

Synthesis of Volatile, Fluorinated β -Ketoiminato Copper(I) Complexes

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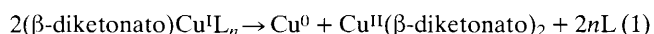
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The fluorinated β -ketoimines, 4-(alkyl)imino-1,1,1,5,5,5-hexafluoropentan-2-one, where alkyl = isopropyl **3** or trifluoroethyl **6**, have been obtained in high yield from the reaction of a silyl ether of hexafluoroacetylacetone with isopropylamine and trifluoroethylamine, respectively, and used to prepare volatile, monomeric copper(I) β -ketoiminato complexes.

There is an extensive chemistry of transition- and main-group metal β -ketoiminato or Schiff-base complexes, where the β -ketoiminato generally acts as a multidentate chelating ligand.¹⁻³ The chemistry of β -ketoiminato complexes of copper has generally centred around the synthesis and characterization of copper(II) complexes as model compounds to study magnetic properties⁴ and biologically important active sites such as haemocyanin.⁵ More recently, copper(II) complexes of fluorinated β -ketoimines were shown to be volatile and were used as metal-organic precursors for the formation of copper films by chemical vapour deposition (CVD).⁶ However, as precursors for copper CVD, copper(II) β -ketoiminato complexes suffer similar drawbacks to their copper(II) β -diketonato counterparts: they do not thermally decompose below 300 °C⁷ and the presence of hydrogen is generally required for the deposition of pure copper films.⁸ More recently, it has been shown that copper(I) β -diketonato compounds, $(\beta\text{-diketonato})\text{CuL}_n$, are suitable for copper CVD by virtue of a thermally induced disproportionation reaction, according to eqn. (1).⁹⁻¹²



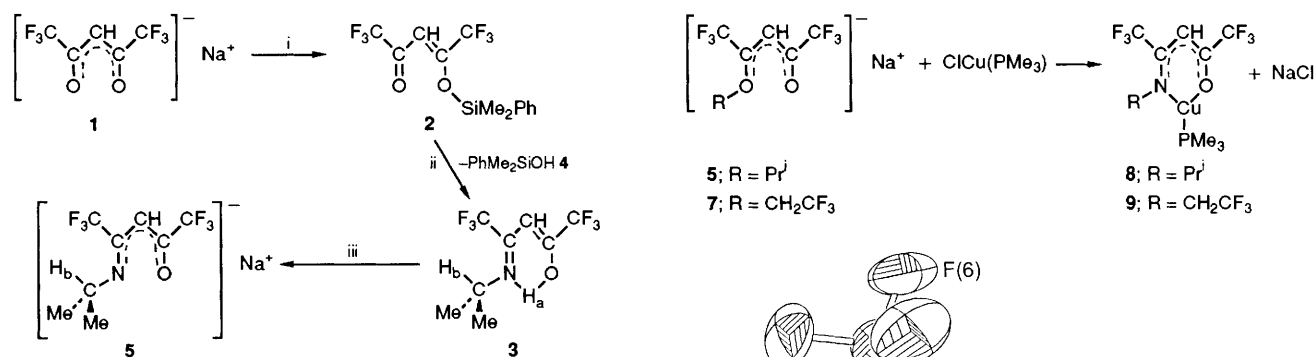
These species deposit pure copper films at low substrate temperatures (100 °C) and at high rates (up to 1 $\mu\text{m min}^{-1}$ at 190 °C).¹² It has been shown that variation of the β -diketonato

substituents and Lewis base (L) ligands influences the selectivity of deposition of copper onto one substrate in the presence of another.^{9,13-15} To explore further the influence of the copper ligands on the disproportionation reaction of eqn. (1) we have prepared the first examples of volatile fluorinated β -ketoiminato copper(I) compounds.

The synthesis of β -ketoimine ligands generally involves the condensation reaction of a β -diketone with a primary amine. However, for fluorinated β -diketones such as hexafluoroacetylacetone (Hhfac), reaction with primary amines to form intermediate N-substituted hemiaminals is dominated by acid-base chemistry and the corresponding primary ammonium salt is generally isolated in high yields [eqn. (2)].¹⁶



To avoid these problems, it has been demonstrated that conversion of the β -diketone to a silyl enol ether is a successful alternative and was utilized for the preparation of copper(II) β -ketoiminato complexes.¹⁷ The free β -ketoimine was then isolated by hydrolysis of the copper(II) complex under acidic conditions. Here we report the synthesis, *direct isolation* and characterization of 4-(alkyl)imino-1,1,1,5,5,5-hexafluoropentan-2-one, where alkyl = isopropyl, **3**; or trifluoroethyl, **6**; and their reactions to form volatile copper(I) complexes.



