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Single-Electron Oxidation of Monomeric Copper(I) Alkyl Complexes: Evidence for Reductive Elimination through Bimolecular Formation of Alkanes

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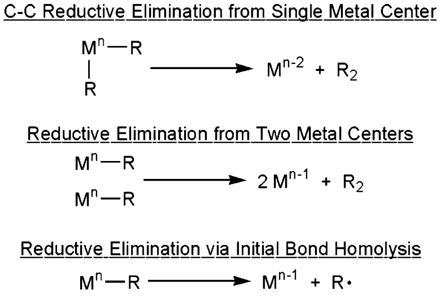
Monomeric Cu(I) alkyl complexes (NHC)Cu(R) (NHC = *N*-heterocyclic carbene; R = Me or Et) and (dtbpe)Cu(Me) (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) have been prepared, isolated, and characterized. Single-electron oxidation of the Cu(I) alkyl complexes upon reaction with AgOTf to form putative Cu(II) intermediates of the type $[(L)Cu(R)]^+$ (L = NHC or dtbpe, R = Me or Et) results in the rapid production of (L)Cu(X) (X = OTf) and R_2. Experimental studies suggest that the reductive elimination of R_2 from Cu(II) occurs through a nonradical bimolecular mechanism. Computational studies of the $Cu-C_{methyl}$ yield bond dissociation enthalpies of $[(SIPr)Cu-CH_3]^{n+}$ (80 kcal/mol for $n = 0$ {Cu(I)} and 38 kcal/mol for $n = 1$ {Cu(II)}).

Introduction

In the area of homogeneous catalysis, the development of well-defined and selective catalytic cycles often requires access to even-electron transformations in preference to odd-electron radical processes. Therefore, relatively strong M−C bonds can be desirable for organometallic systems, and understanding the factors that control M−C bond dissociation enthalpies (BDEs) as well as other metal−ligand BDEs is of fundamental importance.[1−7] In addition to the propensity of a system to initiate M−C bond homolysis and radical chemistry, the mechanism of C−C reductive elimination processes depends on M−C bond energies. For example, the net reductive elimination of M−C bonds can proceed by direct C−C bond formation from a single metal center (formal two-electron reduction of the metal), C−C elimination from two metal centers (formal single-electron reduction of each metal), or initial metal−carbon bond homolysis (formal single-electron reduction of the metal; Scheme 1).[5,8−24]

Scheme 1. Possible Pathways for Elimination of Metal−Carbon Bonds



Copper complexes have played a prominent role in homogeneous catalysis and metal-mediated synthesis of organic molecules.[25−28] Despite the substantial utility of copper com-

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plexes and the integral role of transition metal complexes that possess metal−alkyl or metal−aryl ligands in the field of homogeneous catalysis, the number of copper hydride, alkyl, or aryl complexes that are isolable and well-defined are few, and this is especially true of monomeric systems.[29−32] Copper systems that possess Cu−R (R = alkyl or aryl) or Cu−H bonds are often highly reactive substrates. The reduction of Cu(II) halides with tetraalkyllead has been studied, which may involve Cu(II) alkyl systems.[33] Whitesides et al. have studied the mechanism of decomposition of Cu(I) alkyl complexes in the presence of phosphine ligands,[34,35] and, most germane here, the elimination of alkanes upon reaction of dialkylcuprates with molecular oxygen has been explored.[36]

Recently, Sadighi et al. have reported the synthesis, isolation, and full characterization of the two-coordinate Cu(I) methyl complex (IPr)Cu(Me) (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene).[30] Given the diversity of reactivity available for the Lewis acidic Cu(II) oxidation state, we became interested in exploring the possible preparation of Cu(II) alkyl complexes. To our knowledge, no isolable Cu(II) alkyl complexes have been reported. Herein, we report that single-electron oxidation of a series of two-coordinate Cu(I) complexes of the type (NHC)-Cu(R) (NHC = *N*-heterocyclic carbene, R = methyl or ethyl) and the three-coordinate complex (dtbpe)Cu(Me) {dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane} results in the formation of unstable systems that rapidly undergo reductive elimination of the alkyl ligand to return to the Cu(I) oxidation state.

Results and Discussion

Synthesis of Copper(I) Complexes. The complexes (SIPr)-Cu(OAc) (**1**) and (IMes)Cu(OAc) (**2**) (SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) can be prepared in reactions analogous to the synthesis of (IPr)Cu(OAc).[30] Complexes **1** and **2** have been characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. In addition, single-crystal X-ray diffraction studies of **1** and **2** have confirmed their identity (Figures 1 and 2 and Table 1). Other examples of structural characterization of Cu−carboxylate complexes, including both Cu(I) and Cu(II) oxidation states, have been reported.[30,37−44]

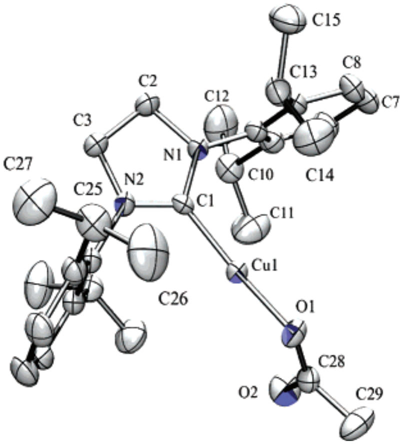

Figure 1. Partially labeled ORTEP of (SIPr)Cu(OAc) (**1**) at 30% probability (hydrogen atoms omitted). Selected bond distances (Å): Cu1−O1 1.838(2), Cu1−C1 1.886(3), O1−C28 1.276(4), O2−C28 1.222(6), C1−N1 1.322(6), C1−N2 1.324(6), C2−C3 1.512(8). Selected bond angles (deg): C1−Cu1−O1 172.5(2), Cu1−O1−C28 125.3(3), O1−C28−O2 125.2(4), O1−C28−C29 120.2(4), Cu1−C1−N2 126.5(3), Cu1−C1−N1 124.4(4), N1−C1−N2 109.1(3).

