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Structural Diversity in Pyridine-*N*-Functionalized Carbene Copper(I) Complexes

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The use of the versatile pyridine *N*-functionalized carbene ligands has allowed the isolation and structural characterization of copper(I) imidazol-2-ylidene complexes of the type {[(3-R)(1-L)imidazol-2-ylidene]CuBr}, where L = 2-picolyl, R = 2,4,6-trimethylphenyl (mesityl), 2,6-$Pr^i_2C_6H_3$; L = 2-pyridyl, R = 2,6-$Pr^i_2C_6H_3$. They were prepared by interaction of the corresponding imidazolium bromides with Cu_2O in chlorinated solvents in the presence of molecular sieves. In the solid state the 2-picolyl derivatives crystallize as dimers or polymers depending on the crystallization conditions, while the 2-pyridyl derivative crystallizes as monomer.

Introduction

There is growing interest in the use of "Arduengo-type" carbenes as ligands on transition metals.[1] Their electronic characteristics are comparable to the well-studied phosphines.[2] The thermodynamic stability of the resulting complexes and the vast opportunities for ligand design promise the discovery of new metal compounds with applications in catalytic,[3] supramolecular, organometallic, and materials chemistry.[4] The synthesis of mixed donor carbene complexes of palladium and silver has been the topic of recent reports by us[5] and others.[6] We focused on *N*-functionalized imidazol-2-ylidene complexes carrying bulky aliphatic (*tert*-butyl) or aromatic (mesityl and 2,6-diisopropylphenyl) substituents on the carbene end, reasoning that this design would show improved catalyst stability and selectivity due to catalytic site isolation. The structural diversity observed with the silver complexes[5b] encouraged us to explore the chemistry of analogous copper compounds. The only previously reported[7] copper(I) imidazol-2-ylidene complex is the homoleptic $[Cu(1,3\text{-dimesitylimidazol-2-ylidene})_2]^+CF_3SO_3^-$, prepared by the interaction of free 1,3-(dimesityl)imidazol-2-ylidene with $[Cu(CF_3SO_3)\cdot 0.5C_6H_6]$ in thf; it was characterized by spectroscopic and analytical methods. Structural data are only available for the copper(I) thiazol-2-ylidene chloride.[8] The scarcity of complexes of this type is surprising, in view of results from a recent theoretical study[9] by Frenking et al., who estimated the copper(I)−carbon bond dissociation energy in imidazol-2-ylidene complexes at 76 kcal/mol, higher than the silver analogues by ca. 15 kcal/mol.

Results and Discussion

Attempts to prepare pyridine *N*-functionalized copper(I) carbene complexes by interaction of the in situ generated carbene with a variety of copper(I) starting materials bearing labile ligands had limited success. However, the corresponding imidazolium salts can be deprotonated by the basic Cu_2O (Scheme 1).

The reaction proceeds best in chlorinated solvents. Furthermore, we found that it can be accelerated at higher temperatures and in the presence of freshly activated molecular sieves (4 Å). Under these conditions

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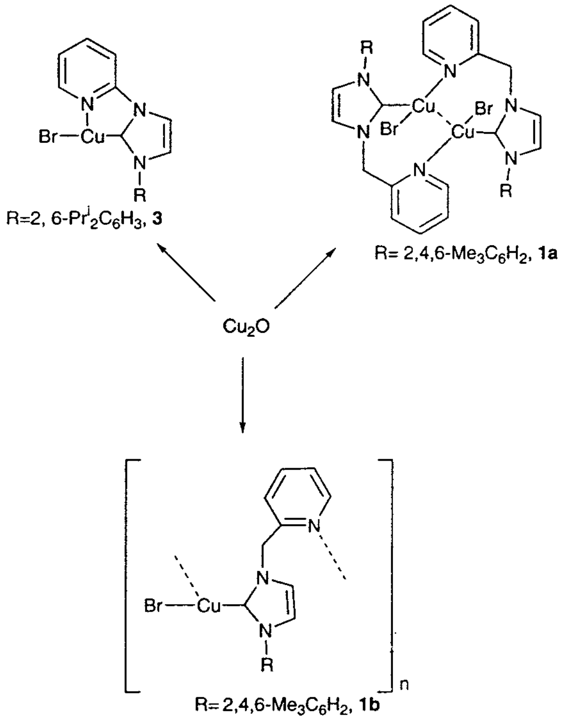
Scheme 1