Scheme 1 i, $-\text{NaCl}$; a, PhMe_2SiCl , Et_2O , room temp., b, reflux 13 h, 79% yield; ii, a, NH_2Pr , -78°C , b, room temp., 20 min; c, distillation (room temp. 10^{-2} Torr), 52% yield; iii, a, NaOMe , Et_2O , -78°C ; b, room temp., 30 min, 87% yield

Compound **3** was synthesized according to the reactions illustrated in Scheme 1.

The sodium salt of hfac, prepared by deprotonation of Hhfac with NaH ,¹⁰ was treated with PhMe_2SiCl in refluxing diethyl ether to form **2** in 79% yield. Compound **2** was isolated by filtration, twice, through Celite followed by removal of the solvent *in vacuo* at 0°C . Reaction of **2** with isopropylamine resulted in formation of **3** together with silanol, **4**. Compounds **3** and **4** were separated by distillation at room temperature under reduced pressure. The sodium β -ketoininato complex **5** was prepared in 87% yield as a white solid from the reaction of **3** with sodium methoxide. Complex **6** was prepared by essentially the same method as compound **3**. Trifluoroethylamine was substituted for the isopropylamine to yield **6** (62%). Compounds **2**, **3** and **6** were isolated and characterized by NMR and mass spectroscopy and by elemental analyses.[†] The reaction of **5** and **7** (the sodium salt of **6**) with ClCuPMe_3

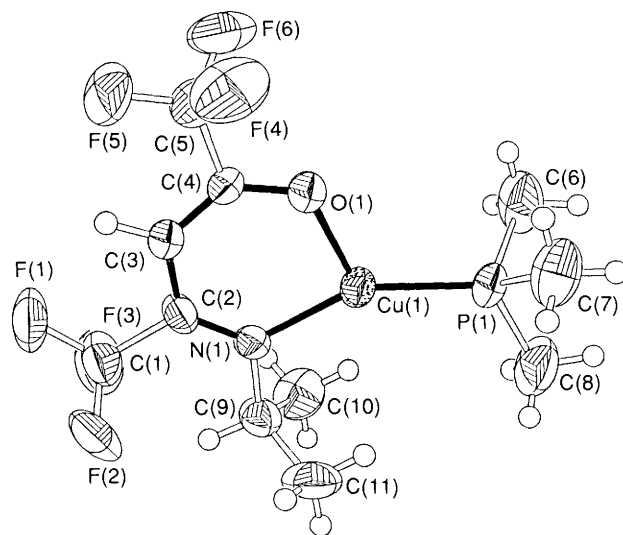


Fig. 1 ORTEP plot of complex **8** emphasizing the coordination environment about copper and showing the atom numbering scheme. Relevant bond lengths are (\AA): $\text{Cu}(1)\text{-P}(1)$ 2.157(2), $\text{Cu}(1)\text{-O}(1)$ 2.002(6), $\text{Cu}(1)\text{-N}(1)$ 1.965(6), $\text{C}(4)\text{-O}(1)$ 1.263(9), $\text{C}(4)\text{-C}(3)$ 1.345(11), $\text{C}(2)\text{-C}(3)$ 1.412(11), $\text{C}(2)\text{-N}(1)$ 1.301(10). Relevant bond angles ($^\circ$): $\text{P}(1)\text{-Cu}(1)\text{-O}(1)$ 115.9(2), $\text{P}(1)\text{-Cu}(1)\text{-N}(1)$ 147.8(2), $\text{O}(1)\text{-Cu}(1)\text{-N}(1)$ 96.2(2).

resulted in formation of copper(I) complexes, (β -ketoininato) CuPMe_3 , as illustrated by Scheme 2.

Compounds **8** and **9** were characterized by NMR and mass spectroscopy and by elemental analysis.[†] Confirmation of the connectivity between the imine and β -diketonato functionalities was derived from ^1H NMR spectroscopy spin-spin coupling. The isopropylmethine proton of **8**, H_b , exhibited a quartet of septet multiplicity arising from coupling to both methyl groups and the three fluorines of the adjacent CF_3 group, five bonds away. Similar coupling was also observed in the free β -ketoinimine **3** where, in addition, H_b also exhibited coupling to H_a (the enolate proton). The trifluoromethylene protons of **9** showed a quartet of quartet coupling with $^3J_{\text{H-F}} = 8.4$ and $^5J_{\text{H-F}} = 1.0$ Hz. However, in contrast to compound **3**, the trifluoromethylene protons of **6** do not exhibit $^5J_{\text{H-F}}$ coupling but show a doublet of quartet pattern due to coupling between the CF_3 and the enolate hydrogen.

