ORGANOMETALLICS

Room Temperature Stable Organocuprate Copper(III) Complex

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Supporting Information

ABSTRACT: The paramagnetic trigonal-planar copper complexes {K(18C6)}- $[Cu^{II}(OC(CH_3)(CF_3)_2)_3]$ (2) and $K[Cu^{II}(OC(C_6H_5)(CF_3)_2)_3]$ (3) have been prepared and characterized, including X-ray crystallography, in 61% and 3% yields, respectively. The latter complex does not form preferentially, because CuBr₂ and $KOC(C_6H_5)(CF_3)_2)_3$ also form the diamagnetic complexes {K(18C6)}- $[K_{2}{Cu^{I}(OC(C_{6}H_{5})(CF_{3})_{2})_{3}}]$ (4) and $\{K(18C6)\}[Cu^{III}(OC(C_{6}H_{4})(CF_{3})_{2})_{2}]$ (5). These species were characterized by X-ray crystallography, UV-vis spectroscopy, ¹H, ¹³C{¹H}, and ¹⁹F{¹H} NMR spectroscopy, and elemental analysis. The unique organocuprate Cu(III) species with $\{O_2C_2\}$ coordination was formed by ortho metalation of two phenyl rings, resulting in trans- $\{O_2C_2\}$ coordination of Cu(III), and is stable at room temperature in the solid state and in dark solutions of THF.

CF₃ Θ CE

■ INTRODUCTION

Inexpensive, earth-abundant copper is active in numerous homogeneous catalytic processes. Organocopper(III) intermediates are believed to play a role in a subset of these, including the Ullmann reaction¹ and cross-coupling² or organocuprate additions.³ Before the turn of the 21st century, organometallic Cu(III) complexes were rare.⁴ The Cu(III) centers in the isolable species were stabilized by chelating ligands or CF3 groups. These complexes include [Cu- $(CF_3)_2(S_2CN(C_2H_5)_2)^{-5}$ $[Cu(CF_3)_4]^{-6}$ $[Cu-N_2CP]^{-6}$ in which N₂CP is the doubly N-confused porphyrin 2-ethoxy-5,10,15,20-tetrapentafluorophenyl-3,7-diaza-21,22-dicarbaporphyrin,⁷ and a unique trigonal-bipyramidal structure, [Cu-(tptm)Cl]⁻, where tptm is tris(2-pyridylthio)methanide.⁸ These reported compounds, however, did not exhibit reactivity of the long-debated and proposed Cu(III) intermediates of catalytic reactions.³

In 2007, Bertz⁹ reported the observation of organocopper-(III) species using rapid-injection NMR spectroscopy (RI-NMR) to study the reactivity of organocopper(I) Gilman reagents with allylic substrates. Subsequently, Gschwind¹⁰ was able to study similar species by low-temperature ¹H and HMBC NMR studies. The high-valent species studied by Bertz et al. were generated in situ under nitrogen at -100 °C.¹¹⁻¹⁴ When they were heated to ambient temperatures, these species underwent reductive elimination to form new C-C bonds.¹³ These spectroscopic observations provided direct evidence for the long-sought Cu(III) intermediates in such cross-coupling reactions.

A reactive family of Cu(III) complexes with monoanionic, triazamacrocyclic ligands has also been prepared by aerobic disproportionation and isolated, and their structural and spectroscopic properties have been studied extensively over the past decade.^{15,16} These aryl–Cu(III) complexes form C–O bonds by reaction with oxygen nucleophiles¹⁷ or reductive elimination¹⁸ and C-N bonds with amide type nucleophiles¹⁹ or reductive elimination.²⁰ The Cu(III) species have been identified and proposed as intermediates both in the Cu(II) catalytic mechanism of C-H methoxylation and amidation of macrocyclic substrates with O₂ as an oxidant²¹ and in Ullmanntype coupling reactions.²²

Subsequently, Cu(II) was reported to react with an azacalix[1]arene[3]pyridine ligand via disproportionation to form an aryl-Cu(III) compound after C-H activation, in which the Cu(I) species is aerobically oxidized to Cu(III).²³ These Cu(III) species react with nucleophiles and alcohols²³ to form C-O bonds²⁴ and halogens to form C-X bonds.²⁵ In addition, the Cu(III) intermediates have been reacted with terminal alkynes and alkynyllithium reagents to form crosscoupled $C_{aryl}-C_{alkynyl}$ bonds.²⁶ Most recently, a one-pot synthesis with Cu(II) yielded $C_{aryl}-C_{alkyl}$ bonds, and independently prepared aryl-Cu(III) species were also used in the cross-coupling reactions.²⁷