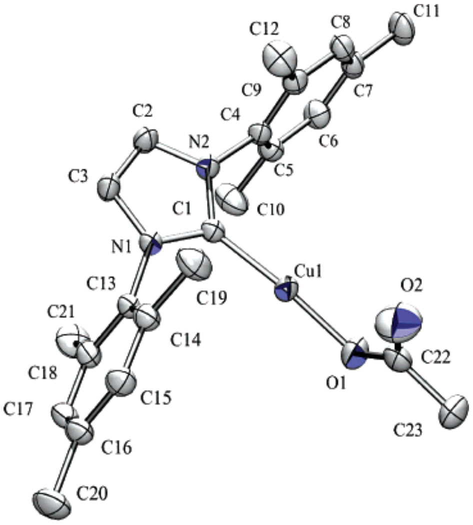

Figure 2. ORTEP of (IMes)Cu(OAc) (**2**) at 30% probability (hydrogen atoms omitted). Selected bond distances (Å): Cu1−O1 1.867(3), Cu1−C1 1.859(3), O1−C22 1.233(5), O2−C22 1.223(6), C1−N1 1.354(3), C1−N2 1.356(3), C2−C3 1.349(4). Selected bond angles (deg): C1−Cu1−O1 171.1(1), Cu1−O1−C22 116.3(3), O1−C22−O2 124.4(4), O1−C22−C23 117.0(4), Cu1−C1−N2 127.6(2), Cu1−C1−N1 128.8(2), N1−C1−N2 103.5(2).

The structures of **1** and **2** reveal nearly linear C1−Cu1−O1 linkages with bond angles of 172.5(2)° and 171.1(1)°, respectively. The Cu−O bond distance of **1** is 1.838(2) Å, while that of **2** is 1.867(3) Å. Thus, the Cu−O bond distances differ by 0.029(4) Å, with the bond length for the SIPr complex **1** being shorter. As previously reported,[30] (IPr)Cu(OAc) exhibits a Cu−O bond distance of 1.850(3) Å, which is intermediate between **1** and **2**. Similar to (IPr)Cu(OAc), the acetate ligands

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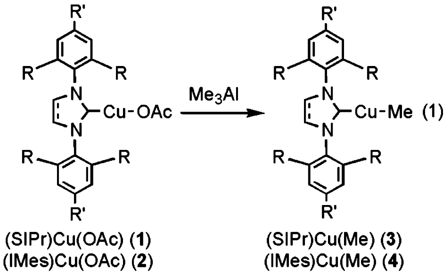
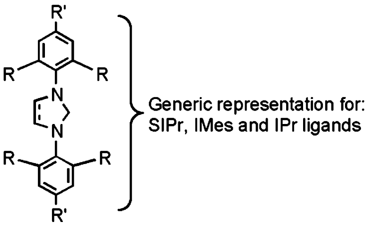
Table 1. Selected Crystallographic Data and Collection Parameters for (SIPr)Cu(OAc)-C_6H_6 (1-C_6H_6), (IMes)Cu(OAc) (2), (dtbpe)Cu(OAc) (5), and (IPr)Cu(OTf) (7)

	1−C_6H_6	**2**	**5**	**7**
empirical formula	$C_{35}H_{47}CuN_2O_2$	$C_{23}H_{27}CuN_2O_2$	$C_{20}H_{43}CuO_2P_2$	$C_{28}H_{36}CuF_3N_2O_3S$
fw	591.29	427.01	441.02	601.19
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a, Å	10.1166(9)	9.4280(6)	15.1868(9)	10.5522(5)
b, Å	16.599(2)	20.037(1)	15.6168(9)	14.2330(7)
c, Å	10.980(1)	11.9928(8)	16.027(1)	20.448(1)
α, deg			98.396(1)	
β, deg	110.600(2)	104.074(1)	98.581(1)	
γ, deg			99.305(1)	
V (Å^3)	1725.9(3)	2197.6(2)	3652.4(4)	3071.1(3)
Z	2	4	6	4
D_{calcd}, g cm^{-3}	1.138	1.291	1.203	1.300
cryst size (mm)	0.12 × 0.14 × 0.50	0.32 × 0.40 × 0.58	0.36 × 0.38 × 0.40	0.25 × 0.38 × 0.40
R_1, wR_2 $\{I > 2\sigma(I)\}$	0.0593, 0.1361	0.0565, 0.1591	0.0434, 0.1122	0.0453, 0.1050
GOF	1.013	1.031	1.035	1.009

of **1** and **2** both exhibit a κ^1-coordination mode, and Sadighi et al. have suggested the possibility that the preferred κ^1-coordination mode (in preference to the κ^2-coordination mode) is the result of an intermolecular interaction between the distal oxygen and a hydrogen of a second carbene ligand.[30] The distance between Cu and the distal oxygen is shorter for the IMes complex **2** (2.831 Å) than for the SIPr complex **1** (3.082 Å) but is similar to that of (IPr)Cu(OAc) {2.868(4) Å}. The similar bond distances of **2** and (IPr)Cu(OAc) suggest that electronic effects of the carbene ligand likely govern the interaction, a result supported by density functional calculations on (NHC)-Cu(acetate), which show conversion of the acetate ligand from κ^2 to κ^1 upon energy minimization, presumably driven by the stability of linear, two-coordinate geometries for d^{10}-Cu(I). If steric effects were dominant, it is anticipated that (IPr)Cu(OAc) and (SIPr)Cu(OAc) (**1**) would exhibit more structural similarity. Furthermore, space-filling diagrams for **1** and **2** (taken from the X-ray structures) suggest more facile access to the Cu center for complex **2** relative to complex **1** (Figure 3).

The reaction of **1** or **2** with $AlMe_3$ produces (SIPr)Cu(Me) (**3**) and (IMes)Cu(Me) (**4**), respectively (eq 1). The Cu(I) methyl complexes have been characterized by ^{1}H and ^{13}C NMR spectroscopy. The methyl groups resonate as singlets at −0.61 ppm for **3** and −0.28 ppm for **4** in the ^{1}H NMR spectrum, which are similar to the resonance at −0.49 ppm for the previously reported complex (IPr)Cu(Me) {IPr = 1,3-bis(2,6)-diisopropylphenyl)imidazol-2-ylidene}.





