Inorg. Chem. **2003**, *42*, 7354–7356

Inorganic Chemistry
Communication

Copper(I) Complexes of a Heavily Fluorinated *β*-Diketiminate Ligand: Synthesis, Electronic Properties, and Intramolecular Aerobic Hydroxylation

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Received September 7, 2003

The aza-Wittig reaction between $Ar^f{-}N{=}PPh_3$ [$Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$] and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione affords a new, highly fluorinated *β*-diketimine, **1**. Metalation by mesitylcopper(I) in benzene gives rise to the Cu(I) *β*-diketiminate as its η^2-benzene adduct, **2a**. Copper(I) carbonyl complexes of **1**, and of three less-fluorinated analogues, have been generated in situ and compared by IR spectroscopy; the two backbone CF_3 groups exert a stronger electronic influence than the four *N*-aryl CF_3 groups. Dinuclear adduct **2b** reacts readily with O_2, leading to *ortho*-hydroxylation of a ligand *N*-Ar^f group.

The aerobic oxidation of organic substrates represents an ongoing goal in synthetic catalysis.[1] Copper(I) complexes, which can react with dioxygen to form strong oxidants,[2,3] some of them capable of C−H bond hydroxylation,[3] are interesting candidates for catalyst precursors. Recently, the reactivity of copper(I) *β*-diketiminate complexes with dioxygen has been studied in detail.[4]

We have now prepared a heavily fluorinated *β*-diketiminate ligand,[5,6] **1**, by a convenient aza-Wittig reaction,[7] and synthesized several copper(I) complexes from it. This ligand is quite electron-poor, as judged by an infrared study of several related (*β*-diketiminate)copper(I) carbonyl complexes. Despite its electron-poor metal center, a copper(I) *β*-diketiminate complex reacts readily with dioxygen, with clean *ortho*-hydroxylation of a ligand *N*-aryl group.[8] The ligand backbone remains unaffected.

Ligand **1** is synthesized in good yield by the aza-Wittig reaction of 2 equiv of [3,5-bis (trifluoromethyl)-phenylimino]-triphenylphosphorane with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione in toluene at 90 °C. We have been unable to prepare this ligand by traditional routes.[9] Reaction of **1** with

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10.1021/ic035056j CCC: $25.00

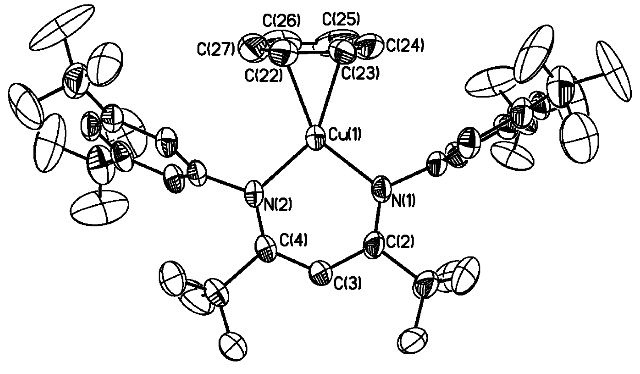
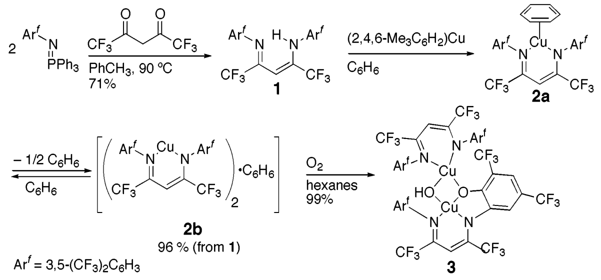


Figure 1. Representation of **2a**, shown as 50% elipsoids. For clarity, all hydrogen atoms were omitted, and only one orientation of each of the aryl CF_3 groups, which were modeled with six fluorines at half occupancy, is shown. Selected bond distances (Å) and angles (deg): Cu(1)−C(22) 2.117(4), Cu(1)−C(23) 2.102(4), C(22)−C(23) 1.385(6), N(1)−Cu(1)−N(1) 99.62(12), C(22)−Cu(1)−C(23) 38.35(17), Cu(1)−C(22)−C(27) 108.1(3), Cu(1)−C(23)−C(24) 106.1(3).

