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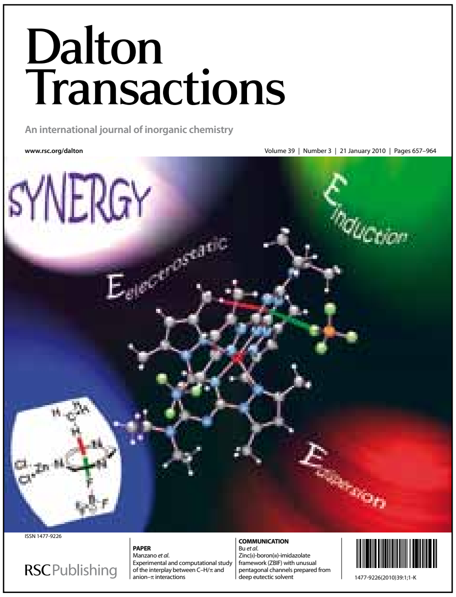

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COMMUNICATION

Thiocyanato-Bridged Copper(I) Cubane Complex and its application in Palladium-Catalyzed Sonogashira Coupling of Aryl halides

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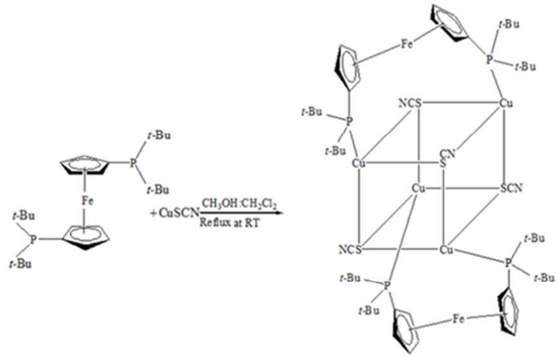
Reaction of copper(I) thiocyanate with 1,1'-bis(di-*tert*-butylphosphino) ferrocene (dtbpf) in 2:1 molar ratio in DCM-MeOH (50:50 V/V) afforded a tetranuclear copper(I) complex $[Cu_4(\mu_3\text{-SCN})_4(\kappa^1\text{-}P,P\text{-dtbpf})_2]$ (**1**) with a cubane-like structure. Complex **1** was shown to be an efficient catalyst in comparison to CuI in Sonogashira reaction. The coupling products were obtained in high yields by using Pd loadings to 0.2 mol% as well as complex-**1** to 0.1 mol%.