Reactive, high-valent complexes are not only used for desired C-H activation but can also be prey to decomposition from unwanted reactions of this same type. Therefore, we are investigating complexes of the late 3d metals with monodentate, oxygen-donating, partially or fully fluorinated ligands. Using these ligands, seen in Scheme 1, the varying degrees of fluorination not only make C-H activation less likely but also reduce both the π -donor character of the O atom and ligand

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Scheme 1. Alkoxide Ligands $^{-}OC_4F_9$ (Perfluoro-*tert*butoxide), $^{-}OC(CH_3)(CF_3)_2$ (Hexafluoro-*tert*-butoxide), and $^{-}OC(C_6H_5)(CF_3)_2$ (Hexafluoro- α -cumyl Alkoxide)



bridging. This effect maintains open coordination sites at metal centers and potentially stabilizes high oxidation states in transition metals. A series of high-spin, three-coordinate alkoxide complexes of the type $[M(OR^F)_3]^-$ were synthesized with $OR^F = OC_4F_9$ and M = Fe(II), Co(II), and Cu(II) (1) via salt metathesis routes.²⁸ The four-coordinate complexes $[M(OR^F)_4]^{2-}$ with M = Co(II), 28 Ni(II)²⁹ and $[M(OR^F)_3(THF)]^{2-}$ with M = Co(II), $Zn(II)^{28}$ were also synthesized. These fluorinated ligands are medium-field ligands, similar to OH^- and F^- , and stronger than NCO⁻, whose character has been shown spectroscopically²⁹ and computationally.³⁰

RESULTS AND DISCUSSION

The partially fluorinated trigonal-planar complex $[Cu(OC-(CH_3)(CF_3)_2)_3]^-(2)$ has now been prepared by a route similar to that for the previously reported²⁸ 1 (Scheme 2). The related

Scheme 2. General Metathesis Synthesis for Cu(II) Tris-Alkoxide Complexes



species $[Cu(OC(C_6H_5)(CF_3)_2)_3]^-$ (3) has also been prepared and revealed much more rich chemical behavior. Herein we report the synthesis, isolation, and characterization of the related and expected Cu(II) complex 3, a trinuclear Cu(I) complex, and a stable organocuprate Cu(III) species, all from the same starting materials.

One equivalent of CuX₂ was reacted with 3 equiv of the potassium alkoxide salt KOC(CH₃)(CF₃)₂ in THF to afford the tris-alkoxide metal species **2**. Removal of presumed KX by filtration and the addition of 18-crown-6 (18C6) in CH₂Cl₂ afforded **2** in good yield (61%). Compound **2** exhibits a solution magnetic moment of 1.95 $\mu_{\rm B}$, consistent with one unpaired electron and an absence of spin–orbit coupling. Recrystallization of **2** resulted in green crystals suitable for X-ray analysis (Figure 1). Data collection parameters and intramolecular metrical parameters for all crystallographic characterizations are provided in the Supporting Information.

A Cu(II) anion in a distorted-trigonal-planar geometry was revealed by single-crystal X-ray diffraction. The six oxygen atoms of 18C6 encapsulate the K⁺ cation, which also displays a single K...O interaction and two K...F interactions to one alkoxide ligand. The average Cu–O bond distance in 2 is 1.840(2) Å, similar to the average Cu–O bond distance of



Figure 1. ORTEP diagram of **2** showing K···F and K···O interactions. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Cu(1)-O(7) = 1.8283(18), Cu(1)-O(8) = 1.8576(15), Cu(1)-O(9) = 1.8349(19); O(7)-Cu(1)-O(8) = 136.69(9), O(8)-Cu(1)-O(9) = 109.42(1), O(9)-Cu(1)-O(7) = 113.88(9).

1.849(7) Å in the only other reported copper complex utilizing this ligand, Ba[Cu(OC(CH₃)(CF₃)₂)₃]₂.³¹ The elongated distance of 1.858(2) Å for Cu(1)–O(8) is due to the bridging interaction of O(8) with the {K(18C6)}⁺ cation. The CuO₃ core in the anion is nearly planar, with the Cu(II) atom displaced by 0.012 Å from the best {O₃} plane. The O(7)–Cu(1)–O(8) angle of 136.69(8)° is much larger than the other two O–Cu–O angles, which are both smaller than 120°.