Scheme 1. Synthesis and Autoxidation of Cu(I) Complexes of **1**

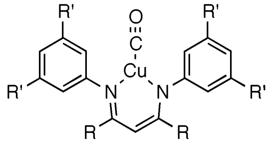


mesitylcopper(I) in benzene solution produces benzene adduct **2a** in high yield. The coordinated benzene is labile, and upon concentration in vacuo, **2a** is converted to the dinuclear benzene adduct **2b** (Scheme 1).

Crystals suitable for X-ray crystallography were grown by slow cooling of a hot hexane/benzene solution of **2a** (Figure 1). The X-ray structure[10] shows **2a** to be a monomeric η^2-benzene adduct. The benzene ring remains essentially planar, and the C(22)−C(23) bond length (1.385(6) Å) is equivalent within error to that of free benzene (1.39 Å),[11] indicating little π-back-bonding from copper.[12] Benzene complexes of copper(I) with poorly donating anions have been structurally characterized;[13] to our knowledge, this is the first such adduct supported by a β-diketiminate ligand.

Table 1. ν_{CO} for Inter-Related (β-Diketiminate)Cu(CO) Complexes

Ligand	R	R'	ν_{CO} (cm^{-1})
1	CF_3	CF_3	2110
4	CF_3	CH_3	2097
5	CH_3	CF_3	2090
6	CH_3	CH_3	2073



We have found analogues without the backbone CF_3 groups to be unstable and have been unable to isolate them.

To assess the electron-withdrawing nature of ligand **1**, less-fluorinated analogues **4**−**6** were synthesized, and the ν_{CO} of the copper carbonyl complexes derived from them were measured (Table 1).[14,15] The all-methyl analogue of **1** gives rise to the lowest carbonyl stretching frequency, resulting from the most electron-rich metal center, as expected. Two CF_3 groups at the ligand backbone exert a larger electron-withdrawing effect than four at the *meta* positions of the *N*-aryl groups: ν_{CO} increases by 24 versus 17 cm^{-1}. Replacement of all methyl groups with CF_3 groups results in an increase in ν_{CO} of 37 cm^{-1}, a substantial effect given the modest metal-to-ligand back-bonding from Cu(I).[16]

Despite the electron-poor nature of ligand **1**, the copper(I) complex **2b** reacts readily with dioxygen. Exposure of a hexane solution of **2b** to dry air leads to the rapid formation of a brown precipitate; the oxidation proceeds in near-quantitative yield after 30 min at room temperature. The ^1H and ^{19}F NMR of the product indicate the formation of an asymmetric, paramagnetic species.

Single crystals of the oxidation product, **3**, were grown by slow diffusion of hexane into a saturated solution of the product complex in C_6F_6. The ^1H and ^{19}F NMR, IR, and UV−vis spectra obtained from the crystals match those of the bulk material. Analysis of a single crystal by X-ray diffraction reveals a dinuclear structure for **3**, in which one of the ligand *N*-aryl groups has been hydroxylated to give a bridging phenolate (Figure 2).[17] The hydroxyl hydrogen atom was detected on the Fourier difference map in the X-ray study, and its presence is further corroborated by the stretch at 3671 cm^{-1} in the IR spectrum of **3**, consistent with other known μ-hydroxocopper complexes.[4a] The structure displays considerable tetragonal distortion at the copper centers; the dihedral angle between the two (β-diketiminate)copper planes is 53.68°.

The UV−vis spectra of starting material **2b** and oxidation product **3**, measured in dichloromethane solution, are shown

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(9) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516.

