DALTON
FULL PAPER

Ligand dynamics in tetracoordinate copper(I) complexes of bis(pyrazolyl)pyridine ligands †

Palanichamy Manikandan, Mahadevan Subramoni, Babu Varghese and Periakaruppan Thangiah Manoharan *

Regional Sophisticated Instrumentation Centre and Department of Chemistry Indian Institute of Technology Madras, Chennai-600 036, India. E-mail: ptm@rsic.iitm.ernet.in

Received 26th February 1998, Accepted 15th July 1998

Several mononuclear and a binuclear copper(I)–phosphine complex with a tridentate ligand, L [2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine] or L′ [2,6-bis(pyrazol-1-ylmethyl)pyridine], have been prepared and characterized. The crystal structure of $[LCu(PPh_2CH_2CH_2PPh_2)CuL][ClO_4]_2$ has been solved. All complexes exhibit interesting molecular dynamics which could be monitored by ^{1}H NMR spectral characteristics arising from the methylene group of the ligand and also from the protons of the pyrazole part of the ligand in some cases. The complexes with unsymmetric phosphine ligands such as PPh_nBu_{3-n} with $n = 1$ or 2 revealed the presence of two conformations with differing populations as evidenced by temperature dependent ^{1}H NMR spectral data. The thermodynamics of these transformations due to the fluxional character of the ligand, L, has been studied by computer simulations of the experimental spectra. The NMR spectral characteristics revealed that the methylene protons are diastereotropic.

Introduction

Nitrogen-containing tridentate ligands have assumed great importance in recent years since their metal complexes could be synthetic models for describing the active sites of metalloproteins such as hemocyanin.[1–8] Studies of copper(I) complexes of such nitrogen containing tridentate ligands and subsequently their reactions with small ligands like CO, O_2, N_3^-, *etc.*, have emphasized their major role in understanding the structure and functionalities of the active sites of copper proteins like hemocyanin, tyrosinase, *etc*.[1–9] Since deoxyhemocyanin and deoxytyrosinase are transparent to most spectroscopic techniques their active sites were probed by complexing them with small soft ligands such as CO, PPh_3, *etc*. We have earlier reported[10] the importance of a tridentate ligand and the formation of a copper(I) complex and its CO adduct in understanding the structural and functional aspects of hemocyanin and tyrosinase. When CO is replaced by phosphine derivatives we have found that these molecules undergo interesting dynamics which could be monitored by NMR spectroscopy in solution.[10] Generally the triphenylphosphine adducts of the copper(I) complexes are stable[11–14] and used as precursors[7,8,15] in several reactions. Recently much attention has also been paid to copper(I) diphosphine complexes because of their potential biological significance.[15] The cytotoxicity and antitumor activity of diphosphine compounds are greatly enhanced when these ligands are complexed with Cu^I.[15–17]

Owing to the strained geometry/structure, certain parts of the ligand when complexed with diamagnetic metal ions[18–20] undergo interesting molecular dynamics; this can be monitored by ^{1}H NMR spectroscopy, if they occur on the 'NMR timescale' typically of the range 1 to 10^{-6} s.[21,22] Since 1953, when Gutoswky and Saiker[23] suggested the possibility of studying such dynamics, there have been reports in this area for several inorganic compounds. One can explore all the phenomena involving internal rotations,[24] fast conformational flips, fluxionality, polytopal rearrangements, "ring whizzing," proton transfer, *etc*. using such Dynamic Nuclear Magnetic Resonance (DNMR) techniques. Barrier energies,[25] rate constants, activation enthalpies and even reaction orders can be obtained from DNMR[26] for such processes by synthesizing the corresponding spectra theoretically. Since all these dynamic processes can significantly affect the chemical behavior, the study of the kinetics of the electron self-exchange by DNMR line broadening techniques becomes possible. Hawkins and Palmer[27] have reviewed the conformational analysis of chelate ring systems by NMR. Although dynamic NMR is an extraordinarily effective probe for dynamic phenomenon, it is complementary to other techniques which probe other timescales relevant to the structural and chemical properties of molecules. We report here the synthesis and structure of several phosphine derivatives of copper(I) complexes. All these complexes undergo very interesting dynamics as a function of temperature which can be monitored by NMR spectroscopy. Energy barrier and thermodynamic parameters have been estimated by simulating these dynamic NMR spectra theoretically.

Experimental

Reagents and physical techniques

Commercially available reagent grade quality chemicals and solvents were used. The compounds, 3,5-dimethylpyrazole and pyridine-2,6-dimethanol were from Aldrich and NaH from Fluka. Commercially available argon and nitrogen gases were purified and dried by passing through P_2O_5, oxygen scavenger[28] and 4 Å molecular sieve columns. The oxygen scavenger was frequently reactivated by passing H_2 over it at 380 °C and the molecular sieve column was reactivated at 400 °C under vacuum or under a nitrogen atmosphere. Solvents were dried and distilled from appropriate drying agents just prior to use[29] under an argon or nitrogen atmosphere. The preparation and handling of air sensitive compounds were carried out by adapting standard Schlenk techniques.[28] Solvents and solutions were

† *Supplementary data available*: variable-temperature NMR spectra. Available from BLDSC (No. SUP 57416, 3 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

deoxygenated by either repeated vacuum/purge cycles (argon) or by bubbling with argon. The samples were stored in an argon atmosphere.