The preparation of 1 and 2 was straightforward, but that of the $[Cu(OC(C_6H_5)(CF_3)_2)_3]^-$ anion proved more challenging. Following synthetic procedures similar to those described above, recrystallization of the proposed $\{K(18C6)\}[Cu(OC (C_6H_5)(CF_3)_2$ yielded a mixture of colorless blocks and yellow plates, coated in dark oil, which were subsequently characterized (vide infra). The best vield (3% based on Cu) of $K[Cu(OC(C_6H_5)(CF_3)_2)_3]$ (3) was obtained as green-yellow plates using a deficiency of alkoxide and no 18C6. Single-crystal X-ray diffraction studies of 3 revealed another Cu(II) center in a distorted-trigonal-planar geometry bound to three monodentate $OC(C_6H_5)(CF_3)_2$ ligands (Figure 2). The average Cu-O bond distance is 1.865(1) Å, which is slightly longer than that of 2. In the absence of 18C6, there are two $K \cdots O_{alkoxide}$ interactions and three K…F interactions to two alkoxides in the asymmetric unit. The CuO₃ core is again nearly perfectly planar, as the copper center is displaced by 0.027 Å from the O(1), O(2), and O(3) plane. The average O-Cu-O angle is 126.64(8)°, slightly larger than the ideal trigonal-planar geometry. Compound 3, like 2, has both wide O(3)-Cu(1)-O(1) (155.29°) and narrow O(1)-Cu(1)-O(2) (90.70°) angles, which are more distorted than those in 2, due to the absence of 18C6 and the resulting closer K…O interactions.

When 18C6 is included in the synthesis from Scheme 2, mostly colorless crystals are obtained in the presence of some yellow plates. X-ray-quality colorless crystals were separated and regrown in CH₂Cl₂ and hexanes at -35 °C, yielding a unique Cu(I) trimer, {K(18C6)}[K₂{Cu(OC(C₆H₅)-(CF₃)₂)₂}₃] (4). Three linear [Cu(OC(C₆H₅)(CF₃)₂)₂]⁻ anions are aligned approximately parallel to one another, and



Figure 2. ORTEP diagram of 3 showing K…F and K…O interactions. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Cu(1)-O(1) = 1.8519(17), Cu(1)-O(2) = 1.8972(17), Cu(1)-O(3) = 1.8473(17); O(1)-Cu(1)-O(2) = 90.69(7), O(2)-Cu(1)-O(3) = 113.95(8), O(3)-Cu(1)-O(1) = 155.28(8).

the ends of this unit are capped by two K⁺ cations, giving an overall monoanionic charge and approximate C_3 symmetry that is balanced by one uncoordinated {K(18C6)}⁺ cation. The anion [K₂{Cu(OC(C_6H_5)(CF₃)₂)₂}₃]⁻ is shown in Figure 3, and a drawing of the anionic molecular structure is given in Figure S1 (Supporting Information). Compound 4 is diamagnetic, and the average Cu–O bond distance is 1.835(1) Å. Each of the two potassium cations not encapsulated by 18C6 has six K…F and three K…O interactions



Figure 3. ORTEP diagram of anion of **4** with extensive K···F and K···O interactions. Only K(1)···F interactions are labeled for clarity. The cation $\{K(18C6)\}^+$ and hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

to three different alkoxide ligands. The potassium atom encapsulated by 18C6 has no K…F or K…O interactions with the anion. The two unique O–Cu–O angles are nearly linear: O(1)–Cu(1)–O(2) at 173.21(6)° and O(3)–Cu(3)–O(3_i) at 171.09(6)°. The highest isolated yield of 4 (13% based on Cu) has been obtained using the synthetic method shown in Scheme 2 with $^{1}/_{3}$ equiv of 18C6 on the basis of the ratio of 18C6 to K⁺ provided by the crystal structure.

Cu(I) derivatives with no 18C6, K[Cu(OC(C_6H_5)(CF₃)₂)₂], and 1 equiv of 18C6 per K⁺, {K(18C6)}[Cu(OC(C_6H_5)-(CF₃)₂)₂], have been independently synthesized from mesitylcopper and hexafluoro- α -cumyl alkoxide.³² The independent preparation of 4 from such sources with ¹/₃ equiv of 18C6 per K⁺ has not been achieved, probably due to the very similar solubilities of 4 and related species with different ratios of 18C6 to K⁺.

The solution electrical conductivity of **4** was measured in THF to determine its degree of electrolyte behavior. The Cu(I) trimer was compared to a 1:1 electrolyte, tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆), and the previously reported 2:1 electrolyte {K(18C6)}₂[Cu(OC₆F₅)₄]³³ (Figure 4). Compound **4** has a conductivity similar to that of the 2:1



Figure 4. Onsager plot of $TBAPF_6$ (squares), $\{K(18C6)\}_2[Cu-(OC_6F_5)_4]$ (triangles), and 4 (diamonds).

electrolyte, indicating only partial dissociation of the three K^+ ions in THF solution, due to the extensive $K \cdots F$ and $K \cdots O$ interactions that maintain the Cu(I) trimer in solution to a degree.