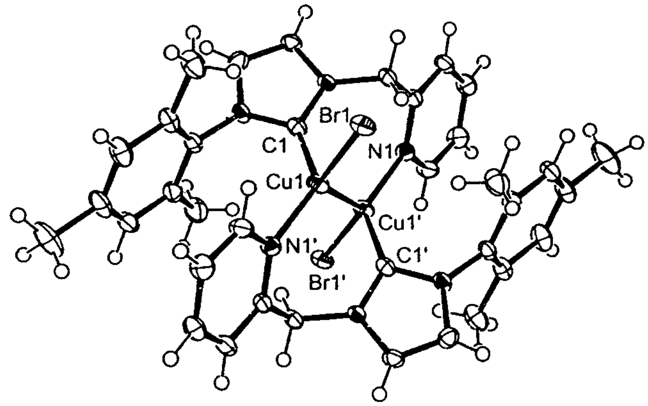


Figure 1. Molecular structure of the dimer **1a**.

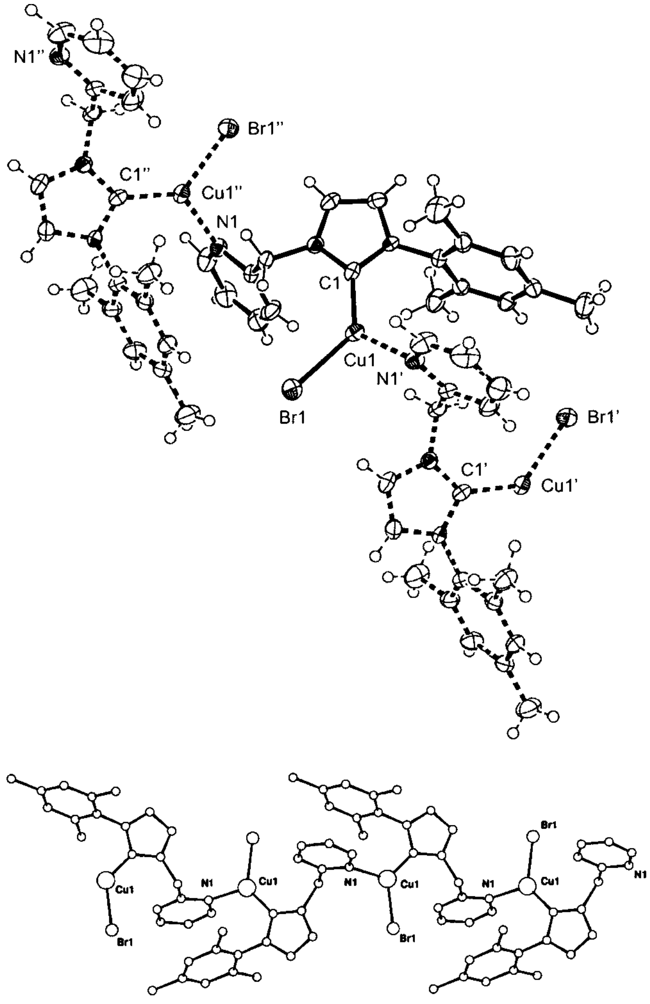


Figure 2. Two views of the structure of the polymer **1b**.

good, reproducible yields of **1**, **2**, and **3** can be obtained. The products are isolated as pale yellow or white, moderately air-sensitive powders. In solution in aprotic solvents they are more sensitive to air. The product stoichiometries were deduced by analytical methods. The ^{1}H NMR spectra are less informative; broad peaks were observed for **3** with minimal coordination shifts. Repeated recrystallizations and variable-temperature studies from 293 to 203 K in CD_2Cl_2 did not result in any improvements, although the band shapes changed noticeably at lower temperatures. We believe that this is a manifestation of nonrigidity in solution. An equilibrium involving mono- and bis(carbene) copper(I) species is another factor that could be contributing to broadening. The ^{1}H NMR spectrum of **2** shows two well-separated broad doublets at 1.05 and 1.20 ppm assignable to the diastereotopic methyls of the isopropyl groups; the protons of the secondary isopropyl carbon, the bridging CH_2, and the aromatic ring give rise to broad unresolved peaks. Finally, the ^{1}H NMR spectrum of **1** shows very broad peaks assignable to the pyridine ring and CH_2 bridge protons and broad peaks due to the mesityl methyls and the carbene ring protons. For all carbene complexes, the carbene carbons could not be observed in the ^{13}C NMR spectrum, even at temperatures above or below ambient or when using long pulse delays.

