high-energy side at 200–280 nm that is referred to the ligand centered charge transitions. On the basis of its intensity and position, the lowest energy transitions at ~ 310 –400 nm ($\epsilon \sim 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) have been tentatively assigned to $\text{M}_{d\pi}\text{-L}_{\pi^*}$ metal to ligand charge transfer transitions (MLCT) [21]. As typical example absorption bands at 205, 212, and 310 nm are depicted in Fig. 1a.

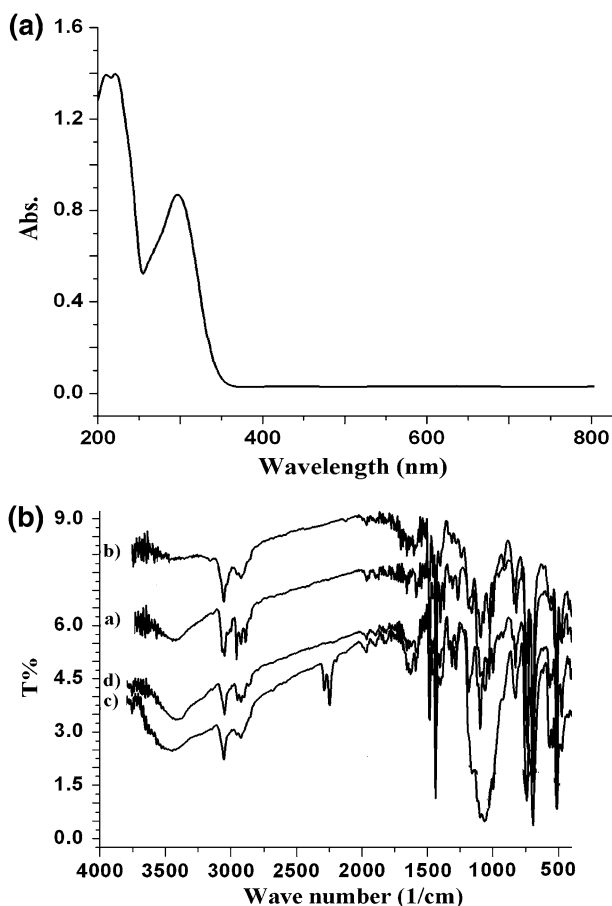


Fig. 1 a UV–Vis spectrum of complex 1 in CHCl_3 at RT. b IR-KBr disk spectra of (a) $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ free ligand, (b) complex 1, (c) complex 2, (d) complex 3

The IR spectra of the complexes have been examined in comparison with the spectra of the free ligands. IR spectra of the desired complexes in particular show main three sets of characteristic absorptions in the range 3,480 cm⁻¹ broad (excepted complex **1**), 3,120 cm⁻¹ sharp and 2,920–2,800 cm⁻¹ multiple, which can be assigned to –H₂O, Ph-CH, and alkyl-CH stretching vibrations, respectively. All the other function group vibrations are appeared at their expected positions as in Fig. 1b.

EDS measurements

To identify and differentiate the chemical composition of the desired complexes **1–3**. The complexes were subjected to EDS measurement as in Fig. 2. All the complexes were found to have signs belong their composition; they contain signs of carbon at 0.2 eV, copper signs at 0.8, 8.1 eV, and phosphine signs at 2 eV. The sign at 2.6 eV in complex **1** was cited to chloride atom (Fig. 2a), this sign was disappeared in complex **2** and **3** (Fig. 2b and c), because the chloride atom was removed by AgBF₄, the presence of fluoride sign at 1.7 eV in both complex **2** and **3** (Fig. 2b and c) confirmed chloride-abstraction from complex **1** to produce complex **2** and **3**.

Thermal studies

The thermal decomposition studies of the complex **1** was investigated in the 0–1,000 °C temperature range under open atmosphere at a heating rate of 10 °C/min. Typical thermal TG and DTA curves are given in Fig. 3.

There is no weight loss in the range 0–380 °C, which indicates the absence of coordinated or uncoordinated water molecules. Such complexes undergo two-step decomposition with weight loss experimentally 90 %, the coordinated chlorides and MeC(CH₂PPh₂) ligands have been de-structured from the complex in between 380 and 450 °C and 450 and 840 °C with exothermic DTA peaks at 440, 475, 585, 675, and 810 °C. The final residue was analyzed by IR spectra and identified as Cupper oxide (Cu₂O, 28 %).