Following the synthetic procedure of Scheme 2 again, but only using THF and no CH_2Cl_2 , recrystallization produces yellow crystals (10%) of the robust organocuprate (III) species $\{K(18C6)\}[Cu(OC(C_6H_4)(CF_3)_2)_2]$ (5) but not the Cu(I) species 4. The anion of 5 is shown in Figure 5, clearly showing ortho metalation of the two phenyl rings and two new Cu–C bonds with an average length of 1.9314(17) Å. Compound 5 is stable at room temperature as a solid and in THF solution in the dark. The fluorinated ligand character and two chelate rings both enhance stability, and the Cu(III) atom sits on an inversion center of this square-planar d⁸ species. There are no K…O or K…F interactions to the anion, as the encapsulating agent 18C6 is closest to a phenyl ring on the alkoxide, similar to the case for 4.

Previous work with hexafluoro- α -cumyl alkoxide was undertaken to stabilize trigonal-bipyramidal geometries,³⁴ and complexes with the same dianionic, four-membered chelate ring as in **5** were structurally characterized³⁵ with M = Ge(IV),³⁶ Sb(III),^{37,38} Bi(III).^{39,40} Hexafluoro- α -cumyl alcohol



Figure 5. ORTEP diagram of anion of **5.** The cation $\{K(18C6)\}^+$ and hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Cu(1)-C(1) = 1.9314(17), Cu(1)-O(1) = 1.8173(12); O(1)-Cu(1)-O(1 i) = 180.00, C(1)-Cu(1)-C(1 i) = 180.00.

was doubly deprotonated by directed dilithiation and added to the p-block halides.^{41,42} The M-C bond distances are generally longer than those of 5, namely 2.133 and 2.162 Å in $[NEt_4][Sb(OC(C_6H_4)(CF_3)_2)_2]^{37}$ and 2.249 and 2.237 Å in $[NEt_4][Bi(OC(C_6H_4)(CF_3)_2)_2]^{.39,40}$ The only structure with M-C bonds similar to those of 5 is $[Ge(OC(C_6H_4)-$ (CF₃)₂)₂],³⁶ with Ge-C distances of 1.896 and 1.900 Å. In other p-block structures with this geometry, lone pairs on the central atoms usually promote a trigonal-bipyramidal structure, rather than square pyramidal. Other structures that have not been structurally characterized include S and Se derivatives.⁴³ Similar work has been done with other p-block elements, such as P⁴¹ and As,⁴² with trigonal bipyramidal structures formed by addition of a nucleophile.⁴¹ Anionic siliconates have also formed similarly. 36,44,45 Most recently, [Ge(OC(C₆H₃-4-CH₃)- $(CF_3)_2$ was used as a ligand to form stable anionic iron(0) complexes.⁴⁶ To the best of our knowledge, 5 is the first transition-metal compound of this dianionic ligand.

¹H NMR spectroscopy reveals distinct resonances for both new diamagnetic compounds, **4** in CD_2Cl_2 and **5** in d_8 -THF, displayed in Scheme 3. The Cu(I) species **4** is robust in all aprotic solvents in the absence of O₂. The reactivity of fluorinated $[Cu(OR)_2]^-$ species with O₂ is discussed elsewhere.³² In contrast, Cu(III) **5** is sensitive to radical species, and poor yields of this compounds are obtained with CH₂Cl₂ as a reaction medium or recrystallization solvent. When the reaction solvent is only THF, path a in Scheme 4, the ¹H NMR (Figure S2, Supporting Information) and ¹³C NMR spectra of the triply recrystallized product displayed predominantly the

Scheme 4. Solvent Dependence of 5 in THF or 4 and 5 in THF/CH₂Cl₂

Cu(II)X ₂	THF, 18C6	{K(18C6)}[Cu(III){OC(C ₆ H ₄)(CF ₃) ₂ } ₂], 5
+ 3 KOC(C ₆ H ₅)(CF ₃) ₂	b) THF/CH ₂ Cl ₂ , 18C6	{K(18C6)}[Cu(III){OC(C ₆ H ₄)(CF ₃) ₂ } ₂], 5 + {K(18C6)}[K ₂ [Cu(I){OC(C ₆ H ₅)(CF ₃) ₂ } ₂] ₃], 4

resonances for the organocuprate Cu(III) species **5**, including a characteristic ¹³C signal¹⁶ for the new, ortho-metalated Cu–C bond. When CH_2Cl_2 was present, path b in Scheme 4, the ¹H NMR spectrum of triply recrystallized material displayed predominantly **4** and a minor amount of **5** (Figure S3, Supporting Information). A similar phenomenon is seen in the ¹⁹F NMR spectra (Figure S4, Supporting Information), in which only **5** is observed in the absence of CH_2Cl_2 , but having used CH_2Cl_2 in the synthesis, a resonance for **4** at –75.49 ppm and a minor resonance at –75.76 ppm for **5** are observed.