The combination of dtbpe and Cu(OAc) yields (dtbpe)Cu(OAc) (**5**) in 66% isolated yield. An X-ray diffraction study of a single crystal of **5** revealed three independent molecules in the crystallographic asymmetric unit. An ORTEP of one molecule is depicted in Figure 4, and data collection and structure solution parameters are given in Table 1. In contrast to the (NHC)Cu(OAc) complexes (see above), in all three molecules, the acetate ligand of **5** is coordinated in a κ^2-mode with varying degrees of asymmetry. The Cu−O bond distances of **5** are substantially elongated (average of 2.146 Å) compared with the Cu−O bond distances of complexes **1** {1.838(2) Å} and **2** {1.867(3) Å}. For the three independent molecules in the solid-state structure of **5**, the Cu−O bond distances are

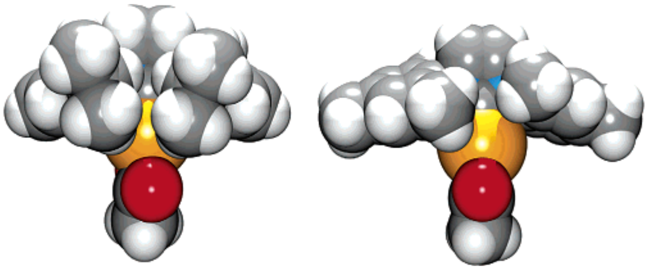


Figure 3. Space-filling diagrams for (SIPr)Cu(OAc) (**1**) (depicted on the left) and (IMes)Cu(OAc) (**2**) (depicted on the right) with view from above the NHC plane.

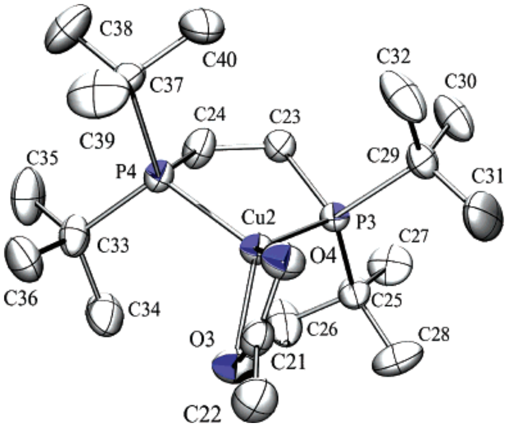


Figure 4. Labeled ORTEP of (dtbpe)Cu(OAc) (**5**) at 30% probability (hydrogen atoms omitted). Selected bond distances (Å): Cu2−O3 2.121(2), Cu2−O4 2.172(2), Cu2−P3 2.2358(7), Cu2−P4 2.2529(8), C21−O3 1.254(4), C21−O4 1.240(3), C21−C22 1.515(4). Selected bond angles (deg): Cu2−O4−C21 88.0(2), Cu2−O3−C21 90.0(2), O3−C21−O4 121.2(2), O3−C21−C22 119.5(3), O4−C21−C22 119.4(3), P3−Cu2−P4 95.87(3), O3−Cu2−O4 60.78(8), P3−Cu2−O3 131.26(7), P4−Cu2−O3 119.32(7), P4−Cu2−O4 122.49(7).

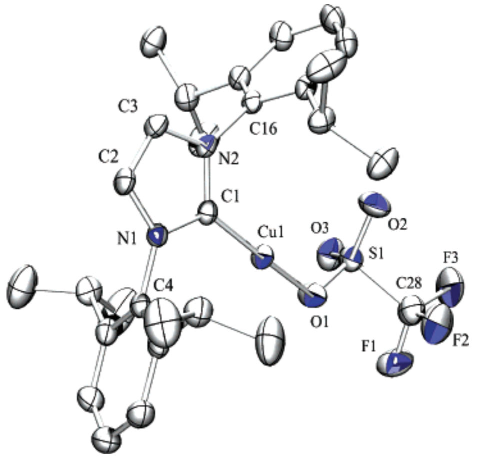
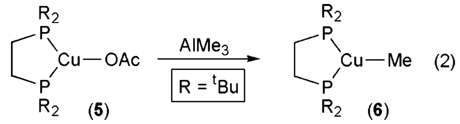


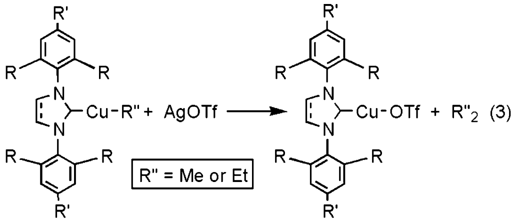
Figure 5. Partially labeled ORTEP of (IPr)Cu(OTf) (**7**) at 30% probability (hydrogen atoms omitted). Selected bond distances (Å): Cu1−O1 1.875(2), Cu1−C1 1.863(3), O1−S1 1.469(3), O2−S1 1.423(3), O3−S1 1.405(3), C1−N1 1.353(4), C1−N2 1.346(4). Selected bond angles (deg): C1−Cu1−O1 175.6(1), Cu1−O1−S1 121.9(1), O1−S1−C28 100.2(2), O1−S1−O3 112.6(2), O1−S1−O2 113.8(2).

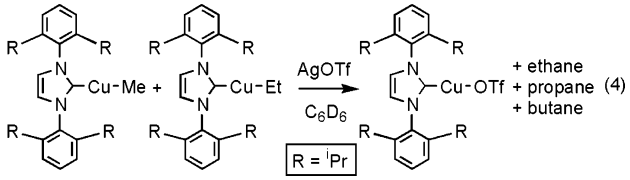
2.078(2)/2.270(2) Å (Δbond length = 0.192 Å), 2.121(2)/2.172(2) Å (Δbond length = 0.051 Å), and 2.086(2)/2.246(2) Å (Δbond length = 0.16 Å).

In a fashion similar to the NHC complexes, the reaction of **5** with $AlMe_3$ produces (dtbpe)Cu(Me) (**6**) (eq 2). The methyl ligand of **6** resonates as a broad singlet at 0.35 ppm in the ^1H NMR spectrum, while the ^{13}C NMR spectrum reveals a broad singlet at −7.1 ppm.