NMR investigations

The ³¹P{¹H} NMR spectra of the desired complexes **1–3** was recorded in CDCl₃ at RT, it revealed one broad singlet signal at –31.1, –20.2, and 10.4 (multi) ppm, respectively. This is consistent with the formation of tetrahedral C_{3v} symmetry complexes with three equivalent phosphorus of the ligand coordinated to the Cu(I) center atom. The broadening of the signal is indicative of fluxional behavior inside these complexes, as in (Fig. 4).

In the ¹H-NMR and ¹³C{¹H}NMR, spectra of the desired complexes have been recorded in CDCl₃ solution to confirm the binding of the ligand to the Cu(I) and their assignments are given in Sect. 2. Several characteristic set of signals are observed attributed to the triphos ligand, CH₃CN and P(CH₂PH)₃. The integration of the ¹H resonances confirms the desired complexes formation.

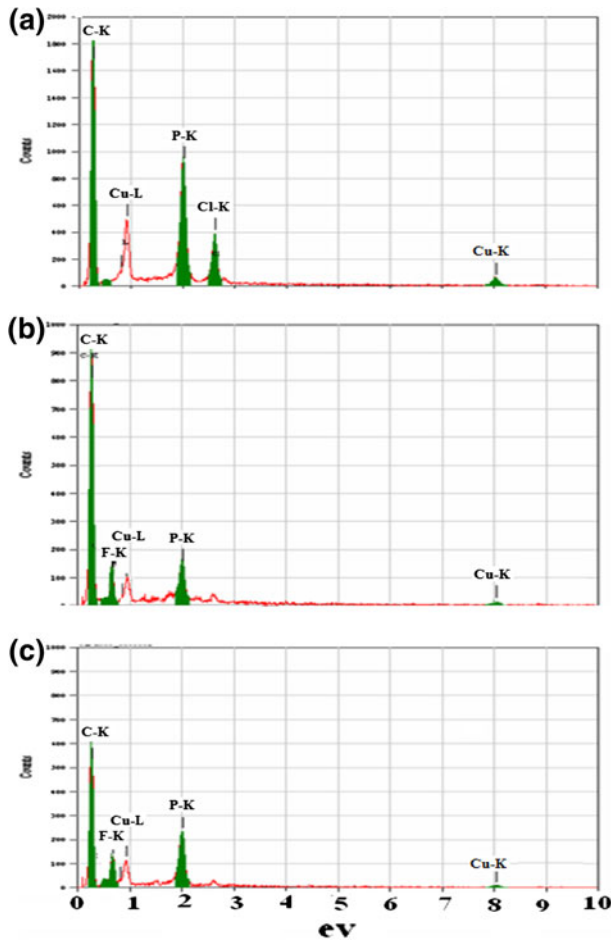


Fig. 2 EDS sings of atomic content in of complex **1** (a), complex **2** (b), and complex **3** (c)

X-ray structural analyses for the complex **1**

The molecular structure of the complex **1** has been determined by single crystal X-ray diffraction and the ORTEP diagram is given in Fig. 5. Complex **1** is crystallized as free solvated isomer with approximate C_{3v} symmetry.

The Cu(I) atom in complex **1** has a distorted tetrahedral environment formed by three P atoms from $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ and one Cl atom. The average for Cu-P bond lengths in the complex (2.292 Å) is very close to the value found (2.2953 Å) in the chloro complex [22] and in both cases are in the expected range for four-coordinate Cu(I) systems (2.304 Å). However, the Cu-Cl distance (2.2587 Å) [22].

A summary of crystal parameters, data collection, and refinement for the crystal structure is given in Table 1, selected bond lengths and angles are listed in Table 2, and atomic coordinates and equivalent isotropic displacement parameters for complex **1** are listed in Table 3.