The observation of Cu(I) and Cu(III) complexes implies disproportionation from a Cu(II) source, but NMR data indicate that the two product oxidation states are not formed simultaneously. Cu(III) 5 is formed first and Cu(I) 4 is only observed upon loss of 5 with excess CH₂Cl₂. ¹H NMR spectra of crude products in d_8 -THF show primarily 5, with evidence for Cu(II) species in several broad resonances (Figure S5, Supporting Information). When the reaction mixture is dissolved in CD₂Cl₂, only weak resonances for 5 are observed between δ 6.9 and 7.1 ppm (Figure S6A, Supporting Information), with the majority component having resonances at δ 7.25 and 7.83 ppm. When the crude product is stirred in CH₂Cl₂ in the dark for 1 h (Figure S6B) or 10 h (Figure S6C), these resonances are maintained. When stirring is carried out in CH_2Cl_2 in the light for 10 h, the remaining resonances for 5 are diminished, and the other diamagnetic product is unchanged (Figure S6D). These resonances are only similar to those of 4 with one 18C6 per three K⁺ ions but match the related monomeric Cu(I) species {K18C6} [Cu{OC(C_6H_5)(CF₃)₂]₂], prepared with a full 1 equiv of 18C6 per K^+ ion.³² It is therefore proposed that excess CH₂Cl₂ acts as a source of H[•] to generate Cu(I) from Cu(III) with two instances of Cu-C cleavage, twoelectron Cu reduction, and regeneration of the C₆H₅ groups. Testing this hypothesis by adding 2 equiv of CD_2Cl_2 to 5 in d_8 -THF revealed no changes in the ¹H NMR spectrum after 24 h, suggesting a small equilibrium constant for any H atom abstraction. Further studies to quantify the reactivity are underway.

Scheme 3. Proton Resonances of the Anions of 4 (in CD_2Cl_2) and 5 (in d_8 -THF) in ppm





Scheme 6. (a) Closest Cu(1)…H_{methyl} Distances for 2 and (b) Closest Cu(1)…H_{ortho} Distance for 3



A mechanism for formation of Cu(III) 5 is proposed in Scheme 5. If a Cu(II) tris-alkoxide is generated in solution, then intramolecular single-electron transfer (SET) from oxygen to copper can create a transient Cu(I) alkoxy radical compound. Such species have been proposed to be subject to nucleophilic attack and reoxidation in the presence of O2.47 We propose that, in this circumstance, the transient Cu(I) species is more reactive than the alkoxides, resulting in oxidative addition of the adjacent ortho-C-H bond. Such a mechanism makes the cumyl alkoxide a directing group for the ortho-metalation process. Although such intermediates have frequently been proposed,⁴⁶ they have rarely been trapped. Oxidative addition of an ortho-C-H bond to Cu(I) creates an anionic five-coordinate Cu(III) hydride species. Loss of H⁺ and alkoxide in solution as the alcohol, $HOC(C_6H_5)(CF_3)_{2}$, regenerates a Cu(II) center. A second iteration of this process would require intermolecular alcohol loss. Evidence for this mechanism includes (i) the absence of intramolecular oxidative addition by the groundstate Cu(I) $[Cu(OC(C_6H_5)(CF_3)_2)_2]^-$ anion³² and (ii) low basicity (and nucleophilicity) of fluorinated alkoxides in general.⁴⁸ No observation of HOC(C_6H_5)(CF_3)₂ in crude ¹H NMR product mixtures was made, but overlap of the OH signal (at δ 3.6 ppm in CD₂Cl₂) with the 18C6 signal(s) near δ 3.5– 3.6 ppm is possible. The introduction of large amounts of CH_2Cl_2 , a known H[•] source,⁴⁹ into the reaction mixture generates the Cu(I) bis-alkoxide species, which is stabilized as the trimer 4 due to the extensive K…F and K…O interactions.

Solution studies also suggest that **5** is susceptible to decomposition in solution in the presence of radicals. UVvis spectroscopy shows that, in THF, **5** has features at 212 and 249 nm ($\varepsilon = 2523 \text{ M}^{-1} \text{ cm}^{-1}$), and one visible feature at 385 nm ($\varepsilon = 251 \text{ M}^{-1} \text{ cm}^{-1}$). When **5** was exposed to light for 10 min, the visible transition diminished, and broadening was observed in the UV region (Figure S7, Supporting Information). Furthermore, **5** has a short lifetime as a solid on exposure to air (maximum of 1 day) and an even shorter lifetime in aerated solutions, with a half-life of approximately 10 min. Complex **5**, however, is not soluble in H₂O under N₂, and a mixture of **5** and H₂O does not show any signs of greenbrown Cu(II) over 1 week (Figure S8, Supporting Information). When d_8 -THF was added, the complex dissolved to form a yellow solution but is remarkably robust over 1 day (Figure S9, Supporting Information). This stability to H⁺ for a d⁸ Cu(III) species is reminiscent of the air stability of orthometalated d⁸ Pt(II)⁵⁰ and Au(III)⁵¹ species with, for example, phenylpyridine. Further mechanistic studies are underway to understand the reactivity of this exceptional Cu(III) bis-aryl complex.