Ferrocenyl diphosphines are very useful ligands for surprisingly wide variety of transition metal catalysed transformations.[1] Although there are many different types of ferrocenyl diphosphines the most common are 1,1'-bis(diphenylphosphino) ferrocene (dppf)[2] and 1,1'-bis(di-*tert*-butylphosphino) ferrocene (dtbpf)[2i,3]. These ligands have significant advantages over other diphosphines which contain alkyl rather than metallocene-backbones.[4] Recently it has been reported that dtbpf is superior to dppf for the Pd-catalyzed α-arylation of ketones and for certain Pd-catalyzed Suzuki couplings.[5,6] Additionally, tetraphosphine ligand $Fc(P)_4{}^{t}Bu$,1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-di-*tert*-butylferrocene, acts as an efficient auxiliary in Sonogashira reaction in presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and copper.[7] Also, the Cu(I) cubane complex of the simple phosphine has been found to be a versatile catalyst for coupling of bromoarenes with pyrazole under relatively mild conditions.[8] We were interested in the structural properties of dtbpf complexes with simple salts, particularly copper(I) and their applications in cross-coupling reactions.[9] Compared to the previously mentioned 1,1'-bis(phosphino)metallocene ligands, dtbpf has not been studied extensively. To date, most of the work with dtbpf has focused on catalytic systems in which dtbpf is a ligand for the palladium catalyst.[10] To the best of our knowledge no structural report has been published on CuX: dtbpf (X=Cl, Br, I, CN, SCN). We decide to undertake this study to better understand the Cu(I) species present in the solid state as well as in solution. Herein we report the first synthesis, spectroscopic characterization, and catalytic properties of a tetranuclear copper(I) complex $[Cu_4(\mu_3\text{-SCN})_4(\kappa^1\text{-}P,P\text{-dtbpf})_2]$ (**1**) which exibits a cubane-like structure. **1** was prepared in high yield as orange crystals by the reaction of CuSCN with 1,1'-bis(di-*tert*-butylphosphino)ferrocene ligand in a dichloromethane: methanol mixture (50:50 V/V) in 2:1 ratio under reflux at room temperature (Scheme 1). **1** is an air-stable, non-hygroscopic solid, soluble in dimethylformamide, dimethylsulfoxide and halogenated solvents but insoluble in petroleum ether and diethyl ether. The complex was fully characterised by IR, UV-Vis, ^1H, and ^{31}P NMR spectroscopy. The molecular structure of **1** was established by single crystal X-ray diffraction measurements. Infra-red spectrum of complex **1** shows the characteristic band at 2126 cm^{-1} corresponding to bridging SCN group (See F-1 supporting material) which is in good agreement with the literature values for bridging thiocyanate group.[11] The ^1H spectrum of **1** shows, two singlets in the range of δ = 4.04-4.25 ppm corresponding to the $\eta^5\text{-}C_5H_4$ protons of the dtbpf ligand. The *tert*-butyl protons of dtbpf were observed as a doublet at δ=1.36 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a single resonance at δ=64.34 ppm for the dtbpf ligand which suggests that all the phosphorus atoms were chemically equivalent (See F-5 supporting material). These chemical shifts are within the accepted range and are comparable to that of the chelating dtbpf ligands.[10c,12] The UV-Vis spectrum of **1** exhibits two bands at 495 and 328 nm in dichloromethane solution (See F-6 supporting material). The lower-energy band at 495 nm can be assigned to the d-d transition and the higher-energy band at



Scheme 1

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† Electronic supplementary information (ESI) available: Full synthetic procedures; experimental and instrumental details; full crystallographic data; additional crystal structure figures; emission figure. CCDC 923839-920724 for **1a** & **1b**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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327 nm has been assigned to intraligand charge transfer. Complex **1** upon excitation at its respective lowest energy band maximum (495 nm) is non-emissive, while on excitation at 327 nm exhibits broad emission at 397 nm (See F-7 supporting material). We tentatively assigned the emission of complex **1** as due to XLCT, CC, and LC transitions due to their broad emission spectrum as dtbpf ligand does not show luminescence in the range of 495-900 nm.

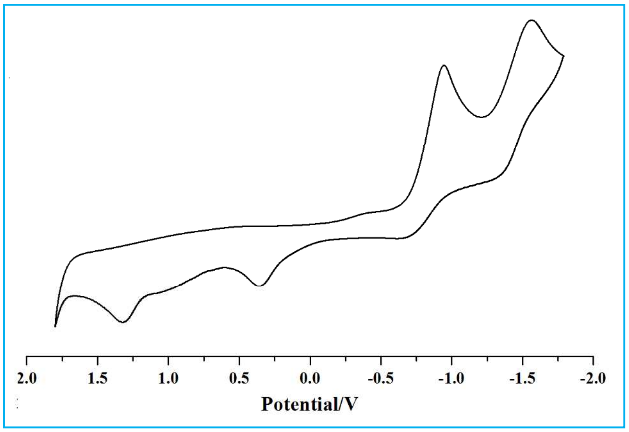

Fig. 1 Cyclic voltammogram of **1** in CH$_2$Cl$_2$/0.1 M [NBu$_4$]ClO$_4$ at 100 mV/s^{-1} scan rate.

The presence of two kinds of oxidation centers in **1**, i.e. iron(II), and copper(I), prompted us to study **1** using cyclic voltammetry (Fig. 1). The oxidation of **1** is chemically quasi-reversible. The first oxidation process is represented by removal of one electron at +0.34 V versus Fc$^{+/0}$. The next oxidation wave at +1.32 V is corresponds to the copper(I/II) oxidation.

