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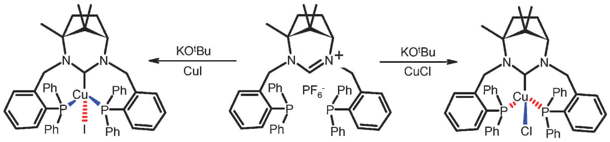

Monovalent chiral-at-copper complexes: halide-controlled diastereoselectivity Q1

Paul D. Newman,* Kingsley J. Cavell* and Benson M. Kariuki

A tridentate diphosphino-NHC ligand coordinates to CuCl to give the chiral-at-copper complex with the S_{Cu} stereochemistry. The same reaction with CuI leads to the diastereomer with the R_{Cu} configuration as the major species in solution.

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Monovalent chiral-at-copper complexes: halide-controlled diastereoselectivity†

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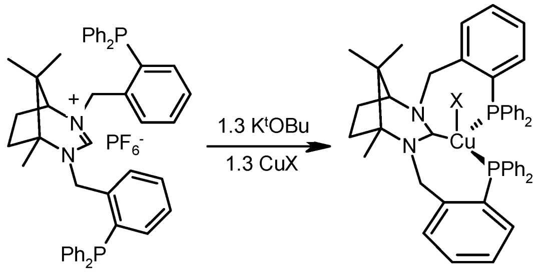
An unusual example of diastereoselectivity has been observed in Cu(κ^3-*P*,*C*,*P*′-1)X complexes where 1 is an asymmetric tridentate ligand containing a bicyclic NHC framework and X is a halide. When X is Cl^-, the S_{Cu} isomer is formed selectively whereas when X = I^- the R_{Cu} diastereomer is preferred.

The extensive literature on stereoselective transformations catalysed by asymmetric metal complexes is dominated by examples where the stereogenic centre(s) resides on the ligand.[1] As such, the chiral source is often remote from the reactive centre (the metal) which might fundamentally restrict effective transfer of chiral information. Conceptually, more efficient 'chirality transfer' should be feasible when the metal itself is a stereogenic centre.[2] These so-called chiral-at-metal complexes are finding increasing use in catalytic asymmetric processes[3] and in materials applications (*e.g.* chiroptical switches, non-linear optics)[4] as the drive to understand the effects of metal-based asymmetry continues. The vast majority of chiral-at-metal complexes are octahedral[2a,5] or 'pseudo-tetrahedral' as in the half-sandwich class of complex.[2a,6] Tetrahedral metal complexes tend to be configurationally labile and consequently examples of their employment in asymmetric catalysis are rare.[7] Monovalent copper typifies this class of complex where rapid ligand exchange leads to facile racemisation/epimerisation and thus examples of chiral-at-metal Cu(I) complexes are extremely rare.[8] One way of trying to restrict this epimerisation is through the use of unsymmetrical, chiral multidentate ligands where appropriate ligand design would enable selective formation of a single diastereoisomer with a specific configuration at the metal. We have been exploring heterodonor derivatives of fused-ring NHCs derived from camphor and have prepared the pro-ligand **1·HPF**^{6} in order to study the coordination chemistry of the diphosphino-carbene, **1**, obtained upon deprotonation of **1·HPF**^{6}. During these studies we discovered some unusual properties of the copper(I) systems Cu(κ^3-*P*,*C*,*P*′-1)X as detailed in this communication.

The desired Cu(κ^3-*P*,*C*,*P*′-1)X complexes were prepared as shown in Scheme 1 and isolated as cream solids in yields of 72, 68 and 89%, respectively. The halides showed variable solubility in toluene, with the iodo complex being more soluble than the bromo while the chloride complex was essentially insoluble. **2c** was crystallised from toluene as colourless blocks suitable for structure determination by single-crystal X-ray techniques.