The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-GSX 400 spectrometer with shifts reported as δ values (in ppm) downfield from an internal standard of $SiMe_4$. Temperature dependent ^{1}H NMR measurements were performed on a JEOL-GSX 400 spectrometer with a JEOL variable temperature controller. The spectra were recorded at various temperature ranges, 333–213 K for $CDCl_3$ and 303–183 K for CD_2Cl_2. Although all the compounds are not very susceptible to air in the solid state, the sample preparation for NMR measurements was done in an argon atmosphere, carefully sealed with a Subaseal rubber septum and parafilm to prevent aerial oxidation. The low temperature measurement was terminated when the line shapes of the spectrum were significantly influenced by the increased viscosity of the sample. For clarity, only the spectral regions giving dynamic information at selected temperatures are plotted. Temperature variation measurements and simulation of corresponding regions was carried out for intervals of 5 to 10 K for estimation of thermodynamic parameters. Infrared spectra were obtained either on a Bruker IFS 66v-FTIR or a Perkin-Elmer spectrometer as KBr pellets and the frequency was calibrated using polystyrene.

Synthesis

CAUTION: although we have experienced no difficulties with the perchlorate salts described, these compounds should be handled with appropriate care as perchlorate salts are potentially hazardous.

The ligands 2,6-bis(pyrazol-1-ylmethyl)pyridine (L′)[30] and 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L)[10] and the copper(I) complexes $[CuL(ClO_4)]\cdot CH_2Cl_2$ **1** and $[CuL(PPh_3)][ClO_4]$ **2** were prepared according to the reported procedures. A general preparative scheme for the copper(I) complexes is given in Scheme 1.

$[CuL(PPh_2Bu^n)][ClO_4]$ 3. The compound was prepared by adding PPh_2Bu (242.3 mg, 1 mmol) in CH_2Cl_2 (20 cm^3) to $[CuL(ClO_4)]\cdot CH_2Cl_2$ (479.8 mg, 1 mmol) in CH_2Cl_2 (20 cm^3) with constant stirring under an argon atmosphere and the solution was allowed to stir for 1 h. To this clear solution deaerated hexane (30 cm^3) was added. The resulting precipitate was washed several times with hexane and then dried. The compound is stable even after exposure to air for a long time. Yield 95% (Found: C, 56.48; H, 5.67; N, 10.99. $C_{33}H_{40}ClCuN_5O_4P$ requires C, 56.57; H, 5.75; N, 10.00%). δ_H ($CDCl_3$, 298 K) 0.7 (3 H, br, CH_3), 0.8 (2 H, br, CH_2), 1.2 (4 H, br, CH_2CH_2), 2.05 (6 H, s, CH_3), 2.4 (6 H, s, CH_3), 4.8–5.3 (4 H, br, CH_2), 5.8 (2 H, s, CH of pz), 7.2–7.4 (10 H, m, CH of Ph), 7.71 (2 H, d, CH of py) and 7.9 (1 H, t, CH of py). δ_C ($CDCl_3$, 298 K) 11.6 (CH_3), 13.8 (CH_3), 15.4 (CH_3), 24.5 (CH_2), 26.5 (CH_2), 27.1 (CH_2), 52.61 (CH_2), 107.02 (CH of pz), 128.7 (CH of py), 128.79 (CH of Ph), 130.00 (CH of Ph), 131.35 (C of Ph), 139.84 (CH of py), 143.03 (C of pz), 149.94 (C of pz) and 154.46 (C of py).

$[CuL(PPhBu^n_2)][ClO_4]$ 4. The compound $PPhBu^n_2$ was prepared by adding 2 equivalents of $LiBu^n$ to $PPhCl_2$ in hexane under an argon atmosphere. A 222.3 mg (1 mmol) amount of it was added to $[CuL(ClO_4)]\cdot CH_2Cl_2$ (479.8 mg, 1 mmol) in CH_2Cl_2 (30 cm^3) under an inert atmosphere with constant stirring. The solution was kept stirring for an hour. The final product was obtained after evaporation of the solvent and purified by repeated washings with diethyl ether and hexane. The resulting colorless product is moderately stable in air. Yield 95% (Found: C, 54.51; H, 6.22; N, 11.01. $C_{31}H_{44}ClCuN_5O_4P$ requires C, 54.70; H, 6.52; N, 10.29%). δ_H ($CDCl_3$, 298 K) 0.65 (6 H, br, CH_3), 1.18 (8 H, br, CH_2CH_2), 1.8 (4 H, br, CH_2), 2.08 (6 H, s, CH_3), 2.25 (6 H, s, CH_3), 5.2 (4 H, br, CH_2), 5.9 (2 H, s, CH of pz), 7.2–7.45 (5 H, m, CH of Ph), 7.65 (1 H, t, CH of py) and 7.91 (2 H, d, CH of py). δ_C ($CDCl_3$, 298 K) 11.09 (CH_3), 13.45 (CH_3), 13.02 (CH_3), 24.15 (CH_2), 26.48 (CH_2), 27.05 (CH_2), 52.0 (CH_2), 106.75 (CH of pz), 122.63 (CH of py), 128.7 (CH of py), 128.79 (CH of Ph), 130 (CH of Ph), 131.35 (C of Ph), 139.84 (CH of py), 141.19 (C of py), 149.10 (C of pz) and 152.90 (C of py).