Single crystals of **1** can be grown either by slow cooling of dichloromethane/ether (**1a**) or from concentrated $CDCl_3$ solutions (**1b**). The molecules are shown in Figures 1 and 2, respectively; important bond lengths and angles and crystallographic data for all the structurally characterized complexes are given in Tables 1 and 2, respectively.

Compound **1a** crystallizes as a centrosymmetric dimer with two ligands bridging the two copper centers. The geometry around the copper is best described as a distorted trigonal pyramid with a bromine occupying the apical position. The angles between the carbene–pyridine and the carbene–phenyl rings are 23.2° and 90.2°, respectively. The Cu···Cu distance of 2.655 Å gives evidence for a weak metal–metal interaction. The Cu–C bond distance of 1.931 Å is within the range characteristic for Cu–C single bonds.

Compound **1b** was crystallized from $CDCl_3$, giving the organometallic/coordination polymer shown in Figure 2. In this case, the copper is found in a trigonal environment with the N(1′), C(1), Br(1), and Cu(1) being on the same plane. The bond distances are comparable to those in the structure of **1a**. The angle between the

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1a, 1b, and 3

1a		1b		3	
Br(1)−Cu(1)	2.5147(4)	Br(1)−Cu(1)	2.3758(7)	C(5)−N(1)	1.330(8)
Cu(1)−C(1)	1.931(2)	Cu(1)−C(1)	1.914(4)	C(5)−N(2)	1.429(8)
Cu(1)−N(1)#1	2.0299(18)	Cu(1)−N(1)#1	2.044(3)	C(6)−C(7)	1.337(9)
Cu(1)−Cu(1)#1	2.6449(6)	N(3)−C(1)	1.351(5)	C(6)−N(2)	1.379(8)
N(2)−C(1)	1.359(3)	N(3)−C(9)	1.396(5)	C(7)−N(3)	1.398(8)
N(2)−C(3)	1.380(3)	C(9)−C(8)	1.328(7)	C(8)−N(3)	1.356(7)
N(3)−C(1)	1.368(3)	C(1)−N(2)	1.356(5)	C(8)−N(2)	1.375(7)
N(3)−C(2)	1.385(3)	N(2)−C(8)	1.382(6)	C(8)−Cu(1)	1.880(6)
		N(1)−Cu(1)#2	2.044(3)	N(1)−Cu(1)	2.454(5)
				Cu(1)−Br(1)	2.2076(10)
C(1)−Cu(1)−N(1)#1	133.88(8)	C(1)−Cu(1)−N(1)#1	125.24(16)	N(1)−C(5)−N(2)	114.4(5)
C(1)−Cu(1)−Br(1)	106.14(7)	C(1)−Cu(1)−Br(1)	130.73(13)	C(7)−C(6)−N(2)	107.1(5)
N(1)#1−Cu(1)−Br(1)	98.08(5)	N(1)#1−Cu(1)−Br(1)	103.43(10)	C(6)−C(7)−N(3)	106.5(5)
C(1)−Cu(1)−Cu(1)#1	70.26(7)	C(1)−N(3)−C(9)	111.2(4)	N(3)−C(8)−N(2)	103.1(5)
N(1)#1−Cu(1)−Cu(1)#1	121.50(6)	C(8)−C(9)−N(3)	106.7(4)	N(3)−C(8)−Cu(1)	136.2(4)
Br(1)−Cu(1)−Cu(1)#1	128.777(17)	N(3)−C(1)−N(2)	103.6(4)	N(2)−C(8)−Cu(1)	119.6(4)
C(1)−N(2)−C(3)	112.05(18)	N(3)−C(1)−Cu(1)	124.2(3)	C(5)−N(1)−Cu(1)	106.1(3)
C(1)−N(3)−C(2)	111.66(19)	N(2)−C(1)−Cu(1)	132.0(3)	C(8)−N(2)−C(6)	111.7(5)
C(3)−C(2)−N(3)	106.4(2)	C(1)−N(2)−C(8)	111.8(4)	C(8)−N(2)−C(5)	121.4(5)
C(2)−C(3)−N(2)	106.7(2)	C(9)−C(8)−N(2)	106.7(4)	C(8)−N(3)−C(7)	111.7(5)
N(2)−C(1)−N(3)	103.15(18)				
N(2)−C(1)−Cu(1)	130.92(16)				
N(3)−C(1)−Cu(1)	122.34(15)				