Oxidation of Copper(I) Methyl Complexes. Reaction of the previously reported (IPr)Cu(Me) with AgOTf should provide access to single-electron transfer to produce the Cu(II) species [(IPr)Cu(Me)][OTf] and Ag(s). The combination of these two reagents in sealed NMR tubes in C_6D_6 cleanly produces the complex (IPr)Cu(OTf) (**7**) and ethane (as determined by ^1H NMR spectroscopy) within 5 min at room temperature (eq 3). Jordan et al. have reported that reactions of Zr(IV) alkyl complexes with Ag(I) salts result in "redox cleavage" of Zr−alkyl bonds.[45,46] Although the preparation of complex **7** has been previously reported,[47] single crystals were grown for a solid-state X-ray diffraction study (Figure 5, Table 1). The triflate ligand is coordinated through a single oxygen atom with a Cu1−O1 bond distance of 1.875(2) Å. As anticipated for two-coordinate Cu(I), the C1−Cu1−O1 linkage is nearly linear, with a bond angle of 175.6(1)°. For the reaction of (IPr)Cu(Me) and AgOTf, the singlet due to ethane appears at 0.82 ppm. A minor resonance slightly above the noise threshold consistent with CH_4 is also detected. The source of the hydrogen atom to yield CH_4 is unknown. Neither performing the reaction in the presence of the radical trap 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) nor using toluene-d_8 as solvent substantially alters the reaction. After 10 min of reaction time, a ^1H NMR spectrum of a C_6D_6 solution of (IPr)Cu(Me) and 0.5 equiv of AgOTf reveals the formation of ethane and an approximately 1:1 molar ratio of (IPr)Cu(Me) and complex **7**. The combination of the previously reported ethyl complex (IPr)Cu(Et) and AgOTf in C_6D_6 produces (IPr)Cu(OTf) and butane as the primary products. Identical observations are made for reactions of (SIPr)Cu(Me) (**3**) and (IMes)Cu(Me) (**4**) with AgOTf in either C_6D_6 or toluene-d_8. The ^1H NMR spectrum of a C_6D_6 solution of (IPr)Cu(Me), (IPr)Cu(Et), and AgOTf (1:1:2 molar ratio) reveals resonances consistent with the production of ethane, propane, and butane as well as (IPr)Cu(OTf) (eq 4).





The observations upon reaction of Cu−methyl complexes with single-electron oxidants are consistent with a reaction pathway that involves initial oxidation of Cu(I) to the unobserved (even at low temperatures) Cu(II) systems [(NHC)Cu(R)][OTf] followed by net reductive elimination of R to reduce Cu(II) to Cu(I). Consistent with a reaction pathway that involves initial single-electron transfer to form Cu(II) and elemental Ag, the combination of (IPr)Cu(Me) and $[Cp_2Fe][PF_6]$ in C_6D_6 produces Cp_2Fe (singlet at ∼4.0 ppm in the ^1H NMR spectrum), ethane, and a single IPr−Cu complex that is likely (IPr)Cu(FPF_5) or [(IPr)Cu(η^2-benzene)][PF_6]. A ^{19}F NMR spectrum of the latter product reveals only a doublet at −68 ppm ($^1J_{FP}$ = 709 Hz). Thus, the PF_6 anion remains intact and is not ruptured to form a Cu−fluoride complex and PF_5. Although the reaction of (IPr)Cu(Me) with ferrocenium demonstrates that outer-sphere electron transfer to form $[(IPr)Cu(Me)]^+$ followed by C−C reductive elimination is a viable pathway, it does not definitely eliminate the possibility of forming Ag(I) alkyl complexes upon reaction of (NHC)Cu(R) systems with AgOTf. However, the decomposition of Ag(I) methyl and ethyl systems has been reported to occur via Ag−C bond homolysis and to produce olefins as well as alkanes,[48] observations that are inconsistent with the transformations involving the (NHC)Cu(R) systems (see below). Thus, it is likely that reaction of AgOTf with (NHC)Cu(R) complexes is proceeding through outer-sphere single-electron transfer to form unobserved $[(NHC)Cu(R)]^+$ intermediates. The subsequent reductive elimination of alkane to re-form Cu(I) likely involves either an initial Cu−C bond homolysis or bimetallic reductive elimination from two metal centers.

We have previously demonstrated that oxidation of Ru(II) complexes of the type TpRu(L)(L′)Me (L, L′ = neutral, two-electron-donating ligands) to Ru(III) in deuterated solvents results in rapid reduction to the Ru(II) systems TpRu(L)(L′)-

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[46] Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111−4113.

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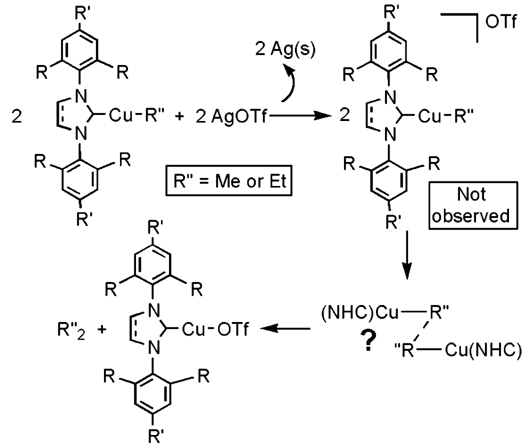
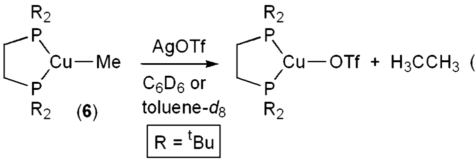
Scheme 2. Proposed Pathway for Conversion of (NHC)Cu(R) and AgOTf to R_2 and (NHC)Cu(OTf) Involves Initial Oxidation to Cu(II) and Bimetallic Elimination of R_2 (NHC = *N*-Heterocyclic Carbene)



OTf with production of CH_3D and perprotio ethane.[49] These transformations likely proceed through a facile Ru−C bond homolysis, as indicated by substantial production of CH_3D in toluene-d_8 {weak benzylic C−H(D) bond increases methane production} and the lack of production of methane/ethane in the presence of radical traps such as TEMPO. *In contrast, regardless of whether the reaction is performed in C_6D_6 or toluene-d_8, oxidation of the copper systems and return to Cu(I) produces predominantly ethane (or butane in the case of R = ethyl) with no evidence for formation of CH_3D. Also, the addition of TEMPO does not alter the reactivity. Thus, a bimetallic pathway for alkane elimination seems likely (Scheme 2).* We currently have no evidence that suggests the nature of the putative bimetallic system that likely precedes alkane elimination.