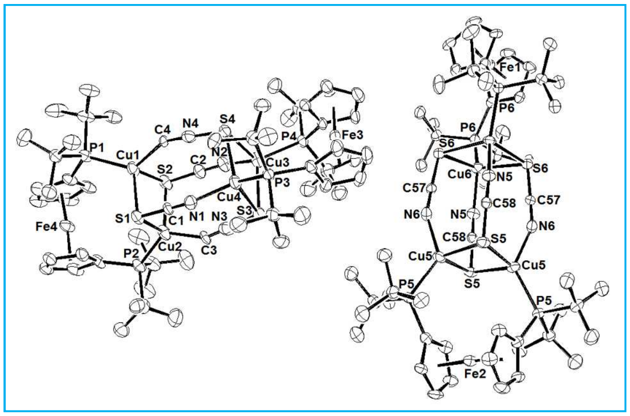

Fig. 2 ORTEP representation of complex **1** with thermal ellipsoids shown at the 30% probability level. Selected bond lengths and angles: Cu(1)-P(1) 2.228(3), Cu(1)-S(1) 2.444(3), Cu(1)-S(2) 2.500(3), Cu(2)-P(2) 2.226(3), Cu(2)-S(2) 2.428(3), Cu(2)-S(1) 2.591(3), Cu(3)-P(4) 2.222(2), Cu(3)-S(3) 2.483(3), Cu(3)-S(4) 2.524(3), Cu(4)-P(3) 2.240(3), Cu(4)-S(4) 2.452(2), Cu(4)-S(3) 2.509(3), Cu(5)-P(5) 2.230(2), Cu(5)-S(5) 2.425(2), Cu(6)-P(6) 2.230(2), Cu(6)-S(6) 2.483(2), N(1)-C(1) 1.161(10), N(2)-C(2) 1.152(11), N(3)-C(3) 1.147(12), N(4)-C(4) 1.156(10), N(5)-C(58) 1.162(9), N(6)-C(57) 1.171(9), P(1)-Cu(1)-S(1) 115.37(9), S(1)-Cu(1)-S(2) 101.97(10), P(1)-Cu(1)-S(2) 111.98(10), P(2)-Cu(2)-S(2) 110.10(11), S(2)-Cu(2)-S(1) 99.81(10), C(1)-S(1)-Cu(1) 101.7(3), C(2)-S(2)-Cu(2) 97.7(4), P(4)-Cu(3)-S(3) 113.31(10), P(4)-Cu(3)-S(4) 116.17(9), S(3)-Cu(3)-S(4) 99.21(9), P(3)-Cu(4)-S(4) 110.29(9), S(4)-Cu(4)-S(3) 100.46(9), P(5)-Cu(5)-S(5) 115.04(9), P(6)-Cu(6)-S(6) 111.99(8), S(6)-Cu(6)-S(6)$^{\#1}$102.03(7), Cu(2)-S(2)-Cu(1) 79.51(9), Cu(3)-S(3)-Cu(4) 79.31(8), Cu(4)-S(4)-Cu(3) 79.62(8), Cu(6)-S(6)-Cu(6)$^{\#1}$ 77.24(7), C(3)-N(3)-S(3) 178.3(9), C(4)-N(4)-S(4) 178.5(8), N(1)-C(1)-S(1) 179.2(9), N(2)-C(2)-S(2) 178.4(10).