Symmetry transformations used to generate equivalent atoms: #1 $-x+1,-y+2,-z+1$

Symmetry transformations used to generate equivalent atoms: #1 $-x,-y,-z$ #2 $-x,-y-1,-z$

Table 2. Summary of Crystallographic Data for 1a, 1b, and 3

	1a	1b	3
chemical formula	$C_{38}H_{42}Br_2Cl_4Cu_2N_6$	$C_{20}H_{19}D_2Br_1C_{l6}Cu_1N_3$	$C_{20}H_{23}N_3BrCu$
fw	1011.48	661.56	448.86
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	8.4260(1)	13.1826(2)	11.4666(3)
b/Å	11.0509(1)	12.8268(2)	12.4772(3)
c/Å	11.4536(1)	16.4122(3)	14.1522(3)
α/deg	85.015(1)		
β/deg	84.737(1)	105.964(1)	99.7489(13)
γ/deg	75.611(1)		
V/Å^3	1026.44(2)	2668.12(8)	1995.53(8)
Z	2	4	4
T/K	150(2)	150(2)	150(2)
μ/mm^{-1}	3.279	2.931	3.104
no. of data collected	17262	26717	10430
no. of unique data	4186	7647	2853
$R_{\rm int}$	0.0584	0.0926	0.0457
final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.0295	0.0560	0.0606
final $R(F^2)$ for all data	0.0756	0.1528	0.1898

phenyl and carbene planes is 81.0° and between the coordination and carbene planes is 11.8°. The polymer chain has a "stretched-helical" conformation. The mesityl rings orient themselves almost parallel to (interplanar angle 19.1°) and above the pyridine rings of the adjacent ligand. The separation between these two rings (3.713 Å) is shorter than the corresponding distance observed in **1a** (3.875 Å). Crystal packing is generally determined by a great number of factors with van der Waals forces being dominant. Because of the close similarity of the corresponding metrical data in **1a** and **1b**, we speculate that the selective crystallization of the polymer from $CDCl_3$ is due to the higher solubility and concentration of monomer and/or dimers in this solvent, allowing chain growth by coordination. Crystallization from dilute solutions in which the monomer and/or oligomers are expected to have limited solubility favors the formation of dimers. Furthermore, we think that the conformational flexibility of the picolyl-functionalized carbene ligand in **1**, in combination with its larger bite angle (when compared with the pyridine-functionalized analogues), is also responsible for the results described here. The degree of association of **1** in solution is not known, but the existence of nonrigid structures was observed by NMR as mentioned earlier.

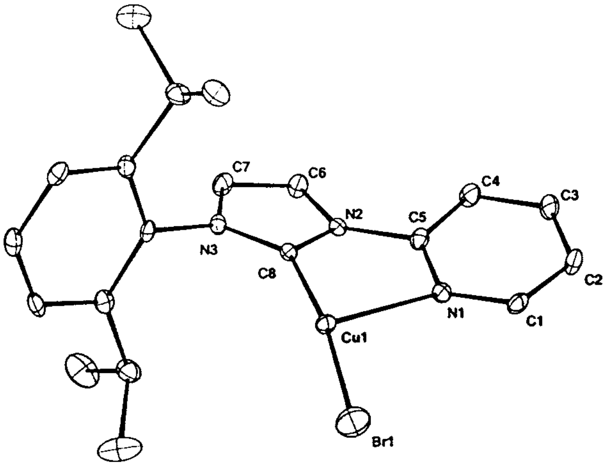


Figure 3. The molecular structure of **3**.