$[LCu(PPh_2CH_2CH_2PPh_2)CuL][ClO_4]_2$ 5. One millimolar equivalent of 1,2-bis(diphenylphosphino)ethane (398.4 mg, 1 mmol) was added to an equimolar amount of complex **1** (479.8 mg, 1 mmol) in CH_2Cl_2 (30 cm^3) with constant stirring under an argon atmosphere. After evaporation of the solvent the final colorless product was recrystallized from dichloromethane and hexane. Yield: 95% (Found: C, 55.72; H, 5.01; N, 10.88. $C_{60}H_{66}Cl_2Cu_2N_{10}O_8P_2$ requires C, 54.80 ; H, 5.06; N, 10.65%). δ_H ($CDCl_3$, 298 K) 1.907 (6 H, s, CH_3), 2.07 (4 H, s, CH_2CH_2), 2.25 (6 H, s, CH_3), 5.02 (8 H, br, CH_2), 5.79 (4 H, s, CH of pz), 7.05 (8 H, t, CH of Ph), 7.23 (8 H, d, CH of Ph), 7.37 (4 H, t, CH of Ph), 7.54 (4 H, t, CH of py) and 7.89 (2 H, d, CH of py). δ_C ($CDCl_3$, 298 K) 11.1 (CH_3), 13.80 (CH_3), 25.12 (CH_2), 51.31 (CH_2), 107.8 (CH of pz), 123.71 (CH of py), 128.12 (CH of Ph), 129.91 (CH of Ph), 132.84 (CH of Ph), 132.51 (C of Ph), 140.39 (CH of py), 141.52 (C of pz), 148.9 (C of pz) and 152.1 (C of py).

$[CuL'(PPh_3)][ClO_4]$ 6. Under argon, a dry and degassed CH_2Cl_2 (50 cm^3) solution of L′ (239.3 mg, 1 mmol) was added to $[Cu(MeCN)_4]ClO_4$ (327 mg, 1 mmol) with stirring. The reaction was immediate. To the resultant faint yellow solution was added (PPh_3 262.3 mg, 1 mmol) and allowed to stir for an hour. The final, colorless product was collected after adding hexane. The compound was recrystallized from CH_2Cl_2–hexane (3:1). Yield 98% (Found: C, 55.89; H, 4.12; N, 11.62. $C_{31}H_{28}ClCuN_5O_4P$ requires C, 56.03; H, 4.25; N, 10.54%). δ_H ($CDCl_3$, 298 K) 5–5.5 (4 H, br, CH_2), 6.25 (2 H, t, CH of pz), 6.75 (2 H, d, CH of pz), 6.85 (2 H, d, CH of pz), 7.16 (6 H, t, CH of Ph), 7.25 (3 H, t, CH of Ph), 7.28 (6 H, d, CH of Ph), 7.59 (1 H, t, CH of py), 7.88 (2 H, d, CH of py). δ_C ($CDCl_3$, 298 K) 55.37 (CH_2), 106.69 (CH of pz), 125.09 (CH of pz), 128.94 (CH of pz), 129.03 (CH of py), 130.27 (CH of Ph), 132.41 (CH of Ph), 132.82 (CH of Ph), 132.98 (C of Ph), 139.78 (CH of py) and 152.65 (C of Ph).

X-Ray crystallography

A dichloromethane–hexane (1:3) solution of compound **5** under argon at room temperature yielded faint yellow plate shaped crystals. A crystal with approximate size 0.2 × 0.2 × 0.1 mm was mounted on an Enraf Nonius CAD-4 diffractometer with a graphite monochromated Mo-Kα X-ray source (λ = 0.71073 Å). The unit cell parameters were obtained using the method of short vectors followed by least squares refinement of 25 reflections with $12 < \theta < 15°$. The two check reflection intensities monitored once every hour showed less than 3% variation during the data collection. After Lorentz-polarization corrections, a semiempirical absorption correction was performed using ψ-scan data. Table 1 shows the experimental crystallographic data.

Compound **5** showed systematic absences for space group *C*2/*c*. The structure was solved by direct methods using SHELXS 86[31] and refined using SHELXL 93.[32] The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$. Final convergence was achieved with $R(F) = 0.0446$, $R' = 0.1344$ for 3734 unique reflections with $I > 2\sigma(I)$. All hydrogen atoms were fixed at geometrically calculated positions and allowed to ride on their parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

CCDC reference number 186/1096.

See http://www.rsc.org/suppdata/dt/1998/3219/ for crystallographic files in .cif format.

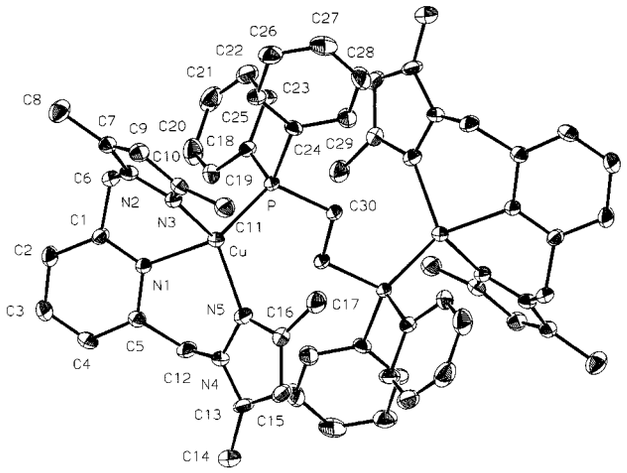
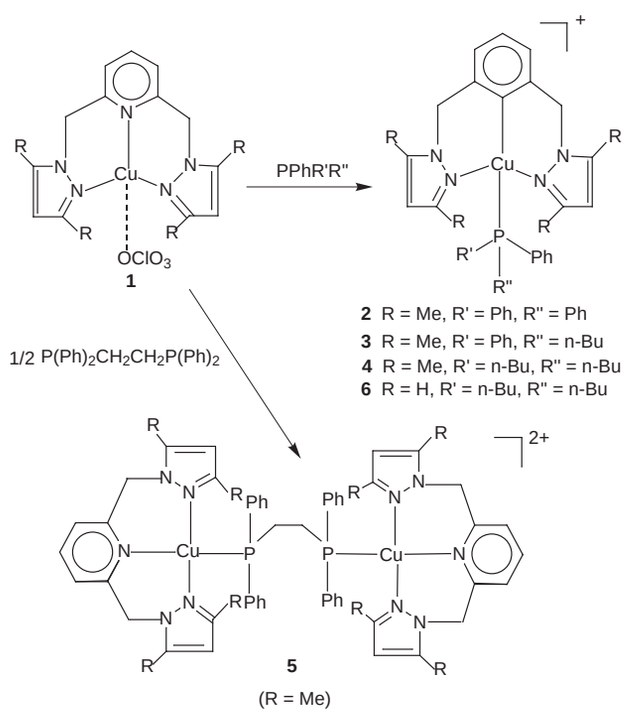