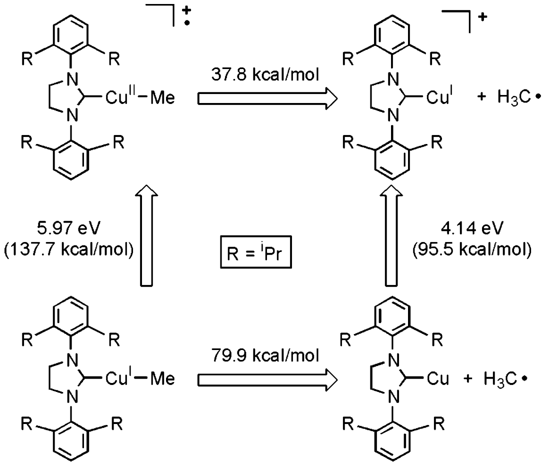
Similar to the (NHC)Cu(Me) complexes, at room temperature the reaction of AgOTf and (dtbpe)Cu(Me) (**6**) in C_6D_6 produces ethane and a diamagnetic Cu complex consistent with (dtbpe)Cu(OTf) (eq 5). Nearly identical observations are made for the analogous reaction in toluene-d_8. In contrast to oxidation of (NHC)Cu(Me) systems, no evidence for formation of methane is observed for the oxidation of complex **6**. Thus, the results are consistent with initial oxidation of complex **6** to the Cu(II) complex [(dtbpe)Cu(Me)][OTf] followed by elimination of ethane to produce (dtbpe)Cu(OTf) in a transformation that does not likely involve Cu−C bond homolysis.



(5)

Computational Results. We have studied the Cu−C BDEs of (SIPr)Cu(Me) and $[(SIPr)Cu(Me)]^+$ using B3LYP/6-31G(d) calculations on the full SIPr models (Scheme 3). At the Cu(I) oxidation state, the Cu−Me bond possesses substantial strength with a calculated BDE of 80 kcal/mol. This value represents a relatively strong metal−carbon (alkyl) bond and may reflect substantial covalent nature for the relatively electronegative transition metal coordinated to a methyl ligand. The calculations reveal that oxidation of the Cu(I) (d^{10}, 14-electron complex) complex (SIPr)Cu(Me) (**3**) to the Cu(II) (d^9, 13-electron complex) system $[(SIPr)Cu(Me)]^+$ significantly decreases the homolytic $Cu-C_{methyl}$ BDE from 80 kcal/mol to 38 kcal/mol. This represents a 53% reduction in BDE upon single-electron oxidation. In comparison, we have recently reported that oxidation of the octahedral Ru(II) (d^6, 18-electron complex) TpRu(CO)(NCMe)(Me) (Tp = hydridotris(pyrazolyl)borate) to the Ru(III) (d^5, 17-electron complex) is calculated to reduce the $Ru-C_{methyl}$ BDE from 49 kcal/mol to 23 kcal/mol, which is an approximately 52% reduction in BDE.[49] *Thus, for two seemingly disparate systems, single-electron oxidation decreases the BDE by a remarkably similar magnitude.* In addition to the calculated decrease in BDE upon conversion of $(SIPr)Cu^I(Me)$ (**3**) to $[(SIPr)Cu^{II}(Me)]^+$ of 42 kcal/mol, the ionization potential of $(SIPr)Cu^I(Me)$ (**3**) (5.97 eV) is calculated to be approximately 1.83 eV (42 kcal/mol) higher than that of (SIPr)Cu (4.14 eV). The calculated $Cu-C_{Me}$ vibrational frequencies for $[(SIPr)Cu^{II}(Me)]^+$ and $(SIPr)Cu^I(Me)$ are nearly identical, ca. 572 cm^{-1}. The calculated $Cu-C_{Me}$ bond lengths are also roughly equivalent, 1.896 Å for the Cu(II) complex and 1.909 Å for the Cu(I) complex **3**, a variation commensurate with literature values for ionic radii differences for both tetrahedral and octahedral Cu(II) and Cu(I) ions [$\Delta r_{ion}\{Cu(I/II)\} \approx 0.03-0.04$ Å].[50] Hence, the computations suggest the possibility that both copper−methyl complexes have intrinsically similar copper−methyl bond thermodynamics and that the lower BDE for the Cu(II)−methyl complex primarily reflects formation of a stable Cu(I) complex upon scission of $[(SIPr)Cu^{II}(Me)]^+$.

Scheme 3. B3LYP/6-31G(d)-Calculated $Cu-C_{methyl}$ Bond Dissociation Enthalpies and Ionization Potentials for $(SIPr)Cu^I(Me)$ (3) (bottom) and $[(SIPr)Cu^{II}(Me)]^+$ (top)



Summary and Conclusions. Transition metal alkyl linkages are often unstable for paramagnetic complexes, and this is largely attributable to an increased predilection toward M−C bond homolysis that results from decreased M−C BDEs. As an example, we recently reported that single-electron oxidation of thermally stable Ru(II) complexes of the type TpRu(L)(L′)R to Ru(III) complexes $[TpRu(L)(L')R]^+$ results in reactivity that is attributable to rapid Ru−C homolysis.[49] These results are consistent with the scarcity of isolable Ru(III) methyl complexes, examples of which are primarily limited to systems with porphyrin ligands that are strongly donating and potentially capable of delocalizing radical spin density. In addition, a recent report by Caulton et al. details the incorporation of a chelating amido ligand to stabilize a Ru(III) dialkyl complex, and similar to the

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Ru(III) porphyrin complexes, the persistence of the Ru(III) dialkyl system is likely attributable to a combination of amido-to-metal donation and delocalization of radical character, steric protection from the ligand set, and low-coordination number.[7,23,51]