As shown in Fig. 2, the X-ray crystal structural analysis of [Cu$_4$(μ_3-SCN)$_4$(κ^1-*P,P*-dtbpf)$_2$] reveals the tetranuclear cubane structure which produces an 18-electron configuration at each copper without the need for any metal-metal bonds**.** The molecule has approximate S_4 symmetry, with copper and thiocyanate arranged in a cubane. The four copper atoms are at the vertices of a tetrahedron. Each Cu^{I} has *pseudo*-tetrahedral coordination provided by the bidentate dtbpf ligands in κ^1-manner and the three bridging thiocyanate groups in μ_3-manner. The tetramer is undistorted with respect to the Cu···Cu separations (3.106-3.204 Å) and the thiocyanate S···S separations (3.813-3.869 Å). The Cu-S, Cu-N and Cu-P bond distances are 2.425(2)-2.598(2) Å, 1.973(9)-2.027(8) Å and 2.222(2)-2.240(3) Å, respectively and comparable with other copper derivatives with ferrocenyl diphosphines.[9,11.12,13] The S-C-N bond angles are in the range of 178.3(9)-179.2(9)° which indicated that thiocyanate groups are linearly coordinated to each copper of the cubane. The S-C and C-N bond distances fall in the range of 1.635(8)-1.657(10) Å and 1.147(12)-1.171(9) Å, respectively. These distances are also within the reported range.[11.13] The two substituted Cp rings in the dtbpf ligand in **1** adopt the antiperiplanar staggered conformation. The self-assembling of **1** contains solvent accessible voids in the crystal 3D lattice (See F-8 supporting material). Crystal packing in complex **1** is stabilised by C-H···S hydrogen bond interactions (See F-9 supporting material). The contact distances for C-H···S interactions are in the range of 2.68-3.00Å. The comparative catalytic activities of the CuI and copper(I) cubane complex [Cu$_4$(μ_3-SCN)$_4$(κ^1-*P,P*-dtbpf)$_2$] (**1**) were investigated in Sonogashira alkynylation of activated and non-activated aryl halides according to the previously established method developed by Hierso et al.[14]. The comparative catalytic performances for the coupling of the activated and non-activated aryl halides with phenylacetylene are reported in Table 1. It can be seen that, without palladium, the system incorporating only either complex **1** or CuI were inefficient (Table 1, entry 1 & 2). We have also found that no reaction occurred in the absence of a copper source and dtbpf (entry 3). As shown in Table 1, we isolated 10% yield of coupling product in the presence of [Pd(allyl)Cl]$_2$/dtbpf (entry 4) with no formation of homocoupling products under these conditions indicating that dtbpf and copper source were crucial to the cross-coupling reaction. Actually, as shown in Table 1, we observed a difference in catalytic activity, that is, complex **1** exhibited higher catalytic activity compared to CuI. In the case of coupling between bromobenzene and phenylacetylene in the presence of either 0.1 mol% of CuI or CuI/dtbpf and 0.2 mol% of [Pd(allyl)Cl]$_2$, the isolated yield of alkynylation product was 20-25%, while alkyne dimerization products were formed in appreciable amounts (entry 5 & 6) so the use of complex **1** in the presence of [Pd(allyl)Cl]$_2$ was more efficient for this coupling. The use of the complex **1** confirmed that the pre-stabilization of copper thiocyanate cubane structure with a bidentate ferrocenyl phosphine ligand promotes the palladium cross-coupling of activated and non-activated aryl halides with phenylacetylene. The desired coupled product in 65-95% yield was obtained (90%, 95%

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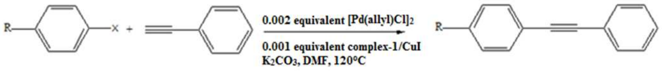
Table 1. Sonogashira Coupling of activated and non-activated aryl halides with Alkynes RC≡CH[a]



Entry	R	X	Copper source	Palladium source ([Pd(allyl)Cl]$_2$)	Alkynylation product yield [%][b]	Alkyne dimerization yield [%][b]
1.	H	Br	0.1 mol% complex **1**		0	0
2.	H	Br	0.1 mol% CuI		0	0
3.	H	Br		0.2 mol%	0	0
4.	H	Br		0.2 mol%/dtbpf	10	no
5.	H	Br	0.1 mol% CuI	0.2 mol%	20	50
6.	H	Br	0.1 mol% CuI	0.2 mol%/dtbpf	25	60
7.	H	Br	0.1 mol% complex **1**	0.2 mol%	90	traces
8.	H	I	0.1 mol% complex **1**	0.2 mol%	95	no
9.	H	Cl	0.1 mol% complex **1**	0.2 mol%	65	30
10.	CH_3	Br	0.1 mol% complex **1**	0.2 mol%	75	traces
11.	CH_3	I	0.1 mol% complex **1**	0.2 mol%	99	No
12.	CH_3	Cl	0.1 mol% complex **1**	0.2 mol%	80	traces