(10) Crystal data for $C_{27}H_{13}N_2F_{18}Cu$: monoclinic, space group $P2_1/n$, a = 8.5814(14) Å, b = 24.486(4) Å, c = 14.198(2) Å, β = 100.135(3)°, V = 2936.8(8) Å^3, Z = 4, ρ_{calcd} = 1.744 g/cm^3, F(000) = 1520. A total of 16229 reflections were collected in the θ range 2.21−25.00° of which 5738 were unique (R_{int} = 0.0415). No absorption correction was applied. The least squares refinement converged normally with residuals of R1 (based on F) = 0.0583, wR2 (based on F^2) = 0.1215, and GOF = 1.315 based on $I > 2\sigma(I)$.

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(14) Full experimental details on the synthesis of ligands and the generation of the Cu(I) carbonyl complexes are provided in the Supporting Information.

(15) For a recent example of metal carbonyl IR stretching frequencies as a measure of ligand electronics, see ref 7b.

(16) Similar differences in stretching frequency have been reported between Cu(CO) complexes of fluorinated and nonfluorinated tris(pyrazolylborate) ligands: Rasika Dias, H. V.; Lu, H.-L. *Inorg. Chem.* **1995**, *34*, 5380−5382.

(17) Crystal data for $C_{48}H_{14}N_4O_2F_{42}Cu_2$: monoclinic, space group: $P2_1/n$, a = 14.102(7) Å, b = 21.704 Å, c = 18.354(8) Å, β = 99.907(7)°, V = 5534(4) Å^3, Z = 4, ρ_{calcd} = 1.925 g/cm^3, F(000) = 3128. A total of 22 451 reflections were collected in the θ range 2.21−23.30° of which 7963 were unique (R_{int} = 0.0674). No absorption correction was applied. The least squares refinement converged normally with residuals of R (based on F) = 0.0444, wR2 (based on F^2) = 0.1153, and GOF= 1.024 based on $I > 2\sigma(I)$.

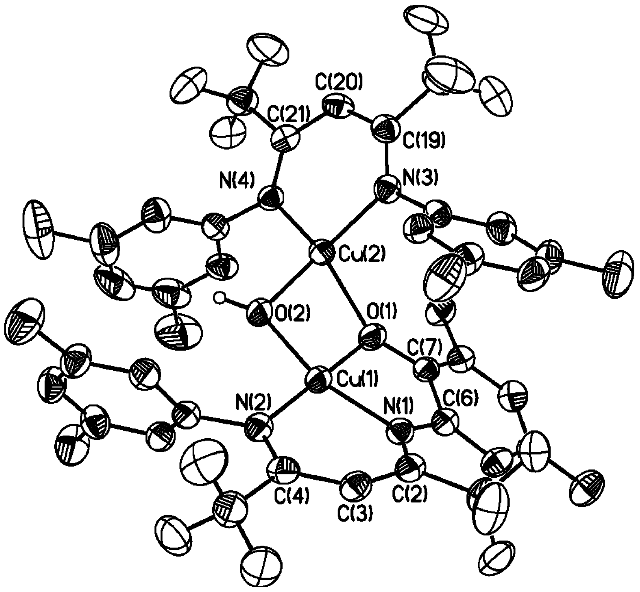

Figure 2. Representation of **3**, shown as 50% elipsoids. For clarity, the following were omitted: the fluorine atoms of all aryl CF_3 groups, all hydrogen atoms except for the hydroxyl proton, and a cocrystallized C_6F_6 molecule. Selected interatomic distances (Å) and angles (deg): Cu(1)−Cu(2) 2.9345(12), Cu(1)−O(1) 1.935(3), Cu(2)−O(1) 2.028(3), Cu(1)−O(2) 1.908(3), Cu(2)−O(2) 1.911(3), O(1)−C(7) 1.325(4), N(1)−Cu(1)−N(2) 97.05(12), N(3)−Cu(2)−N(4) 97.31(13), O(1)−Cu(1)−O(2) 78.92(11), O(1)−Cu(2)−O(2) 76.57(10), Cu(1)−O(1)−Cu(2) 95.51(11), Cu(1)−O(2)−Cu(2) 100.41(12).