Fig. 1 A ZORTEP view of cationic part of $[LCu(PPh_2CH_2CH_2PPh_2)CuL][ClO_4]_2$ **5**. For clarity, hydrogen atoms and perchlorate anions are not shown.



Scheme 1

Results and discussion

Crystal structure of $[LCu(PPh_2CH_2CH_2PPh_2)CuL][ClO_4]$ 5

The experimental crystallographic data for compound **5** are summarized in Table 1, selected bond distances and angles in Table 2. Fig. 1 represents the ZORTEP[33] diagram of the cationic part of **5**. The asymmetric unit contains half of the molecule, the second copper atom, Cu(2), is related to Cu(1) by crystallographic inversion. The two copper units are bridged by the diphosphine ligand. Each copper is co-ordinated by three nitrogens of the ligand and one phosphorus from the bridging diphosphine ligand. The pyridine nitrogen, N(1), is co-ordinated to Cu with Cu–N(1) 2.111(4) Å and the other two nitrogens [N(3) and N(5)] of the pyrazolyl groups are at relatively shorter distances from copper, *viz*. 2.091(4) Å and 2.052(4) Å respectively. The Cu–P distance is 2.2163(14) Å, comparable to that found for $[CuL(PPh_3)]^+$ **2** [2.212(1) Å].[10] The bond angles around copper vary from 89.0(2) [N(1)–Cu–N(3)] to 125.67(11)° [N(1)–Cu–P]. Thus the geometry around copper can be represented as a distorted tetrahedron. One of the Cl–O distances [Cl–O(3) 1.406(12) Å] is longer than the others [Cl–O(1) 1.363(8), Cl–O(2) 1.349(13), Cl–O(4) 1.338(8) Å]. The O–Cl–O bond angles vary from 101.0(9) to 114.9(6)°. This variation in bond distances and angles may be due to the high thermal motion. The C(1)–N(1)–C(5) bond angle is 118.2(4)°, smaller than expected. The mean planes of the chelating rings N(1)C(5)C(12)N(4)N(5)Cu and CuN(1)C(1)C(6)N(2)N(3) assume boat conformations. None of the aromatic rings deviate from planarity.

Table 1 Crystal data for compound **5**

Chemical formula	$C_{66}H_{66}Cl_2Cu_2N_{10}O_8P_2$
Formula weight	1315.19
T/K	298(2)
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	23.769(2)
b/Å	14.386(2)
c/Å	20.284(3)
β/°	100.61(3)
U/Å^3	6817(2)
Z	4
μ/mm^{-1}	0.805
Reflections collected	6420
Independent reflections	5183
Final indicies [$I > 2\sigma(I)$]	$R = 0.0446$, $R' = 0.1344$

Table 2 Selected bond distances (Å) and angles (°) for compound **5**

Cu–N(5)	2.052(4)	Cu–N(1)	2.111(4)
Cu–N(3)	2.091(4)	Cu–P	2.2163(14)
N(5)–Cu–N(3)	120.6(2)	N(5)–Cu–P	115.77(13)
N(5)–Cu–N(1)	93.9(2)	N(3)–Cu–P	109.58(11)
N(3)–Cu–N(1)	89.0(2)	N(1)–Cu–P	125.67(11)

Variable temperature NMR studies and simulations

Six four-co-ordinate copper(I) compounds have been prepared with tridentate N donor ligands, L and L′, the fourth co–ordination site being filled either by oxygen of perchlorate or phosphorus of phosphine derivatives. The room temperature ^{1}H NMR spectra of the ligand portion of the compounds are essentially similar except for the methylene proton region. Proton resonance assignments and signal positions of all the complexes are given in the Experimental section. The methylene protons of the ligand part and the pyrazole protons of the ligand in some cases (**3** and **4**) exhibit interesting molecular dynamic processes as a function of temperature which can be monitored by ^{1}H NMR spectroscopy. The symmetry and bulkiness of the group the fourth co-ordination site play a major role in the dynamic properties of the complexes. From the dynamic NMR results one can categorize three classes: (i) compounds which exhibit an isotropic signal for methylene protons (**1**); (ii) compounds which exhibit diastereotropic character for methylene protons (**2**, **5** and **6**) and (iii) compounds which possess diastereotropic methylene protons as well as different conformations (**3** and **4**).