Similar to our previous observations with TpRu(L)(L′)R systems, calculations suggest that single-electron oxidation of the even-electron Cu(I) methyl complexes to odd-electron Cu(II) complexes renders the Cu−C bonds easier to break. However, in contrast to observations made for $[\mathrm{TpRu^{III}(L)(L')R}]^+$ systems,[49] the Cu(II) methyl complexes appear to undergo decomposition through a pathway that does not involve metal−carbon bond homolysis to generate a radical species. Rather, we propose a bimolecular pathway that results in the elimination of ethane (or butane for Cu−Et bonds) and reduction of two metal centers, each by a single electron. In each case in deuterated solvents, a *small* amount of CH_4 is potentially formed with no evidence for the formation of CH_3D, which likely indicates that C−H reductive elimination from the putative bimolecular copper species is also possible. Although oxidation from Cu(I) to Cu(II) apparently decreases the Cu−C BDEs by a similar magnitude compared to the TpRu systems, the initial metal−carbon BDE for $\mathrm{Cu^{I}{-}C}$ is calculated to be approximately 31 kcal/mol more substantial (or, ∼64% greater) than the $\mathrm{Ru^{II}{-}C}$ BDE. Thus, even though oxidation of Cu(I) to Cu(II) results in less stable complexes, the corresponding Cu(II)−C bonds apparently remain strong enough to kinetically suppress Cu−C bond homolysis and are, in fact, calculated to be only 11 kcal/mol weaker ($\mathrm{Cu^{II}{-}C}$ BDE ≈ 38 kcal/mol) than the BDE of the stable (at room temperature) TpRu(CO)(NCMe)Me ($\mathrm{Ru^{II}{-}C}$ BDE ≈ 49 kcal/mol) complex. Similar to Ru(III) systems (see above), the incorporation of donating ancillary ligands capable of spin delocalization may allow isolation of relatively stable Cu(II) alkyl or aryl complexes and access to reactivity from these species.

Experimental Section

General Methods. All procedures were performed in a glovebox under an inert atmosphere of dinitrogen or using standard Schlenk techniques. The glovebox atmosphere was maintained by periodic nitrogen purges and monitored by an oxygen analyzer $\{O_2(g) < 15\ \mathrm{ppm}$ for all reactions$\}$. Benzene, toluene, THF, and hexanes were purified by reflux over sodium followed by distillation. Diethyl ether was used as received. Benzene-d_6 and toluene-d_8 were distilled over sodium, degassed by three freeze−pump−thaw cycles, and stored over 4 Å molecular sieves. All reactions performed on an NMR scale utilized J-Young NMR tubes with Teflon screw caps or in NMR tubes sealed with rubber septa. ^1H and ^{13}C NMR measurements were performed on either a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer (operating frequencies for ^{13}C NMR spectra were 100 and 75 MHz, respectively) and referenced to TMS using resonances due to residual protons in the deuterated solvents (^1H NMR) or the ^{13}C resonances of the deuterated solvents. ^{19}F spectra were recorded on a Varian Mercury instrument operating at a frequency of 376.5 MHz with C_6F_6 as external standard. Elemental analyses were performed by Atlantic Microlabs, Inc. Trimethylaluminum in hexanes, TEMPO, silver triflate, ferrocenium hexafluorophosphate, and anhydrous ethanol were obtained from Sigma Aldrich, Cu(I) acetate was obtained from Strem Chemical, and these reagents were used as received. The ligands IMes, SIPr, and dtbpe as well as the complexes (IPr)Cu(OAc), (IPr)Cu(Me), (IPr)Cu(Et), and (IPr)Cu(OTf) were prepared according to literature procedures.[30,47,52−54]

(SIPr)Cu(OAc) (1). A round-bottom flask was charged with SIPr (0.177 g, 0.500 mmol), Cu(OAc) (0.059 g, 0.50 mmol), and toluene (15 mL), and the resulting solution was stirred for 2 h at room temperature. The solution was filtered through Celite, approximately half of the solvent was removed in vacuo, and hexanes were added to form a white precipitate. The solid was collected by vacuum filtration and dried in vacuo (0.165 g, 64%). Crystals suitable for a solid-state X-ray diffraction study were grown at room temperature by slow diffusion of pentane into a benzene solution of **1**. ^1H NMR (C_6D_6, δ): 7.16−7.12 (overlapping with solvent peak, 2H, *para*-CH of aryl group), 7.04 (d, $^3J_{HH} = 7$ Hz, 4H, *meta*-CH), 3.16 (s, 4H, NC*H*), 2.99 (sept, $^3J_{HH} = 6$ Hz, 4H, C*H*(CH_3)$_2$), 1.90 (s, 3H, CO_2CH_3), 1.53 (d, $^3J_{HH} = 7$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH} = 7$ Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, δ): 204.8 (N*C*Cu), 147.2, 135.4, 130.4, 125.0, 112.1 (aryl of SIPr ligand and N*C*H), 29.5 {*C*H(CH_3)$_2$}, 25.9 {CH(*C*H$_3$)$_2$}, 24.3 (CH(*C*H$_3$)$_2$). (Note: the resonances due to the carbonyl and methyl groups of the acetate ligand were not observed. For (IPr)Cu(OAc), these resonances are observed at 128.9 and 24.2 ppm, respectively, and they could be coincidental with other observed resonances for complex **1**.) Anal. Calcd for $C_{29}H_{41}CuN_2O$: C, 67.87; H, 8.05; N, 5.46. Found: C, 67.85; H, 8.02; N, 5.45.