Confirmation of the monomeric nature of **8** was derived in the solid state from a single crystal X-ray diffraction study.[‡]

[‡] *Crystal data:* $\text{C}_{11}\text{H}_{17}\text{CuF}_6\text{NOP}$; $M_w = 387.80$, monoclinic, $P2_1/c$, $a = 10.935(2)$, $b = 14.371(3)$, $c = 11.4720(2)$ \AA , $\beta = 107.34(3)^\circ$, $U = 1720.6$ \AA^3 ; $Z = 4$; $D_c = 1.497$ g cm^{-3} ; $\mu(\text{Mo-K}\alpha) = 14.15$ cm^{-1} ; $T = 297$ K, Siemens P4/V. An empirical correction for absorption was applied to the data. Of the 2387 data collected (max $2\theta = 45^\circ$), 1371 were both observed ($F \geq 4\sigma(F_o)$) and independent. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. At coverage, $R(F) = 5.02$, $R(wF) = 5.07\%$, $\text{GOF} = 1.24$, highest unassigned peak in the final difference map = 0.34 $e \text{\AA}^{-3}$. All computations used SHELXTL-PLUS software systems (G. Sheldrick, Siemens Corp., Madison, WI). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[†] *Selected spectroscopic data for 2:* ^1H NMR (C_6D_6 , 20°C , 250 MHz) δ 7.47 (m, 2H, C_6H_5), 7.13 (m, 3H, C_6H_5), 6.01 (s, 1H, CH), 0.45 (s, 6H, CH_3); ^{13}C NMR (C_6D_6 , 20°C , 62.9 MHz) δ 177.7 (q, J 36 Hz, CO), 155.1 (q, J 36 Hz, CO), 133.8 (s, C_6H_5), 133.3 (s, C_6H_5), 130.9 (s, C_6H_5), 128.1 (s, C_6H_5), 119.0 (q, J 288 Hz, CF_3), 115.8 (q, J 291 Hz, CF_3) 100.1 (s, CH), -1.50 (s, Me). **3:** ^1H NMR (C_6D_6 , 20°C , 250 MHz) δ 10.5 (s, br, 1H, NH), 5.71 (s, 1H, CH), 3.36 (m, br, 1H, CHMe_2), 0.59 (d, J 6.38 Hz, 6H, Me); ^{13}C NMR (C_6D_6 , 20°C , 62.9 MHz) δ 179.6 (q, J 34.5 Hz, CO), 152.9 (q, J 32.4 Hz, CN), 119.4 (q, J 278 Hz, CF_3), 117.4 (q, J 288 Hz, CF_3), 85.2 (q, J 4.2 Hz, CH), 48.4 (q, J 2.2 Hz, CHMe_2) 23.3 (s, Me). MS (30 eV, m/z): 249 (23%), $[\text{CF}_3\text{COCH}_2\text{CN}(\text{Pr}^i)\text{CF}_3]^+$; 234 (6%) $[\text{CF}_3\text{COCH}_2\text{CN}(\text{CHMe})\text{-CF}_3]^+$; 180 (16%), $[\text{COCH}_2\text{CN}(\text{Pr}^i)\text{CF}_3]^+$ or $[\text{CF}_3\text{COCH}_2\text{CN}(\text{Pr}^i)]^+$; 138 (50%), $[\text{CF}_3\text{COCH}_2\text{CN}]^+$ or $[\text{COCH}_2\text{CNCF}_3]^+$; 69 (2%), $[\text{CF}_3]^+$; 43 (100%), $[\text{Pr}^i]^+$; 28 (27%), $[\text{CHMe}]^+$. **6:** ^1H NMR (C_6D_6 , 20°C , 250 MHz) δ 10.1 (s, br, 1H, NH), 5.73 (s, 1H, CH), 3.14 (q, J 7.9 Hz, 2H, CH_2); ^{13}C NMR (C_6D_6 , 20°C , 62.9 MHz) δ 181.1 (q, J 35.8 Hz, CO), 152.8 (q, J 32.7 Hz, CN), 123.0 (q, J 278 Hz, CF_3), 118.9 (q, J 278 Hz, CF_3), 116.7 (q, J 288 Hz, CF_3), 88.7 (q, J 5.0 Hz, CH), 45.7 (q, J 35.5 Hz, CH_2). **8:** (Yield 77%). ^1H NMR (C_6D_6 , 20°C , 250 MHz) δ 6.08 (s, 1H, CH), 4.05 (m br, 1H, CHMe_2), 1.0 (d, J 6.0 Hz, 6H, CH_3), 0.59 (d, J 7 Hz, 9H, PMe_3); ^{13}C NMR (C_6D_6 , 20°C , 62.9 MHz) δ 168.5 (q, J 31 Hz, CO), 154.9 (q, J 25 Hz, CN), 120.6 (q, J 257 Hz, CF_3), 84.5 (s, br, CH), 53.2 (s br, CHMe_2), 26.5 (s, Me), 14.2 (d, J 25 Hz, PMe_3); ^{31}P NMR (C_6D_6 , 20°C , 101.2 MHz) δ -45.9 (s br). MS (30 eV, m/z): 387 (7%), $[\{\text{CF}_3\text{COCHCN}(\text{Pr}^i)\text{CF}_3\}\text{-CuPMe}_3]^+$; 290 (5%), $[\{\text{CHCN}(\text{Pr}^i)\text{CF}_3\}\text{CuPMe}_3]^+$; 248 (7%), $[\text{CF}_3\text{COCHCN}(\text{Pr}^i)\text{CF}_3]^+$; 215 (25%), $[\text{Cu}(\text{PMe}_3)_2]^+$; 139 (100%), $[\text{CuPMe}_3]^+$; 124 (3%), $[\text{CuPMe}_2]^+$; 75 (15%), $[\text{PMe}_3]^+$; 63 (3%), $[\text{Cu}]^+$; 61 (3%), $[\text{PMe}_2]^+$; 43 (6%), $[\text{Pr}^i]^+$. **9:** (Yield 82%). ^1H NMR (C_6D_6 , 20°C , 250 MHz) δ 6.02 (s, 1H, CH), 3.97 (q, J 8.4 Hz, 2H, CH_2), 0.58 (d, J 7.4 Hz, 9H, PMe_3); ^{13}C NMR (C_6D_6 , 20°C , 62.9 MHz) δ 171.0 (q, J 30.6 Hz, CO), 159.6 (q, J 25.7 Hz, CN), 124.4 (q, J 278 Hz, CF_3), 119.8 (q, J 287 Hz, CF_3), 118.7 (q, J 278 Hz, CF_3), 85.8 (s br, CH), 56.6 (q, J 31 Hz, CH_2), 14.5 (d, J 23 Hz, PMe_3); ^{31}P NMR (C_6D_6 , 20°C , 101.2 MHz) δ -44.4 (s br). Satisfactory elemental analyses were obtained for compounds **2**, **3**, **5**, **8** and **9**.