Proton NMR spectra of complex 1. We had earlier reported[10] the variable temperature ^{1}H NMR spectra for compound **1** in $CDCl_3$ solution down to 213 K. Signals due to the methylene protons are slightly broadened at higher temperatures and as the sample was cooled no splitting was observed; however, the signals due to the methylene protons and those of CH_2Cl_2, the solvent of crystallisation, separate at low temperatures as a result of sharpening of the peaks. This single resonance of the methylene protons of the ligand reveals that not only the methylene groups of both arms of the ligand are identical but also that the protons on the individual methylene groups are magnetically equivalent in solution. Owing to its small size, the

Table 3 Resonance positions and coupling constants of methylene and pyrazole protons

Compound (solvent)	Conformer	Chemical shift (δ) of methylene protons		J/Hz	Chemical shift (δ) of pyrazole protons
		A	B		
1 ($CDCl_3$)	—	5.23		—	5.95
2 ($CDCl_3$)	—	5.27	4.73	14	5.80
5 (CD_2Cl_2)	—	5.14	4.65	14	5.79
6 ($CDCl_3$)	—	5.54	4.86	14	6.25
3 ($CDCl_3$)	sym.	5.37	4.83	15	5.37
	asym.	5.27	4.74	15	5.84
4 ($CDCl_3$)	sym.	4.98	4.43	10	5.78
	asym.	4.94		—	5.34

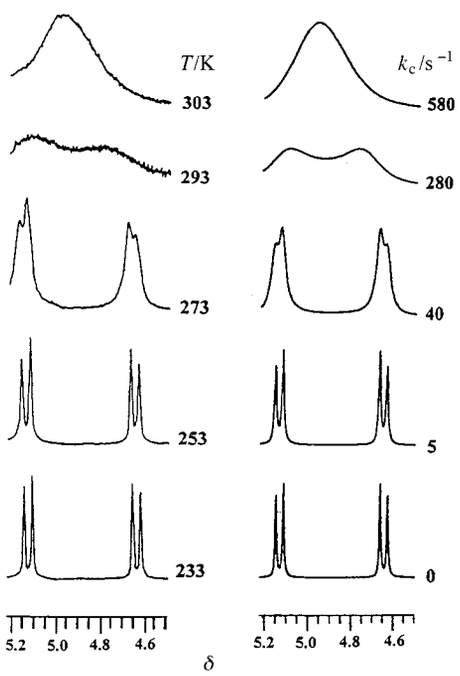


Fig. 2 Variable temperature ^{1}H NMR spectra of the methylene region (left) for the compound $[LCu(PPh_2CH_2CH_2PPh_2)CuL][ClO_4]_2$ **5** and the corresponding computer simulations (right) in CD_2Cl_2 solvent.

perchlorate ion rotates freely which makes the methylene protons experience more or less the same ring current effect from the pyrazole and pyridine groups and as a result the methylene protons are isotropic.

Dynamics of the methylene group of complexes 2, 5 and 6. Variable temperature ^{1}H NMR spectra of the methylene region of compounds **2**, **5** and **6** show a similar pattern in principle but small differences exist. Hence, only the spectra of **5** in the temperature range 233–303 K are shown in Fig. 2 as representative. The methylene protons of **2**, **5** and **6** show a broad signal at room temperature in solution but a relatively sharp singlet for **1**. On raising the temperature these signals sharpen considerably. The broad signal at room temperature splits gradually into two broad signals on cooling. As the temperature is lowered further, these signals sharpen followed by splitting. The signals resemble an AB quartet at lower temperatures for all the compounds. If the methylene protons are magnetically equivalent one would normally expect a sharp signal. However, the variable temperature ^{1}H NMR studies in solution indicate the inequivalence of the methylene protons with a weak coupling between them ($\delta > J$).[18–20] Exchange narrowing at high temperatures reveals the equivalence of two protons of the methylene group due to dynamic exchange. Coalescence occurs at 298 (±2) K for all these compounds though the chemical shifts for the methylene protons are different (*cf.* Table 3). The spectra of other protons of the molecule are not notably affected in the temperature range studied.

The inequivalent nature of the methylene protons could be rationalized from available crystallographic structural information. The crystallographic least squares plane analyses of complexes **2**[10] and **5** indicate the chelating rings assume boat conformations. Thus the methylene protons have to be in axial and equatorial positions of the boat conformation of the chelating ring. Thus the methylene protons are diastereotropic and become distinguishable on the NMR timescale at low temperatures. The difference in the chemical shifts of proton A and B of this CH_2 group may be rationalized as follows: the restricted motion of the phenyl groups of phosphine derivatives and the flip-flop motions of pyrazole groups (with respect to pyridine) are possibly slowed at low temperatures and hence the methylene protons located at the axial and equatorial positions experience differing ring current effects. The differing chemical shifts of protons A and B may also be due to their differing proximity to the metal centre which can cause a differential shielding to them. The increase in temperature increases these two rate processes, making these protons experience similar shielding and hence a single broad line followed by sharpening is observed on the NMR timescale. Computer simulations of the methylene protons of compounds **2**, **5** and **6** using this presumed molecular dynamics model easily reproduce the experimental spectra as shown in Fig. 2 for compound **5**. The simulations were performed by using chemical shift, coupling constant and rate constant parameters. The calculated chemical shift and coupling constant values are listed in Table 3. The rate constant values are shown on the corresponding simulated spectra.

The compounds were also analysed by ^{13}C NMR spectroscopy at room temperature (r.t.) and 233 K. Complete assignment of the peaks at r.t. is given in the Experimental section. Only one signal appears at *ca.* δ 51–53 which corresponds to methylene carbon at r.t. and 233 K. This clearly indicates the absence of any dissociation of the ligand arms. It also gives additional proof for the equivalence of two methylene groups of the ligand.

However, the dynamically exchange narrowed lines at high temperatures (above the coalescence point) especially for complexes **2** and **5** have slightly higher chemical shifts than those observed at around the coalescence temperature. This may be due to the elongation of the Cu–P bond necessitated by free rotation of the triphenylphosphine group with respect to this bond.