(IMes)Cu(OAc) (2). A round-bottom flask was charged with IMes (0.152 g, 0.500 mmol), Cu(OAc) (0.059 g, 0.50 mmol), and toluene (15 mL), and the resulting solution was stirred overnight at room temperature. The solution was filtered through Celite, and approximately half of the solvent was removed in vacuo. Hexanes were added to form a white precipitate. The solid was collected by vacuum filtration and dried in vacuo (0.162 g, 76%). Crystals suitable for a solid-state X-ray diffraction study were grown at room temperature by layering a benzene solution of **2** with pentane. ^1H NMR (C_6D_6, δ): 6.67 (s, 4H, *meta*-CH), 5.97 (s, 4H, NC*H*), 2.06 (s, 6H, *para*-CH_3), 2.05 (s, 3H, CO_2CH_3), 2.02 (s, 12H, *ortho*-CH_3). ^{13}C NMR (C_6D_6, δ): 180.9 (N*C*Cu), 139.5, 136.0, 135.2, 130.0, 122.1 (aryl of IMes ligand and N*C*H), 24.1 (CO_2CH_3), 21.7 (*para*-CH_3), 18.4 (*ortho*-CH_3). (Note: similar to complex **1**, the resonance due to the carbonyl of the acetate ligand for complex **2** was not observed and is presumed to be coincident with a resonance in the range of 120 to 130 ppm.) Anal. Calcd for $C_{23}H_{27}CuN_2O$: C, 64.69; H, 6.37; N, 6.56. Found: C, 65.26; H, 6.36; N, 6.29.

(SIPr)Cu(Me) (3). To a precooled Schlenk flask (−60 °C) charged with (SIPr)Cu(OAc) (**1**) (0.200 g, 0.393 mmol) and diethyl ether (4.0 mL) was added a solution of ether (0.5 mL), $AlMe_3$ (0.5 mL of a 1.0 M solution in hexanes, 1 mmol), and ethanol (60 μL, 1 mmol). The solution was stirred at −60 °C for 1 h followed by an additional hour of stirring at room temperature. Approximately half of the solvent was removed in vacuo, and hexanes were added to form a white precipitate. The solid was collected by vacuum filtration and dried (0.156 g, 84%). To prevent slow decomposition, complex **3** was stored in an inert atmosphere at −20 °C. ^1H NMR (C_6D_6, δ): 7.18 (t, $^3J_{HH} = 7$ Hz, 2H, *para*-CH), 7.08 (d, $^3J_{HH} = 7$ Hz, 4H, *meta*-CH), 3.17 (s, 4H, NC*H*), 3.07 (sept, $^3J_{HH} = 7$ Hz, 4H, C*H*(CH_3)$_2$), 1.52 (d, $^3J_{HH} = 7$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.21 (d, $^3J_{HH} = 7$ Hz, 12H, CH(C*H*$_3$)$_2$), −0.61 (s, 3H, Cu−C*H*$_3$). ^{13}C NMR (C_6D_6, δ): 182.8 (N*C*Cu), 147.3, 136.0, 130.0, 124.8 (phenyl of IPr ligand), 54.0 (N*C*H), 29.5 (*C*H(CH_3)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), −11.6 (Cu*C*H$_3$). Complex **3** decomposes over a period of days under inert atmosphere, and its instability precludes satisfactory elemental analysis.

(IMes)Cu(Me) (4). To a precooled Schlenk flask (−60 °C) charged with (IMes)Cu(OAc) (**2**) (0.168 g, 0.393 mmol) and diethyl ether (4.0 mL) was added a solution of ether (0.5 mL), $AlMe_3$ (0.5 mL of a 1.0 M solution in hexanes, 1 mmol), and ethanol (60 μL, 1 mmol) . The solution was stirred at −60 °C for 1 h, removed from the cold bath, and stirred an additional hour at room temperature. Approximately half of the solvent was removed in

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(51) Alexander, C. S.; Rettig, S. J.; James, B. R. *Organometallics* **1994**, *13*, 2542−2544.

vacuo, and hexanes were added to form a white precipitate. The solid was collected by vacuum filtration and dried (0.115 g, 77%). To prevent slow decomposition, complex **4** was stored in the solid state under an inert atmosphere at −20 °C. ^{1}H NMR (C_6D_6, δ): 6.69 (s, 4H, *meta*-CH), 6.00 (s, 4H, NC*H*), 2.08 (s, 6H, *para*-CH_3), 2.06 (s, 12H, *ortho*-CH_3), −0.28 (s, 3H, Cu−C*H*$_3$). ^{13}C NMR (C_6D_6, δ): 184.7 (N*C*Cu), 139.1, 136.5, 135.1, 129.8, 121.2 (aryl of IMes ligand and N*C*H), 21.4, 18.3 (*C*H$_3$ of IMes ligand), −11.6 (Cu−*C*H$_3$). Complex **4** decomposes over a period of days under inert atmosphere, and its instability precludes satisfactory elemental analysis.

(dtbpe)Cu(OAc) (5). Cu(OAc) (0.293 g, 2.40 mmol) was added to a colorless solution of dtbpe (0.690 g, 2.2 mmol) in THF (20 mL). The solution immediately turned dark brown and was stirred for 4 h, at which time an orange slurry was present. The solution was filtered through Celite to remove the orange solids, and the filtrate was reduced in vacuo to approximately 2 mL. Hexanes (∼10 mL) were added to form a white precipitate, which was collected by vacuum filtration and dried (0.707 g, 76% yield). ^{1}H NMR ($CDCl_3$, δ): 2.02 (s, 3H, OCOC*H*$_3$), 1.77 (vt, $N = 5$ Hz, 4H, methylene C*H*$_2$), 1.20 (vt, $N = 13$ Hz, 36H, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, δ): 178.6 (s, O*C*OCH$_3$), 33.4 (vt, $N = 9$ Hz, *C*(CH$_3$)$_3$), 30.3 (vt, $N = 9$ Hz, C(*C*H$_3$)$_3$), 23.2 (s, OCO*C*H$_3$), 20.6 (vt, $N = 26$ Hz, methylene *C*H$_2$). ^{31}P NMR ($CDCl_3$, δ): 26.4 (s). Anal. Calcd for $C_{20}H_{43}Cu_1O_2P_2$: C 54.46; H 9.83; O 7.26. Found: C 54.39; H 9.97; O 7.20.