Fig. 1 shows the two independent molecules in the unit cell of **2c**. Each of the pseudo-tetrahedral copper centres is coordinated by the two phosphines and the central carbon of the κ^3-**1** ligand with the coordination sphere being completed by an iodide. The two molecules are a diastereomeric pair and, as the two phosphorus donors are inequivalent, the copper atoms are stereogenic with opposing absolute configurations at the Cu(I) centre. For the upper structure in Fig. 1 the CIP priority of P2 is higher than that of P4 and the complex has the *R* configuration at the metal (R_{Cu}). Similar application of CIP rules defines the complex shown in the lower part of Fig. 1 as the S_{Cu} isomer. The Cu-P bond lengths are comparable in both structures (average = 2.299(8) Å) and similar to the average values of 2.342 Å, 2.295 Å and 2.318(2) Å reported for the Cu-P bonds in the related compounds $Cu(PPh_3)_3I$,[9] Cu(L)I (where L is a tripodal triphosphine) and $[Cu_2(\kappa^2\text{-dppe})_2(\mu\text{-dppe})I_2]$ (the value quoted is that for the bidentate dppe).[10] Although the Cu-C bond lengths are not as accurate as we would like, there is a clear disparity between the two molecules with the R_{Cu} complex having the longer bond at 2.09(2) Å compared to 1.95(2) Å in the S_{Cu} complex; these values are longer than those reported for linear *bis*(5-NHC) systems.[11] As



1·HPF$_6$

2a: X = Cl
2b: X = Br
2c: X = I

Scheme 1 Preparation of the Cu(I) complexes.

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† Electronic supplementary information (ESI) available: Experimental procedures and crystallographic data. CCDC 879396. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33036a

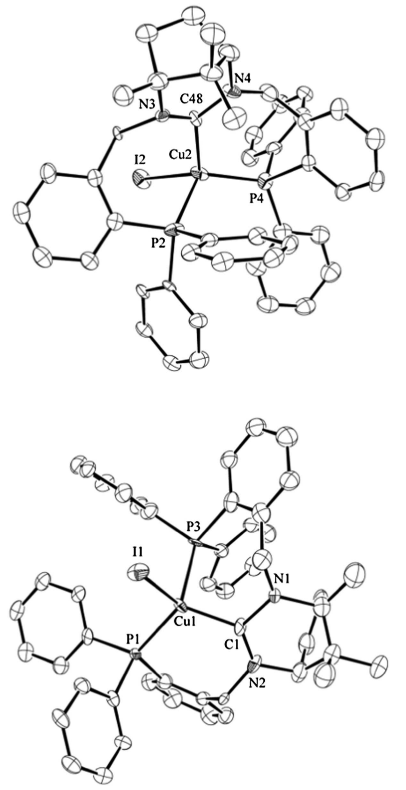

Fig. 1 Ortep views of the two independent molecules of **2c**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles(°) for **2c**: Cu1-P1 2.276(7), Cu1-P3 2.310(6), Cu1-I1 2.705(4), Cu1-C1 1.95(2), Cu2-P2 2.321(8) Cu2-P4 2.290(8), Cu2-I2 2.687(4), Cu2-C48 2.09(2), P1-Cu1-P3 120.1(3), I1-Cu1-P1 107.4(2), I1-Cu1-P3 100.2(2), I1-Cu1-C1 119.7(6), P1-Cu1-C1 112.3(6), P3-Cu1-C1 97.1(8), P2-Cu2-P4 118.9(3), I2-Cu2-P2 100.5(2), I2-Cu2-P4 106.5(2), I2-Cu2-C48 117.9(6), P2-Cu2-C48 98.5(6), P4-Cu2-C48 114.2(6), N1-C1-N2 113.8(19), N3-C48-N4 117(2).

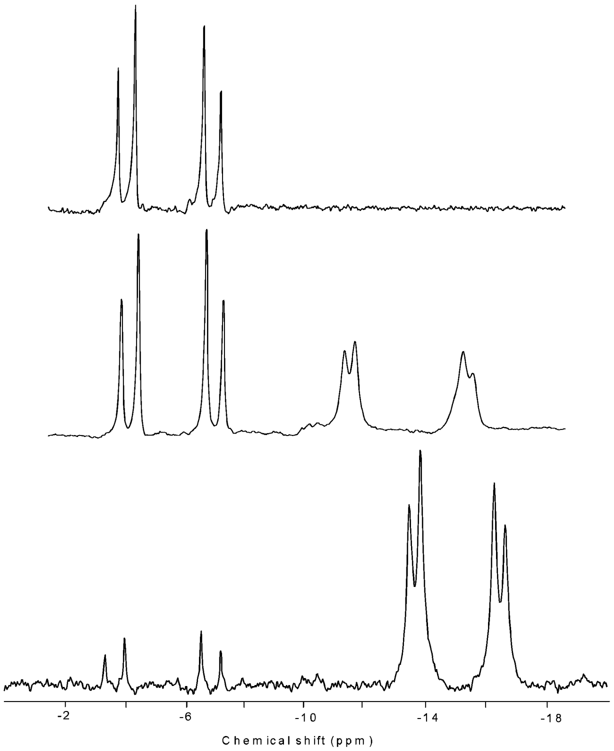

Fig. 2 $^{31}P\{^1H\}$ NMR spectra of **2a** (top), **2b** (middle) and **2c** (bottom) recorded in $CDCl_3$ at 223 K.