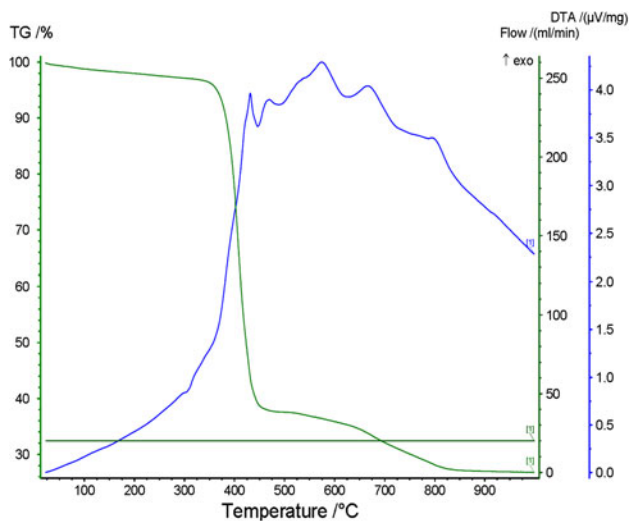


Fig. 3 TG and DTA thermal curves of complex **1**

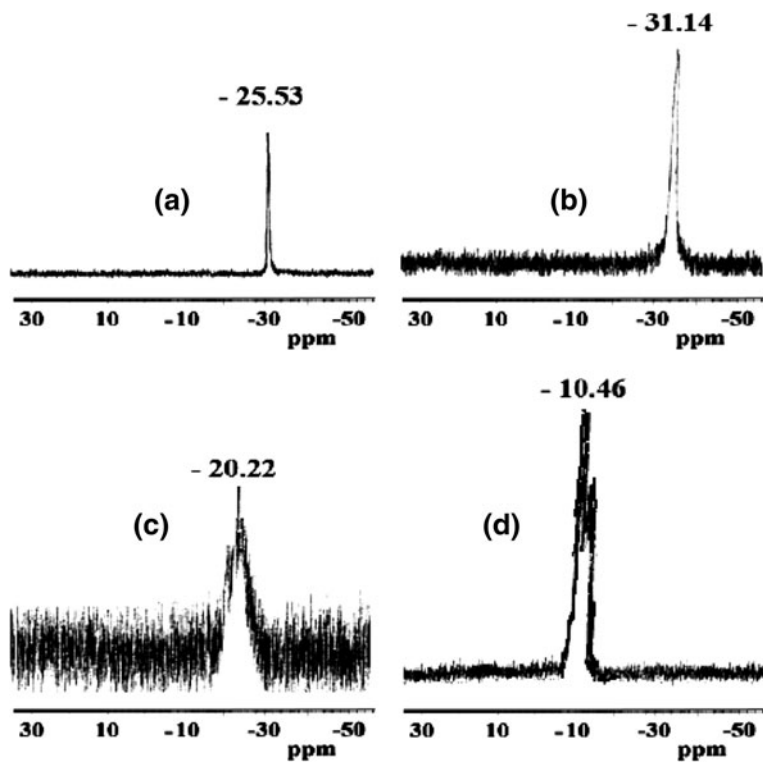


Fig. 4 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum free ligand (a), **1** (b), **2** (c), and **3** (d), in CDCl_3 at RT