(dtbpe)Cu(Me) (6). A slurry of complex **5** (0.578 g, 1.3 mmol) in diethyl ether (10 mL) was stirred in a bath at −60 °C for 30 min. Ethanol (0.2 mL, 3.4 mmol) was added to a solution of 2.0 M $AlMe_3$ (1.7 mL, 3.4 mmol) in ether (5 mL), which bubbled vigorously upon mixing. This solution was slowly added to the solution of **5**, and the resulting solution was stirred at −60 °C for 1 h. After allowing to warm to room temperature, the volatiles were removed in vacuo. A minimal amount of hexanes (approximately 3 mL) was added, resulting in the formation of a precipitate after storage overnight at −20 °C under N_2. The white product was collected by vacuum filtration and dried (0.136 g, 25% yield). ^{1}H NMR (C_6D_6, δ): 1.46 (br s, 4H, C*H*$_2$), 1.09 (vt, $N = 13$ Hz, 36H, C(C*H*$_3$)$_3$), 0.35 (br s, 3H, Cu−C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ): 34.5 (vt, $N = 6$ Hz, *C*(CH$_3$)$_3$), 31.3 (vt, $N = 10$ Hz, C(*C*H$_3$)$_3$), 22.1 (vt, $N = 23$ Hz, methylene *C*H$_2$), −7.1 (br s, Cu*C*H$_3$). ^{31}P NMR (C_6D_6, δ): 33.1 (s). Complex **6** decomposes over a period of days under inert atmosphere, and its instability precludes satisfactory elemental analysis.

(IPr)Cu(OTf) (7). The synthesis and characterization of this complex have been previously reported.[47] X-ray-quality crystals of this complex were grown from a solution of CH_2Cl_2 layered with pentane.

Oxidation of Cu(I) Methyl Complexes. Some representative experiments are given. *(IPr)Cu(Me):* To a colorless solution of (IPr)Cu(Me) (0.010 g, 0.021 mmol) and C_6D_6 (0.5 mL) in an NMR tube sealed with a rubber septum was injected a solution of AgOTf (0.006 g, 0.023 mmol) and C_6D_6 (0.1 mL). The solution immediately turned dark brown. ^{1}H NMR revealed clean formation of one copper complex, identified as (IPr)Cu(OTf), and the organic product ethane. *(SIPr)Cu(Me):* To a colorless solution of (SIPr)Cu(Me) (**3**) (0.010 g, 0.021 mmol) and C_6D_6 (0.5 mL) in an NMR tube sealed with a rubber septum was injected a solution of AgOTf (0.006 g, 0.023 mmol) and C_6D_6 (0.1 mL). The solution immediately turned dark brown. ^{1}H NMR revealed clean formation of one copper complex, identified as (SIPr)Cu(OTf), and ethane. *(SIPr)Cu(Me)* (***3***) *in toluene-d_8:* To a colorless solution of (SIPr)Cu(Me) (**3**) (0.010 g, 0.021 mmol) and toluene-d_8 (0.5 mL) in an NMR tube sealed with a rubber septum was injected a solution of AgOTf (0.006 g, 0.023 mmol) and toluene-d_8 (0.1 mL). The solution immediately turned dark brown. ^{1}H NMR revealed clean formation of one copper complex, identified as (SIPr)Cu(OTf), and ethane. *(dtbpe)Cu(Me)* (***6***)*:* To a colorless solution of (dtbpe)Cu(Me) (**6**) (0.007 g, 0.017 mmol) and C_6D_6 (0.5 mL) in an NMR tube sealed with a rubber septum was injected a solution of AgOTf (0.005 g, 0.024 mmol) and C_6D_6 (0.1 mL). The solution immediately turned dark brown. ^{1}H NMR revealed clean formation of one copper complex, identified as (dtbpe)Cu(OTf), and the organic product ethane. *(IPr)Cu(Et):* To a colorless solution of (IPr)Cu(Et) (0.010 g, 0.021 mmol) and C_6D_6 (0.5 mL) in an NMR tube sealed with a rubber septum was injected a solution of AgOTf (0.006 g, 0.029 mmol) and C_6D_6 (0.1 mL). The solution immediately turned dark brown. ^{1}H NMR revealed clean formation of one copper complex, identified as (IPr)Cu(OTf), and the organic product butane. *(IPr)Cu(Me) with [Cp_2Fe][PF_6]:* To a colorless solution of (IPr)Cu(Me) (0.010 g, 0.021 mmol) and C_6D_6 (0.5 mL) in an NMR tube sealed with a rubber septum was injected a solution of [Cp_2Fe][PF_6] (0.008 g, 0.023 mmol) and C_6D_6 (0.1 mL). The solution immediately turned yellow-orange. ^{1}H NMR revealed clean formation of a single copper complex, likely either (IPr)Cu(PF_6) or (IPr)Cu(F), and the organic product ethane. *(IPr)Cu(Me) with TEMPO:* To an orange-brown solution of (IPr)Cu(Me) (0.010 g, 0.021 mmol), TEMPO (0.017 g, 0.11 mmol), and C_6D_6 (0.5 mL) in an NMR tube sealed with a rubber septum was injected a solution of AgOTf (0.006 g, 0.023 mmol) and C_6D_6 (0.1 mL). The solution immediately turned dark brown. ^{1}H NMR revealed clean formation of one copper complex, identified as (IPr)Cu(OTf), and ethane.

Computational Methods. All calculations were carried out utilizing the Gaussian03 package.[55] The B3LYP functional (Becke's three-parameter hybrid functional[56] using the LYP correlation functional containing both local and nonlocal terms of Lee, Yang, and Parr)[57] and VWN (Slater local exchange functional[58] plus the local correlation functional of Vosko, Wilk, and Nusair[59]) were employed in conjunction with the 6-31G(d) all-electron basis set. Closed-shell (diamagnetic) and open-shell (paramagnetic) species were modeled within the restricted and unrestricted Kohn−Sham formalisms, respectively. All systems were fully optimized without symmetry constraint, and analytic calculations of the energy Hessian were performed to conform species as minima and to obtain enthalpies in the gas phase at 1 atm and 298.15 K.

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Supporting Information Available: Complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for (SIPr)Cu(OAc) (**1**), (IMes)Cu(OAc) (**2**), (dtbpe)Cu(OAc) (**5**), and (IPr)Cu(OTf) (**7**). ^{1}H and ^{13}C NMR spectra of all new Cu methyl complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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