In evaluating the mechanism proposed in Scheme 5, it is also informative to examine the shortest Cu(1)···H distances in 2 and 3, shown in Scheme 6. The average $Cu(1)\cdots H_{methyl}$ distance in 2 of the closest six hydrogen atoms on the three methyl substituents is 2.9880(3) Å. The two shortest distances are 2.8262(3) Å for Cu(1)…H(20A) and 2.8679(3) Å for $Cu(1)\cdots H(20C)$, both from the copper to the methyl substituent of the O(8) alkoxide involved in the interaction with 18C6. The average $Cu(1)\cdots H_{ortho}$ distance in 3 is 2.6940(2) Å. The shortest distance, $Cu(1)\cdots H(27)$, however, is much shorter than the other two at 2.4905(2) Å. This shortest distance from Cu(1) to H_{ortho} on the O(3) alkoxide ligand shows the strong potential for oxidative addition. Although the hydrogen atoms were not located in the difference map and were placed in calculated positions, the $Cu(1)\cdots C(27)$ distance of 2.940 Å in 3 agrees with our evaluation of the placement of hydrogen atoms, as the $Cu(1)\cdots C(27)$ distance is clearly the shortest copper-carbon distance in either 2 or 3. It would be particularly interesting to compare 5, with the still unknown $\{K(18C6)\}[Cu(OC(C_6H_5)-$

 $(CF_3)_2)_3$], to see how the C···H distances change upon diminished K⁺ interactions with alkoxides, and its synthesis is currently under investigation.

CONCLUSION

Our unique organocuprate Cu(III) species 5 contains two trans ortho-metalated phenyl rings and is stable at room temperature in the solid state and in dark THF solution. This compound does not react with H₂O in the absence of O₂ over several hours, though it does react in minutes in solution in air. To the best of our knowledge, this is the first stable organometallic Cu(III) structure with O-donor ligands, instead of the commonly used N-donor ligands. The relative stability of 5 to reductive elimination is likely due to the two chelate rings with trans-disposed Cu-C bonds. The formation of this compound from Cu(II) starting materials suggests that other less stable and more reactive Cu(III) species may also be present in the $\{Cu(OR)_2\}$ systems for potential use in oxidative-addition and reductive-elimination chemistry. The search for similar $[Cu(OR)_2]$ species that can activate external C-H bonds is currently underway.

EXPERIMENTAL SECTION

General Procedures. Ligand synthesis and copper complex preparations were performed at room temperature in an MBraun purified N2-filled drybox or using standard Schlenk techniques under an atmosphere of N2 or Ar. The anhydrous solvents dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), hexanes, and Et₂O were purified with an Ar-filled MBraun solvent purification system (SPS) equipped with dual columns of anhydrous Al₂O₃. The deuterated solvent CD₂Cl₂, used for NMR samples, and the internal reference ¹⁹F standard trichlorofluoromethane (CFCl₃) were both dried by refluxing over CaH2; d8-THF (C4D8O) was dried over molecular sieves. All solvents were stored over molecular sieves in an N2-filled drybox. Celite was dried overnight in vacuo while being heated to 125 °C with an oil bath. The reagent 18-crown-6 (18C6) was obtained from commercial sources and recrystallized from toluene and hexanes. Potassium hydride (KH) was obtained as a mineral dispersion (30 wt %) and was purified by washing with hexanes and drying in vacuo prior to storage in the drybox. The fluorinated alcohols HOC₄F₉, $HOC(CH_3)(CF_3)_2$, and $HOC(C_6H_5)(CF_3)_2$ were purchased from Oakwood Chemicals or Matrix Scientific and were dried over sieves before being stored in the drybox. Potassium ligand salts used in metathesis reactions were prepared as described previously.²⁸ Tetra-nbutylammonium hexafluorophosphate (TBAPF₆) was triply recrystallized from CH2Cl2 and hexanes. All other reagents were obtained commercially and used without any further purification.

Physical Methods. NMR spectra were recorded on Varian 400 MHz spectrometer at room temperature. Chemical shifts (δ) for ¹H, ¹³C{¹H}, COSY, and HSQC NMR spectra were referenced to the resonance of residual protio solvent (¹H) or the ¹³C{¹H} resonance of the solvent. Chemical shifts (δ) for ¹⁹F NMR spectra were referenced to internal CFCl₃. Solution-phase magnetic susceptibility was determined via the Evans method^{52,53} in CD₂Cl₂ with (Me₃Si)₂O as the internal reference and reported after the appropriate diamagnetic corrections.⁵⁴ UV–vis data were collected with a Shimadzu UV-3600 spectrophotometer. Conductivity studies were performed at room temperature in the drybox using a Fisher Scientific Traceable Portable Conductivity Meter (Model No. 09-326-2). Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ) or by Atlantic Microlab, Inc. (Norcross, GA).