Compound **3** crystallizes as a monomer with copper in a "T-shaped" coordination geometry; the copper is displaced perpendicularly from the coordination plane defined by C(8), N(1), and Br(1) by 0.1359 Å. The bite angle of the ligand, as measured by the C(8)−Cu(1)−N(1) at 76.5°, is in the range observed for chelates of the bipy family (75.5−81.1°). The five-membered chelate ring is essentially planar. The angles between the coordination plane and the carbene- and pyridine-planes are 13.8° and 10.6°, respectively. The angle between the phenyl and the carbene rings is 84.2°. The Cu(1)−C(8) distance of 1.880 Å is comparable to that found in the thiazol-2-ylidene complexes and longer than the theoretically predicted value (1.848 Å); however, it is shorter than other known copper(I)−carbon bonds (1.90−1.96 Å).[10] The Cu−C bond distance in **3** is shorter than the ones observed in **1a** and **1b**. Although the nucleophilic carbene−metal bond is considered to have only a purely σ-component (negligible metal to carbene π-back-bonding contribution),[2] it is conceivable that minor π-back-bonding in **1a** and **1b** is suppressed by the unfavorable conformation of the carbene ring relative to the coordination plane of the metal. In **3** the conformation imposed by the ligand backbone favors carbene carbon−metal π-interaction. Some metal electron density (in **1a**) is also involved in the Cu−Cu interaction. The Cu(1)−Br(1) and Cu(1)−N(1) bonds at 220.8 and 2.454 Å, respectively, are not unusual.

Compound **3** is the first example of a structurally characterized monomeric imidazol-2-ylidene copper complex. The presence of the bulky 2,6-$Pr^i_2C_6H_3$ group on the carbene moiety and the conformational rigidity of the five-membered chelate ring formed prevent association to oligomeric or polymeric structures.

Conclusions

We have shown that pyridine-*N*-functionalized Cu(I) carbene complexes can be easily prepared, and we have structurally characterized the first example of the monomeric Cu(I) imidazol-2-ylidene complex. The Cu−C bond in this compound is shorter than a Cu−C single bond and comparable to the bond length observed in thiazol-2-ylidene complexes. Furthermore, by using picolyl-*N*-functionalized carbene ligands, which exhibit larger bite angles and backbone flexibility, we obtained dimeric and polymeric materials.

Experimental Section

Analyses were carried out by the University College, London, microanalytical laboratory. NMR data were recorded on Bruker AMX-300 and AM 360 spectrometers, operating at 300 and 360 MHz (^{1}H), respectively. The spectra were referenced internally using the signal from the residual protiosolvent (^{1}H) or the signals of the solvent (^{13}C). Commercial chemicals were from Acros, Aldrich, and Avocado. All solvents were dried over the appropriate drying agents and distilled under nitrogen. The *N*-functionalized imidazolium salts[5b] and Cu_2O[11] were prepared as described in the literature.

Synthesis of the Complexes. General Method. The manipulations were carried out under nitrogen. A suspension of the substituted imidazolium salt, slight excess of Cu_2O, and 4 Å molecular sieves in dichloromethane or 1,2-dichloroethane was heated at 35 or 90 °C for 3−12 h, respectively. After completion, the volatiles were removed under vacuum and the resulting solid was washed with ether and extracted into thf. Filtration of the solution and evaporation of the volatiles under vacuum produced moderately air-sensitive solids.