Dynamics and conformers in complexes 3 and 4. Fig. 3 shows the variable temperature ^{1}H NMR spectra of pyrazole and methylene group protons of $[CuL(PPh_2Bu^n)][ClO_4]$ **3** in $CDCl_3$ in the temperature region 213–323 K. At r.t. the signals due to both methylene and pyrazole CH protons are broad and at high temperatures (>293 K) the methylene proton signals are relatively sharp while those of the pyrazole CH proton broaden. On cooling, the methylene protons give a broad doublet around

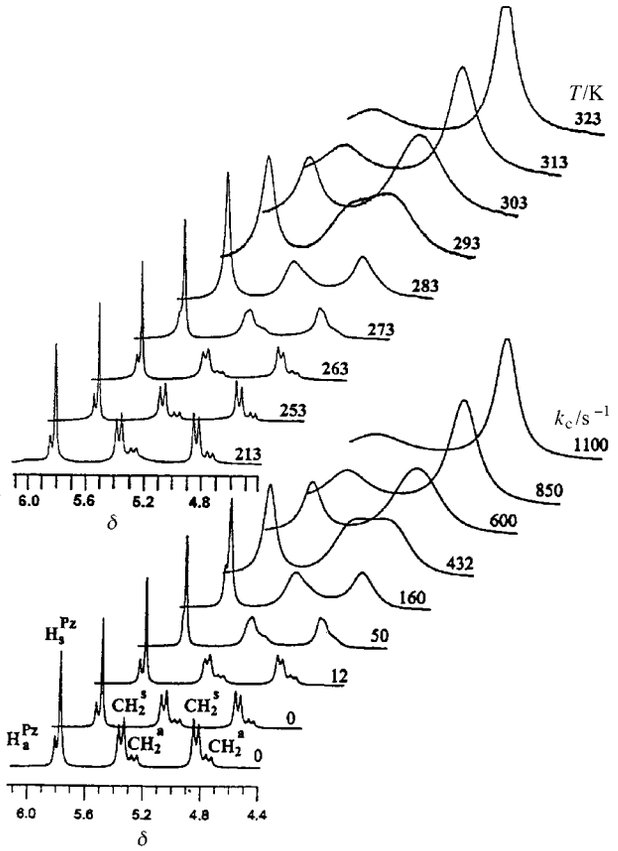


Fig. 3 Temperature variation of the ^{1}H NMR spectra of the methylene and pyrazole regions of [CuL(PPh$_2$Bu)][ClO$_4$] **3** in CDCl$_3$ (left) and the corresponding computer simulated spectra (right) (a = asymmetric, s = symmetric, pz = pyrazole).

283 K with asymmetric line shape. At 213 K the spectrum is composed of two different doublets of doublets with differing intensities. The evolution of this spectral character is clear on going from 323 to 213 K. The low temperature spectrum (spectral region δ 5.5 to 4.6) contains two typical AB patterns with differing intensities, one being approximately five times as intense as the other. It is interesting that, in addition to these methylene protons, the pyrazole CH protons also undergo dynamics. The highly broadened line at 323 K, becomes sharper on lowering the temperature; at about 273 K and below there appears an additional signal and both become even sharper on further lowering of temperature. The intensity ratio of 5 : 1 is as clearly seen from the sharp signals at 213 K in exact correspondence to the ratio of intensities of the two doublets of doublets observed for the methylene protons. The ^{1}H NMR signals due to other parts of the ligand do not undergo notable changes except for slight sharpening or narrowing with temperature.

Fig. 3 shows that the experimental and simulated spectra are in good agreement. The rate constants were calculated only for the methylene protons at different temperatures. The pattern is that of an AB system arising from the two environmentally non-equivalent methylene protons. The diastereotropic nature of the methylene protons and chemical shift non-equivalence of protons A and B occur for the same reason discussed above for compounds **2**, **5** and **6**. The observation of two AB patterns for methylene protons with different intensities could be due to the rotation of the *n*-butyldiphenylphosphine group with respect to the Cu–P bond which would in turn create two conformers, *viz*. symmetric or unsymmetric staggered with a CuN$_3$ chromophore (say symmetric rotamer and unsymmetric rotamer). At this point it is difficult to say which rotamer is more populated, though the symmetric one is expected to be more so.

The temperature dependent ^{1}H NMR spectra of complex **4** containing PPhBu$^n_2$ down to 213 K in CDCl$_3$ are similar to

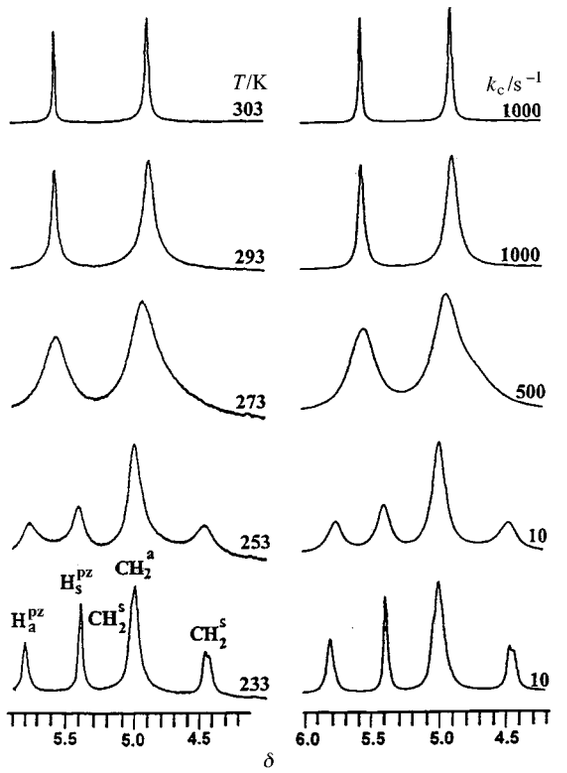
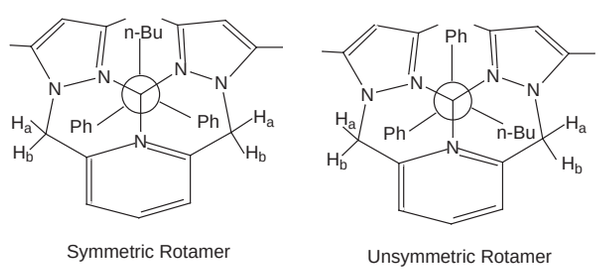
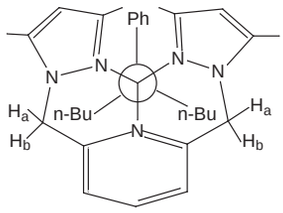