Compound **8** crystallized in the space group $P2_1/c$. The atom numbering scheme together with a view of the molecule emphasizing the copper coordination environment is shown in Fig. 1. The copper atom possesses a distorted trigonal-planar coordination environment consisting of O(1) and N(1) of the β -ketoiminato ligand and P(1) of trimethylphosphine. The O(1)–Cu(1)–N(1) angle (96.2°) is similar to the O–Cu–O bite angle observed for (β -diketonato)Cu(phosphine) compounds. However, the O(1)–Cu(1)–P(1) and N(1)–Cu(1)–P(1) angles of 115.9 and 147.8° , respectively, are distinctly asymmetric, probably as a result of steric interactions between the isopropyl group, the methyl groups of PMe_3 and the adjacent CF_3 group. Other angles and distances in this complex are not noteworthy in this context, within the limits of error on the data.

Compounds **3** and **6** are volatile and colourless liquids. Compound **8** is a volatile, low-melting (60°C), yellow solid and **9** is a liquid at room temperature. These compounds sublime or distil at 45 and 35°C at 10^{-2} Torr, respectively. Both compounds **8** and **9** are sensitive to atmospheric oxygen. CVD of **8** over the temperature range 150 – 250°C results in deposition of copper on Pt-coated silicon substrates. Studies are in progress to investigate the influence of the β -ketoiminato, and Lewis-base ligands on the mechanism and selectivity of copper CVD via thermally induced disproportionation from these complexes and will be reported elsewhere.

We thank the National Science Foundation (grant number CHE-9107035) for support of this research. T. T. K. acknowledges support from the NSF PYI program number CTS-9058538. M. H. S. thanks the NSF chemical instrumentation program for the purchase of a low-field NMR spectrometer.

Received, 8th October, 1991; Com. 1/05107E

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