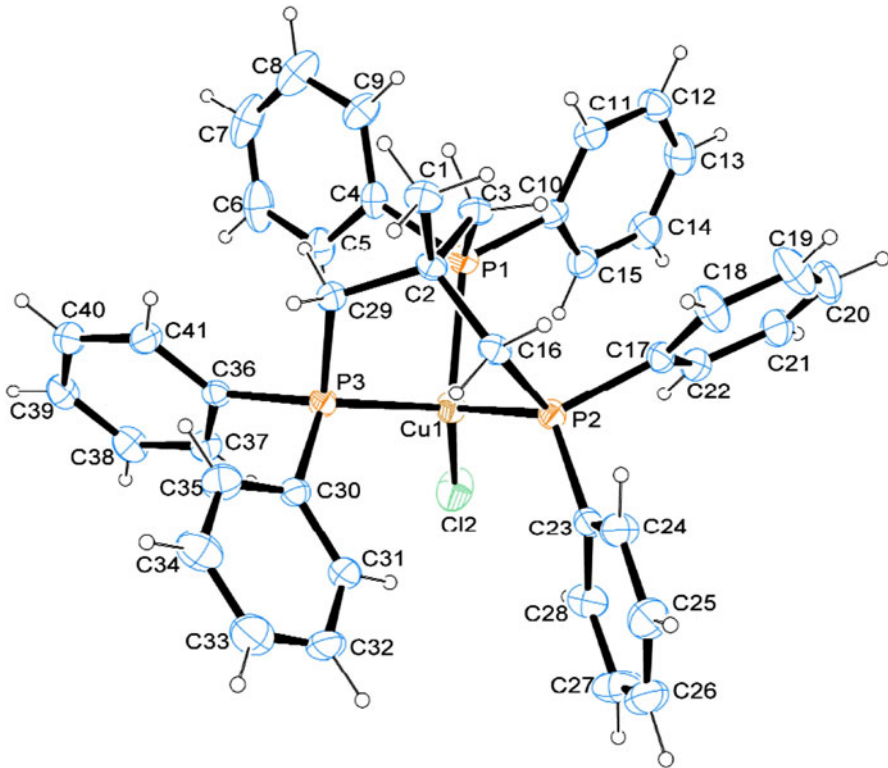


Fig. 5 Labeled ORTEP diagram of complex **1** with thermal probability

Table 2 Bond lengths [Å] and angles [°] for complex **1**

P(1)–Cu(1)	2.2930(15)	Cl(2)–Cu(1)–P(2)	125.84(5)
P(2)–Cu(1)	2.2819(14)	Cl(2)–Cu(1)–P(1)	120.22(5)
P(3)–Cu(1)	2.2954(14)	P(2)–Cu(1)–P(1)	92.08(4)
Cl(2)–Cu(1)	2.2587(14)	Cl(2)–Cu(1)–P(3)	120.77(5)
		P(2)–Cu(1)–P(3)	95.92(5)
		P(1)–Cu(1)–P(3)	94.22(4)

Conclusions

The desired Cu(I) complexes were made available through direct synthesis using equivalent tripodal triphosphine ligand in good yield. The structure of the complexes was characterized by several physical measurements, EA, FAB-MS, IR, UV–Vis, ^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$ NMR, TG/DTA and X-ray single crystal. In solid state using X-ray single crystal structure of complex characterized as regular tetrahedral, which was also confirmed by liquid $^{31}\text{P}\{^1\text{H}\}$ NMR.

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **1**

	X	Y	Z	U (eq)
C(1)	10324(2)	7197(4)	4171(2)	55(1)
C(2)	10020(2)	7825(3)	4914(2)	43(1)
C(3)	10589(2)	8317(4)	5419(2)	48(1)
C(4)	10680(2)	7271(4)	7011(2)	55(1)
C(5)	10296(2)	6869(4)	7635(3)	73(1)
C(6)	10501(3)	5850(6)	8113(3)	100(2)
C(7)	11069(4)	5225(5)	7961(4)	111(2)
C(8)	11443(3)	5599(5)	7343(4)	101(2)
C(9)	11247(3)	6614(4)	6864(3)	74(1)
C(10)	11023(2)	9869(3)	6736(2)	47(1)
C(11)	11634(2)	9921(3)	6434(3)	59(1)
C(12)	12078(2)	10816(4)	6683(3)	69(1)
C(13)	11922(3)	11670(4)	7267(3)	78(1)
C(14)	11319(3)	11641(4)	7584(3)	76(1)
C(15)	10861(2)	10748(4)	7330(2)	63(1)
C(16)	9584(2)	8952(3)	4616(2)	46(1)
C(17)	10032(2)	11482(4)	5173(2)	48(1)
C(18)	10364(2)	11650(5)	4472(3)	80(2)
C(19)	10816(3)	12600(6)	4402(3)	101(2)
C(20)	10944(3)	13424(5)	5028(4)	92(2)
C(21)	10630(2)	13261(4)	5723(4)	80(2)
C(22)	10171(2)	12285(4)	5793(3)	60(1)
C(23)	8705(2)	11072(3)	4829(2)	49(1)
C(24)	8641(2)	11169(4)	4025(2)	66(1)
C(25)	8114(3)	11784(5)	3696(3)	82(2)
C(26)	7646(2)	12321(5)	4161(4)	87(2)
C(27)	7705(2)	12255(5)	4948(4)	91(2)
C(28)	8229(2)	11618(4)	5299(3)	65(1)
C(29)	9633(2)	6736(3)	5343(2)	47(1)
C(30)	8265(2)	7157(4)	5387(2)	49(1)
C(31)	7842(2)	8185(4)	5338(3)	71(1)
C(32)	7306(2)	8101(6)	4825(4)	94(2)
C(33)	7191(3)	6987(6)	4405(3)	93(2)
C(34)	7597(2)	5963(5)	4469(3)	81(1)
C(35)	8121(2)	6044(5)	4948(2)	66(1)
C(36)	8856(2)	5914(3)	6673(2)	45(1)
C(37)	8534(2)	6160(4)	7365(2)	53(1)
C(38)	8398(2)	5171(5)	7884(2)	65(1)
C(39)	8586(2)	3923(5)	7728(3)	64(1)
C(40)	8909(2)	3667(4)	7044(3)	66(1)

Table 3 continued

	X	Y	Z	U (eq)
C(41)	9046(2)	4642(3)	6522(3)	56(1)
P(1)	10401(1)	8694(1)	6463(1)	48(1)
P(2)	9387(1)	10274(1)	5314(1)	44(1)
P(3)	8984(1)	7280(1)	6013(1)	45(1)
Cl(2)	8895(1)	10073(1)	7617(1)	88(1)
Cu(1)	9328(1)	9243(1)	6504(1)	50(1)

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