[a] All reactions were carried out using 3.38 X 10^{-3} mol activated and non-activated aryl halides, phenylacetylene (2 equivalent), K_2CO_3 (2 equivalent), 0.1 mol% of **1**/CuI with 0.2 mol% of [Pd(allyl)Cl]$_2$ and the catalytic system stirred at 120°C over 20 h in 10 mL of DMF under nitrogen.
[b] Isolated yield.

and 65%, respectively, Table 1 entries 7, 8, and 9) by employing 0.1 mol% of **1**, 0.2 mol% of the palladium source, and the non-activated iodo, bromo or chlorobenzene. Under the same catalytic conditions the electron-rich 4-bromotoluene, 4-iodotoluene and 4-chlorotoluene were efficiently coupled resulting in yields of over 75-99% (75%, 99% and 80%, respectively, Table 1 entries 10, 11, and 12). The stability of complex **1** during the course of tandem catalytic reaction was checked by ^{31}P and ^{1}H NMR experiments. Upon mixing the complex **1** with 0.5 equivalent of the [Pd(allyl)Cl]$_2$ and heating for 2 h at 120°C, a portion of the dtbpf ligand is transferred to palladium, giving rise to the palladium complex [PdCl(μ^1-C_3H_5)(κ^2-*P,P*-dtbpf)], clearly characterized in the ^{31}P NMR by two signals at 64.38 ppm (complex **1**) and 57.27 ppm (palladium complex) of almost equal intensity (See F-11 & F-12 supporting material). Upon heating the mixture for 20 h at 120°C, the total transfer of the ligand from copper to palladium centre has been observed (See F-13 supporting material).

In conclusion, we have synthesized and characterized the cubane tetranuclear Cu(I) complex [Cu$_4$(μ_3-SCN)$_4$(κ^1-*P,P*-dtbpf)$_2$] in the solid state and in solution. The ^{31}P NMR study shows that complex **1** is unstable during the course of tandem catalytic reaction and dtbpf ligand migrates to palladium(II) from copper(I) which promotes palladium Sonogashira cross-coupling of activated and non-activated aryl halides.

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Notes and references

§ Crystal data for **1a** (CCDC 923839): $C_{56}H_{88}Cu_4Fe_2N_4P_4S_4$, FW= 1435.28, orthorhombic, Aba2, *a* = 32.8531(4) Å, *b* = 32.0553(6) Å, *c* = 21.0880(3) Å, V = 22208.1(6) Å^3, T = 150(2) K, Z = 12, μ, mm^{-1} = 1.742, d_{calc}, g cm^{-3} = 1.288, R_1 [I > 2σ(I)] = 0.0466, wR_2 = 0.1012, S = 1.093. Crystal data for **1b** (CCDC 920724): $C_{56}H_{88}Cu_4Fe_2N_4P_4S_4$, FW= 1435.28, orthorhombic, Aba2, *a* = 32.822(3) Å, *b* = 32.088(2) Å, *c* = 21.1255(9) Å, V = 22249(3) Å^3, T = 293(2) K, Z = 12, μ, mm^{-1} = 1.739, d_{calc}, g cm^{-3} = 1.285, R_1 [I > 2σ(I)] = 0.0755, wR_2 = 0.1298, S = 1.119. For **1a** & **1b**, the SQUEEZE option in PLATON was used to remove the disordered solvent molecules.

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Graphical Abstract: Synopsis and Pictogram

The synthesis and characterization of a tetranuclear copper(I) complex $[Cu_4(\mu_3\text{-}SCN)_4(\kappa^1\text{-}P,P\text{-}dtbpf)_2]$ with a cubane-like structure is reported. This complex was shown to exhibit efficient catalytic activity compared to CuI in Sonogashira reaction by using Pd loadings to 0.2 mol% as well as complex-**1** to 0.1 mol%.