expected for a complex with two 7-membered chelates the coordination geometry is distorted with bond angles ranging from ~97° to ~120°. The coordination reported here is quite distinct from a related $PC_{NHC}P$ ligand which shows an unusual binding mode at Cu(I) with the NCN carbon bridging two metal centres[12] (a motif that is more common for monovalent silver).[13]

Although the solid-state structure of **2c** is a 1 : 1 mixture of diastereomers, a clear preference for one isomer is evident in solution as the room temperature $^{31}P\{^1H\}$ NMR spectrum consists of a single, albeit broadened, AB pattern at $\delta_P = -13.9$ and -16.0 ppm with a $^2J_{P\text{-}P}$ value of 40 Hz. When the spectrum was recorded at 223 K (Fig. 2), two AB patterns assignable to the two diastereomers of **2c** were observed in an approximately 1 : 3 ratio with the minor set at -3.6 and -6.9 ppm having a $^2J_{P\text{-}P}$ value of 77 Hz compared to the smaller value of 45 Hz for the major set at -13.6 and -16.4 ppm. In addition there are two small, broad resonances around -10 and -19 ppm which may indicate the presence of species containing bidentate forms of **1**. The resonances for the major isomer remain somewhat broadened even at 223 K indicating a degree of fluxionality. The origin of this broadening is not known but it could result from conformational interconversion;[14] Cu-P bond breaking is not implied at temperatures below 298 K as the $^2J_{P\text{-}P}$ coupling is always observable. Signal broadening is also evident in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2c** where all resonances are affected at RT. The ^1H NMR recorded at 223 K clearly shows the presence of the two isomers in an approximately 3 : 1 ratio as determined by integration of appropriate signals most notably the singlets for the methyl groups. The major isomer at all temperatures is characterised by a diagnostic CH_3 resonance to high-field of TMS ($\delta_H = -0.67$ ppm) in the ^1H NMR spectrum. Unfortunately the broadening removes any fine structure from the resonance assigned to the carbene carbon in the $^{13}C\{^1H\}$ NMR spectrum which is seen as a broad peak at 213.3 ppm, a value that compares to $\delta_C = 209.2$ ppm in [Cu(7-NHC^{Mes})Cl] and 208.7 ppm in [Cu(7-NHC^{Mes})I]).[15b] The AB pattern for the minor isomer of **2c** persists up to 265 K whereupon it starts to become broad. At 273 K there is only a very broad resonance seen at ~ -6 ppm which is lost altogether as the temperature is raised further.

In contrast to **2c**, only a single diastereomer is observed for **2a** at all accessible temperatures in $CDCl_3$ with an invariant $^{31}P\{^1H\}$ NMR spectrum consisting of a simple, unbroadened AB set of doublets at $\delta_P = -3.2$ and -5.8 ppm ($^2J_{P\text{-}P} = 80$ Hz). The ^1H NMR spectrum is not complicated by the presence of the other diastereomer and four doublets are seen for the necessarily inequivalent benzylic methylene hydrogens and three singlets with typical chemical shifts for the three methyl groups. Only ten aliphatic carbon resonances are seen in the $^{13}C\{^1H\}$ NMR spectrum and the single NCN carbon appears as a triplet at δ_C 200.2 ppm with a $^2J_{C\text{-}P}$ coupling constant of 31.5 Hz. The position of this resonance is close to

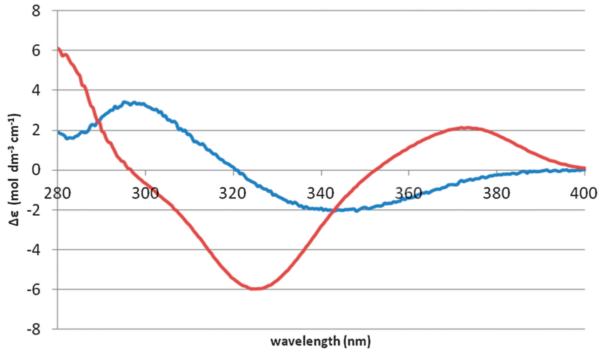

Fig. 3 ECD spectra of **2a** (—) and **2c** (—) recorded in $CHCl_3$ at RT.