X-ray Crystallography. Single-crystal X-ray diffraction data for complexes 2 (green blocks), 3 (yellow blocks), and 4 (colorless blocks) were collected on APEX-CCD-detector equipped Bruker diffractometers with Mo K α radiation. Data for a yellow block crystal of 5 were collected at 100 ± 1 K on a Bruker Proteum-R system equipped with a CCD area detector, Cu K α radiation and an Oxford

Cryostream 700 low-temperature device. All crystals were mounted on a cryoloop with Paratone-N oil and cooled under a stream of nitrogen gas. Data were corrected for absorption using semiempirical, multiscan methods. All structures were solved by heavy-atom methods, and the remaining non-hydrogen atoms were located from subsequent difference maps. Data were integrated using the Bruker SHELXTL software program and scaled using the SADABS software program. Solution was by direct methods (SHELXS), and all non-hydrogen atoms were refined anisotropically by full-matrix least squares (SHELXL-97). Hydrogen atoms were treated as idealized contributions and were placed in calculated positions with appropriate riding models.

Synthesis of {K(18C6)}[Cu(OC(CH₃)(CF₃)₂)₃] (2). A solution of KOC(CH₃)(CF₃)₂ (0.3222 g, 1.46 mmol) was added to an orangebrown slurry of CuBr₂ (0.1059 g, 0.474 mmol) in THF. The reaction mixture turned cloudy blue-green and was stirred at room temperature overnight. The cloudy blue-green solution was filtered through Celite to remove KBr and triturated three times with CH₂Cl₂. A solution of 18C6 (0.1196 g, 0.453 mmol) in CH₂Cl₂ was added, and the resultant green solution was stirred overnight at room temperature. The solution was filtered to remove more residual KBr, and CH₂Cl₂ was removed in vacuo. The crude product was recrystallized from CH₂Cl₂ and hexanes. The green crystalline product was isolated in 61% yield (0.2504 g). Large green crystals suitable for single-crystal X-ray diffraction were grown from the same recrystallization mixture at -35°C. UV–vis (CH_2Cl_2 ; λ_{max} , nm (ϵ , cm⁻¹ M⁻¹)): 315 (3820), 778 (153). Anal. Calcd for $\{\{K(18C)\}[Cu(OC(CH_3)(CF_3)_2)_3]\},\$ KC24H33O9F18Cu: C, 31.67; H, 3.65; F, 37.57. Found: C, 31.69; H, 3.47; F, 35.36. The fluorine analysis is likely low due to incomplete F combustion. μ_{eff} (Evans method, CD_2Cl_2) = 1.95 μ_{B} .

Synthesis of K[Cu(OC(C₆H₅)(CF₃)₂)₃] (3). A solution of KOC- $(C_6H_5)(CF_3)_2$ (0.2101 g, 0.744 mmol) was added to an orange-brown slurry of CuBr₂ (0.0810 g, 0.363 mmol) in THF. The reaction mixture turned cloudy brown-green and was stirred at room temperature overnight. The cloudy brown-green solution was filtered through Celite to remove KBr and triturated three times with CH₂Cl₂. The brown solution was stirred in CH₂Cl₂ for 3 h and filtered to remove more residual KBr, and CH2Cl2 was removed in vacuo. The crude product was recrystallized from CH2Cl2 and hexanes at -35 °C. Recrystallization resulted in yellow blocks coated in dark oil, and they were extracted and washed with a mixture of hexanes and CH_2Cl_2 (80/ 20) and isolated in 3% yield on the basis of Cu (0.0082 g). A small amount of yellow-green crystals suitable for single-crystal X-ray diffraction were grown from the recrystallization mixture at -35 °C. Due to the low yield of the reaction only structural crystallographic characterization is provided at this time.