[3-(Mesityl)-1-(2-picolyl)imidazol-2-ylidene]cuprous Bromide, 1. This was prepared following the general method from 0.20 g (0.55 mmol) of [3-(mesityl)-1-(2-picolyl)imidazolium] bromide and 0.04 g (0.27 mmol) of Cu_2O in dichloromethane (30 cm^3) by heating at 35 °C for 12 h. The product was obtained as a moderately air-sensitive white solid in ca. 60% yield. Mp: 170−5 °C (dec). Found: C 47.12, H 4.16, N 8.77. Calcd for $(C_{18}H_{19}CuBrN_3)_2CH_2Cl_2$: C 47.96, H 4.35, N 9.07. (Slightly lower carbon analyses were obtained due to partial loss of volatile CH_2Cl_2.) X-ray quality crystals were obtained by cooling slowly a saturated dichloromethane/ether solution to −30 °C (**1a**) or from a saturated $CDCl_3$ solution (**1b**). The ^{1}H NMR spectra in $CDCl_3$ at room temperature show the following peaks: δ 2.20 [s, 6H, $C_6H_2(o\text{-}CH_3)_2(CH_3)$], 2.35 [s, 3H, $C_6H_2(CH_3)_2(p\text{-}CH_3)$], 5.2 (s, br, 2H, CH_2 bridge), 6.2 and 6.5 (two doublets, 2H, imidazol-2-ylidene protons), 7.0 [s, 2H, $C_6H_2(o\text{-}CH_3)_2(CH_3)$], 7.3, 7.7, and 8.6 (very broad 4H pyridine ring protons).

[3-(2,6-Diisopropylphenyl)-1-(2-picolyl)imidazol-2-ylidene]cuprous Bromide, 2. It was prepared as **1a** from 0.20 g (0.48 mmol) of [3-(2,6-diisopropylphenyl)-1-(2-picolyl)-imidazolium] bromide and 0.05 g (0.4 mmol) of Cu_2O in 1,2-dichloroethane (30 cm^3) by heating at 90 °C for 3 h. Yield: 60%. Mp: 180−5 °C (dec). Found: C 54.49, H 5.66, N 8.66. Calcd for $C_{21}H_{25}CuBrN_3$: C 54.49, H 5.44, N 9.08. The ^{1}H spectra in CD_2Cl_2 at room temperature show broad peaks at δ 1.05 and 1.2 [broad doublets, 12H, $(CH_3)_2CH$], 2.8 [partially resolved septet, 2H, $(CH_3)_2CH$)], 5.4 (broad singlet, bridging CH_2), 7.3, 7.4, and 8.0 (6H, aromatic).

[3-(2,6-Diisopropylphenyl)-1-(2-pyridyl)imidazol-2-ylidene]cuprous Bromide, 3. It was prepared as **1a** from 0.10 g (0.26 mmol) of [3-(2,6-diisopropylphenyl)-1-(2-pyridyl)-imidazolium] bromide and 0.04 g (0.26 mmol) of Cu_2O in dichloromethane (20 cm^3) by heating at 35 °C for 12 h. A white moderately air-sensitive powder formed. Yield: 65%. X-ray quality crystals were obtained by layering a saturated $CDCl_3$ solution with ether. Mp: 170 °C. Found: C 53.73, H 5.48, N 8.99. Cald for $C_{20}H_{23}BrN_3$: C 53.52, H 5.16, N 9.36. The ^{1}H spectra in CD_2Cl_2 at room temperature show broad peaks at δ1.1 [12H, $(CH_3)_2CH$], 2.8 [2H, $(CH_3)_2CH$)], 7.3, 7.4, and 8.0 (6H, aromatic).

X-ray Crystallography. Cell dimensions and intensity data were collected at 150 K using a Nonius KappaCCD area detector diffractometer mounted at the window of a FR591 rotating anode generator operating at 50 kV, 90 mA, with a molybdenum target [λ(Mo Kα) = 0.71069 Å]. The crystal-to-detector distance was 30 mm, and ϕ and ω scans with a κ offset were employed to access a complete set of unique reflections with a suitable redundancy. Data collection and processing were carried out using dirAx,[12] DENZO,[13] and maXus[14] run within the Nonius COLLECT[15] program. The crystals were mounted on a glass fiber with silicon grease. An empirical absorption correction was made by the SORTAV[16] method from symmetry-related measurements. The structures were solved by heavy-atom Patterson (**1a**, **1b**) and direct methods (**3**) (SHELXS-97).[17] Refinement was carried out by full-matrix

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[10] See footnote 10 in ref 7.

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least-squares techniques (SHELXL-97).[18] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model.

Acknowledgment. We thank the EPSRC and the university of Southampton for support and Dr. Robert P. Tooze for helpful discussions.

Supporting Information Available: Complete tables of bond distances, bond angles, anisotropic thermal parameters, and fractional atomic coordinates for **1a**, **1b**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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