that seen for related complexes of monodentate 6-NHCs (δ_C 196.7 and 202.4 ppm)[15] but is slightly upfield that of a monodentate 7-NHC derivative.[13b]

The spectroscopic differences highlighted above indicate that the single isomer observed for **2a** at all temperatures is only seen as a minor species for **2c** at temperatures below 265 K and the thermodynamically favoured isomer is different for **2a** and **2c**. It also suggests that **2a** is configurationally stable whereas **2c** undergoes exchange quite readily which enables its crystallisation as a racemic-at-metal solid. It is noteworthy that solvent-induced chirality-switching in Cu(I) systems containing asymmetric ligands with hydrogen-bond donors/acceptors has been noted previously,[16] but the factors controlling stereoselection in these systems are quite distinct from the present complexes. Indeed the halide-controlled diastereoselection seen here is surprising and the underlying reasons for it remain unclear. In order to attempt an explanation it is essential to identify which isomer is preferred by each of the complexes **2a** and **2c**. This can be answered upon inspection of the ^{1}H NMR spectra of **2a** and **2c**. As mentioned above, the major isomer of **2c** has a methyl resonance upfield of TMS (broad peak at −0.56 ppm in $CDCl_3$ at RT and a sharp peak at −0.67 ppm at −60 °C in d_8-THF) which is not present in the ^{1}H NMR spectrum of **2a** (the highest field methyl group resonates at $\delta_H = 0.34$ ppm). The upfield position of this resonance indicates a location over one or more of the aromatic rings; this is only possible in the R_{Cu} isomer where the methyl group that is '*endo*' with respect to the NCN link is in close contact (3.619 Å from the carbon atom of the methyl to the centroid of the ring) with one of the phenyl substituents on a phosphorus donor (Fig. 1). This defines the major isomer of **2c** as the R_{Cu} diastereomer and hence **2a** is assigned the S_{Cu} configuration (there are no close contacts between the aromatic rings and the methyls as is evident from the lower structure in Fig. 1).

The ECD spectra of **2a** and **2c** are shown in Fig. 3. Although the origin of the bands observed in the spectral region highlighted in Fig. 3 are not known for certain, the low energy transitions in the 340–400 nm range are likely to be of a MLCT nature. There are clear distinctions between the ECD spectra of the two diastereomers with **2a** giving a positive absorption around 275 nm that is absent from the spectrum of **2c**. There is a corresponding peak in the electronic spectrum of **2a** at 370 nm (ε = 470 mol dm^{-3} cm^{-1}) before a large absorption band starts at around 325 nm. The electronic spectrum of **2c** does not show this small initial band as the large absorption starts at higher wavelength (~ 375 nm).

The observation of an inverse diastereoselectivity for **2a** and **2c** led us to examine the corresponding bromo complex **2b** with the expectation that neither isomer would be favoured in this complex. Observation of the ^{31}P{^{1}H} NMR spectrum of **2b** at RT was inconclusive as extensive broadening was evident but examination of the ^{31}P{^{1}H} NMR spectrum at 223 K showed the expected two AB sets of resonances in a roughly 1 : 1 ratio ($\delta_P = -3.2, -6.5$ ppm with $^2J_{P\text{-}P} = 80$ Hz and $\delta_P = -11.7, -16.3$ ppm with $^2J_{P\text{-}P} = 48$ Hz (Fig. 2). Upon raising the temperature the behaviour of **2b** mimics that already discussed for **2c** although the two separate ^{31}P{^{1}H} resonances for the S_{Cu} isomer did not coalesce until 298 K.

An unusual diastereoselection has been observed in [Cu(κ^3-*P*,*C*,*P*-**1**)X] with the R_{Cu} isomer being preferred when X = I^- and S_{Cu} when X = Cl^-. Diastereomer distributions in non-halo Cu(I) complexes of κ^3-**1** are currently being investigated as is the extension to other tetrahedral or pseudo-tetrahedral d^{10} systems such as Pt(0) and Zn(II).

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