Synthesis of $\{K(18C6)\}[K_2\{Cu(OC(C_6H_5)(CF_3)_2)_2\}_3]$ (4). A solution of $KOC(C_6H_5)(CF_3)_2$ (0.3952 g, 1.40 mmol) was added to an orange-brown slurry of CuBr₂ (0.1036 g, 0.464 mmol) in THF. The reaction mixture turned cloudy brown-green and was stirred at room temperature overnight. The cloudy brown-green solution was filtered through Celite to remove KBr and triturated three times with CH₂Cl₂. A solution of 18C6 (0.0371 g, 0.140 mmol) in CH₂Cl₂ was added, the resultant brown solution was stirred for 3 h and filtered to remove more residual KBr, and CH2Cl2 was removed in vacuo. The crude product was recrystallized from CH2Cl2 and hexanes at -35 °C for several days. Recrystallization resulted in large colorless blocks coated in dark oil. The crystals were extracted, washed with a mixture of hexanes and CH₂Cl₂ (80/20), and isolated in 13% yield based on Cu (0.0408g). Large colorless crystals suitable for single-crystal X-ray diffraction were then grown at -35 °C. UV-vis (THF; λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 212 sh, (39,850), 244, (10,700). Anal. Calcd for {{K(18C6)} K_2 [Cu(OC(C₆H₅)(CF₃)₂]₃}, $K_3C_{66}H_{54}O_{12}F_{36}Cu_3$: C, 39.03; H, 2.68; 33.68. Found: C, 39.05; H, 2.45; F, 33.48. ¹H NMR (δ , ppm, CD₂Cl₂): 3.63 (s, 24H, -CH₂); 7.18 (dd, J = 7.6, 7.6 Hz, $12H_{1}H_{b}$; 7.26 (t, J = 7.6 Hz, 6H, H_{c}); 7.88 (d, J = 7.6 Hz, $12H_{1}H_{a}$). ¹⁹F NMR (δ , ppm, CD₂Cl₂): -75.49 (s).

Synthesis of {K(18C6)}[Cu(OC(C_6H_4)(CF₃)₂)₂] (5). A solution of KOC(C_6H_5)(CF₃)₂ (0.7688 g, 2.72 mmol) was added to an orangebrown slurry of CuBr₂ (0.2011 g, 0.900 mmol) in THF. The reaction mixture turned cloudy brown-green and was stirred at room temperature overnight. The cloudy brown-green solution was filtered through Celite to remove KBr. A solution of 18C6 (0.2380 g, 0.9011 mmol) in THF was added, the resultant green-brown solution was stirred for 3 h and filtered to remove more residual KBr, and THF was removed in vacuo. The resulting green-brown oil was triturated three times with diethyl ether. The product was dissolved in diethyl ether, and the green solution was decanted. Yellow powders were then recrystallized from THF and diethyl ether. Recrystallization resulted in large yellow plates, which were isolated in 10% yield based on Cu (0.0512 g). Large yellow crystals suitable for single-crystal X-ray diffraction were then grown at -35 °C. UV-vis (THF; λ_{max} nm (ε , M⁻¹ cm⁻¹)): 212 sh (24350), 249 (2523), 385 (251). Anal. Calcd for {{K(18C6)}[Cu(OC(C₆H₄)(CF₃)₂)₂]}, KC₃₀H₃₂O₈F₁₂Cu: C, 42.32; H, 3.79; F, 26.78. Found: C, 42.53; H, 3.98; F, 26.53. ¹H NMR (δ, ppm, d_8 -THF): 3.53 (s, 24H); 6.87 (dd, ${}^{4}J_{c'} = 7.3$ Hz, ${}^{3}J_{c'} = 14.6$ Hz, 2H, $H_{c'}$); 6.96 (dd, ${}^{4}J_{b'}$ = 7.3 Hz, ${}^{3}J_{b'}$ = 14.6 Hz, 2H, $H_{b'}$); 7.04 (dd, ${}^{4}J_{d'}$ = 1.4 Hz, ${}^{3}J_{d'}$ = 7.3 Hz, 2H, H_d); 7.44 (br d, J = 8.0 Hz, 2H, H_{a'}). ¹H NMR resonances were assigned according to results of a ¹H-¹H COSY spectrum (Figure S10, Supporting Information). 13 C NMR (δ , ppm, d_{s} -THF): 71.09 (s, $C_{12}H_{24}O_{6}$); 124.06 (s, C_{d}); 125.68 (s, $C_{c'}$); 127.70 (s, $C_{b'}$); 133.05 (s, $C_{a'}$); 154.49 (s, $OC(ipso-C_6H_4)(CF_3)_2$); 176.00 (s, OC(ortho-metalated-C₆H₄)(CF₃)₂). ¹³C NMR signals were assigned according to the results of a ${}^{1}H^{-13}C$ HSQC spectrum (Figure S11, Supporting Information). ¹⁹F NMR (δ , ppm, d_8 -THF): -75.76 (s).

ASSOCIATED CONTENT

S Supporting Information

Figures, tables, and CIF files, X-ray crystallographic data, ¹H NMR, ¹⁹F NMR, UV–vis, ¹H–¹H COSY, and ¹H–¹³C HSQC spectra, and Cambridge Structural Database search parameters. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC files 911310 (2), 911311 (3), 911312 (4), and 911315 (5) also contain supplementary crystallographic data for this paper. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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Notes

The authors declare no competing financial interest.

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