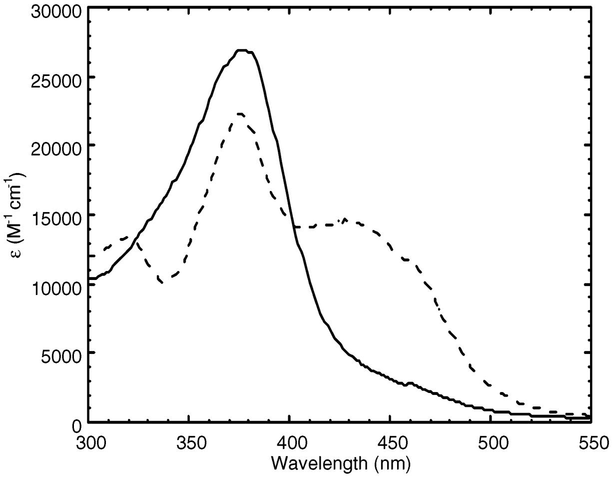

Figure 3. UV−vis spectra of **2b** (—) and **3** (- - -) in CH_2Cl_2.

in Figure 3. The starting material spectrum shows a single absorption at 379 nm ($\epsilon = 26\,900$ M^{-1} cm^{-1}). The spectrum of dinuclear Cu(II,II) complex **3** displays an absorption maximum at 376 nm ($\epsilon = 22\,300$ M^{-1} cm^{-1}), with new bands at 320 nm ($\epsilon = 13\,300$ M^{-1} cm^{-1}) and at 430 nm ($\epsilon = 14\,700$ M^{-1} cm^{-1}). This pattern is reminiscent of that observed upon oxygenation of other copper(I) β-diketiminates,[4c] even though the oxidation state obtained in this case is different.

The magnetic susceptibility of **3** been measured for a powder sample using a SQUID magnetometer. The effective magnetic moment μ_{eff}, at ambient temperature and a field strength of 0.5 T, is 1.95 μ_B; the magnetic behavior is consistent with weak antiferromagnetic coupling between the two copper(II) centers.[18] For comparison, the square planar bis[(β-diketiminate) copper(II) μ-hydroxide] reported by Dai and Warren has a smaller effective magnetic moment, 1.39 μ_B.[4a]

Intramolecular aerobic hydroxylation of an aryl group is well-precedented;[2b,3a,b] in this case, the aryl group is oxidized cleanly and rapidly despite the presence of two electronically deactivating CF_3 groups. Reaction of other (β-diketiminate)-copper(I) species with O_2 generally gives rise to dimeric Cu(III) μ-oxo complexes, or to monomeric Cu(III) η^2-peroxo complexes, depending on the ligand.[4] Aerobic oxidation of the β-diketiminate ligand backbone, which has been reported for Cu(II) and Zn(II) complexes,[19] was not observed in the oxidation of **2**.

In conclusion, an aza-Wittig reaction, using 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, affords the new, heavily fluorinated β-diketimine ligand **1** in good yield. This ligand is quite electron-poor, as reflected by the infrared stretching frequencies for four inter-related copper(I) carbonyl complexes. Nonetheless, a benzene adduct of its copper(I) complex reacts rapidly with dry air under ambient conditions, generating an oxidizing intermediate sufficiently powerful to hydroxylate a ligand-based 3,5-bis(trifluoromethyl)phenyl group, while leaving the diketiminate backbone unchanged. The chemistry of related complexes, protected against *N*-aryl group oxidation, is currently under investigation.

Acknowledgment. We gratefully acknowledge Prof. Stephen J. Lippard for donation of an IR spectrometer, and Prof. Daniel G. Nocera for the use of his UV−vis spectrophotometer. Dr. Daniel Grohol kindly assisted us in obtaining magnetic susceptibility data. We thank these colleagues and Prof. Christopher C. Cummins for helpful discussions. We also thank the MIT Department of Chemistry for support of this research through a startup grant, and the MIT School of Science for a generous grant from the James H. Ferry, Jr. Fund. We gratefully acknowledge a Lester Wolfe predoctoral fellowship for D.S.L. We also acknowledge NSF Awards CHE-9808061 and DBI-9729592 for supporting our NMR facilities.

Supporting Information Available: Experimental details (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) See Supporting Information for plots of χ and of μ_{eff} versus *T* (Figure S1).

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