Fig. 4 Temperature variation of the ^{1}H NMR spectra of the methylene and pyrazole regions of [CuL(PPhBu$_2$)][ClO$_4$] **4** in CDCl$_3$ solvent (left) and the corresponding computer simulated spectra (right) (a = asymmetric, s = symmetric, pz = pyrazole).

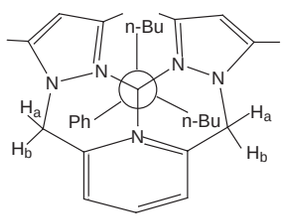


those of **5** but with a difference and hence are a bit more complicated, Fig. 4. At high temperatures (303 K) both pyrazole (CH) and methylene protons give relatively sharp signals. On lowering the temperature both signals broaden and the shape of the methylene proton signals is unsymmetric. At about 253 K both the peaks split further into broad doublets; in the case of methylene, in contrast to complexes **2** and **3**, the peak splits into unequal doublets followed first by narrowing and later resolution. Also in the case of pyrazole CH the two broad signals have unequal intensities and sharpen as the temperature is lowered, with about 50 Hz separation between them.

Excellent simulation has been achieved based on the assumption that there are two conformers with different populations for the methylene protons at low temperatures. One of the two conformers exhibits an AB quartet (due to diastereotropic methylene protons) and the other a slightly broad singlet (isotropic methylene protons). The existence of two conformers may be due to symmetric and unsymmetric arrangements of the two *n*-butyl and one phenyl group of PPhBu$_2$ with respect to the CuN$_3$ chromophore, similar to what has been discussed for compound **3** (*i.e.* symmetric and unsymmetric staggered rotamers). Though the presence of two conformers is evident, the isotropic nature of the methylene protons in one conformer is not understood clearly. It may result in almost similar chemical shifts of the two protons. The diastereotropic nature of the methylene protons and inequivalent chemical shifts from



Symmetric Rotamer



Unsymmetric Rotamer

protons A and B in one of the conformers should occur for the same reason discussed earlier for compounds **2**, **5** and **6**.

Furthermore, the ^{13}C NMR spectrum of complex **4** in $CDCl_3$ solvent at r.t. gives only one signal each for the methylene and pyrazole CH groups. However, at 233 K the latter gave two signals (δ 106.98 and 105.68) which obviously indicates the presence of two different pyrazole manifestations at lower temperatures, and only one signal even at 233 K for the methylene group which probably indicates the signals due to the two conformers appear at the same position. However, it is interesting that the ratio of the populations of the asymmetric to symmetric conformer remains at 0.8 : 1 as measured by ^1H NMR spectroscopy of the pyrazole and methylene protons.

In addition, the variable temperature ^1H NMR measurements carried out in different solvents, CD_3COCD_3, CD_2Cl_2 and $CDCl_3$, confirm the presence of both conformers though the resolutions are much better in $CDCl_3$ rather than in the other two solvents. As a result, there is little variation in the coalescence temperature and hence the thermodynamic parameters in the different solvents.[18–20]

Simulation and estimation of energy barrier and thermodynamic parameters. Line shape analyses have been carried out using a modified version of DNMR 5.[21] Input parameters for the simulations were the resonance positions of A and B, coupling constants, relaxation time T_2, populations and rate constant. The T_2 varied from 35 to 45 ms for the methylene protons. For complexes **2**, **5** and **6** only the methylene region has been simulated; for **3** and **4** both the methylene and pyrazole proton regions have been simulated. Thermodynamic parameters were estimated by employing the Arrhenius and Eyring eqns. (1) and (2). The rate constants, k_c, obtained by fitting the experimental

$$k_c = A \exp(-E_a/RT) \quad (1)$$

$$k_c = (kT/h) \exp(-\Delta H^{\ddagger}/RT) \exp(\Delta S^{\ddagger}/R) \quad (2)$$

data were used to construct an Arrhenius plot of ln k_c *vs.* $1/T$ and a least squares analysis of the data gave the energy barrier, E_a. Similarly, the thermodynamic parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were obtained from least squares analysis of the data from an Eyring plot of $\ln(k_c/T)$ *vs.* $1/T$. The free energy of activation ($\Delta G^{\ddagger}$) at the coalescence point was calculated from eqn. (3)

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T_c \Delta S^{\ddagger} \quad (3)$$

where T_c is the coalescence temperature. The results of the least squares analysis are given in Table 4. Though no quantitative comparison of thermodynamic parameters can be made, a gross look at the derived parameters shows that they are comparable to such data obtained for similar compounds.[20] The increase in activation barrier energy in the order **4** < **3** < **2** is understandable since the replacement of phenyl by Bu^n should facilitate the Cu–P free rotation. As expected this energy for **6** is much less than that for **2** because of the absence of a methyl group in the former. Such specific trends are noticeable for the enthalpy and energy of activation. However, what is puzzling is the entropy part, though such variations and lack of trends have been reported earlier.[20,34]

Table 4 Estimated energy barriers and thermodynamic parameters for methylene groups of complexes **2**–**6**

Compound	ΔE_a [a]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	$\Delta G^{\ddagger}$ [a]
2 $[CuL(PPh_3)]^+$	76.43	73.93	55.44	57.41
3 $[CuL(PPh_2Bu)]^+$	53.17	50.64	−22.27	57.27
4 $[CuL(PPhBu_2)]^+$	44.51	42.35	−36.97	52.85
5 $[LCu(PPh_2CH_2CH_2PPh_2)CuL]^{2+}$	61.34	59.04	6.30	60.92
6 $[CuL'(PPh_3)]^+$	54.95	52.53	−14.99	57.00

[a] In kJ mol^{-1}. [b] In J K^{-1} mol^{-1}.

Acknowledgements

One of the authors (P. M.) thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India for a fellowship. The work was financially supported by two projects: one by the Department of Science and Technology, Government of India, New Delhi (SP/S1/47/90) and the other by the CSIR, both awarded to P. T. M.

References

1 K. D. Karlin and J. Tyeklsr (Editors), *Bioinorganic Chemistry of Copper*, Chapman & Hall, New York, 1993.
2 K. D. Karlin, R. W. Cruse, M. S. Haka and Y. Gultneh, *Inorg. Chim. Acta.*, 1986, **125**, L43.
3 K. D. Karlin, M. S. Haka, R. W. Cruse, G. J. Meyer, A. Faroog, Y. Gultneh, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1988, **110**, 1196.
4 K. D. Karlin, R. W. Cruse, Y. Gultneh, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1984, **106**, 3372.
5 N. J. Blackburn, R. W. Strange, A. Farooq, M. S. Haka and K. D. Karlin, *J. Am. Chem. Soc.*, 1988, **110**, 4263.
6 L. Casella, O. Carugo, M. Gullotti, S. Garofani and P. Zanello, *Inorg. Chem.*, 1993, **32**, 2056.
7 N. Kitajima and Y. Moro-oka, *Chem. Rev.*, 1994, **94**, 737.
8 N. Kitajima, K. Fujisawa and Y. Moro-oka, *J. Am. Chem. Soc.*, 1989, **111**, 8975.
9 E. I. Solomon, *Copper Proteins*, ed. T. G. Spiro, Wiley, New York, 1981; vol.3, pp. 41–108.
10 P. Manikandan, B. Varghese and P. T. Manoharan, *J. Chem. Soc., Dalton Trans.*, 1996, 371.
11 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens and S. J. Lippard, *Inorg. Chem.*, 1976, **15**, 1155.
12 B. Mohr, E. E. Brooks, N. Rath and E. Deutsch, *Inorg. Chem.*, 1991, **30**, 4541.
13 M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1065.
14 E. L. Muetterties, *Inorg. Chem.*, 1965, 4, 769.
15 S. J. Berners-Price, C. K. Mirabelii, R. K. Johnson, L. F. Faucette, F. L. McCabe and P. J. Sadler, *Inorg. Chem.*, 1987, **26**, 3383.
16 R. K. Johnson, C. K. Mirabelli, L. F. Faucette, F. L. McCabe, B. M. Sutton, D. L. Bryan, G. R. Girard and D. T. Hill, *Proc. Am. Assoc. Cancer Res.*, 1985, **26**, 254.
17 J. Diez, M. P. Gamasca, J. Gimeno, A. Tiripichio and M. T. Camellini, *J. Chem. Soc., Dalton Trans.*, 1987, 1275.
18 J. A. Goodwin, L. J. Wilson, D. M. Stanbury and R. A. Scott, *Inorg. Chem.*, 1989, **28**, 42.
19 D. K. Coggin, J. A. Gonzalez, A. M. Kook, D. M. Stanbury and L. J. Wilson, *Inorg. Chem.*, 1991, **30**, 1115.
20 D. K. Coggin, J. A. González, A. M. Kook, C. Bergman, T. D. Brennan, W. R. Scheidt, D. M. Stanbury and L. J. Wilson, *Inorg. Chem.*, 1991, **30**, 1125.
21 G. Binsch, *Dynamic Nuclear Magnetic Resonance Spectroscopy*, eds. L. M. Jackaman and F. A. Cotton, Academic Press, New York, 1975, p. 45.
22 J. D. Salter, V. Šik, S. A. Williams and T. Adatia, *J. Chem. Soc., Dalton Trans.*, 1996, 643.
23 S. Gutoswky and Saiker, *J. Chem. Phys.*, 1953, **21**, 1688.
24 H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 219.
25 G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 411.
26 R. S. Drago, *Physical Methods in Chemistry*, W. B. Saunders Company, London, 1977.
27 G. J. Hawkins and J. A. Palmer, *Coord. Chem. Rev.*, 1982, **44**, 1.
28 D. F. Shriver and M. A. Drezdzon, *Manipulation of air sensitive compounds*, 2nd edn., Wiley-Interscience, New York, 1986.

29 D. D. Perrin and W. L. F. Armerego, *Purification of laboratory chemicals*, 3rd edn, Pergamon, New York, 1988.
30 S. Mahapatra, R. N. Gupta and N. Mukherjee, *J. Chem. Soc., Dalton Trans.*, 1991, 2911.
31 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
32 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.
33 L. Zsolnai and H. Pritzkowm, ORTEP program for personal computer, University of Heidelberg, 1994.
34 R. H. Holm, *Dynamic Nuclear Magnetic Resonance Spectroscopy*, eds. L. M. Jackaman and F. A. Cotton, Academic Press, New York, 1975, p. 317.

Paper 8/01622D