2173.3(3) Å^3, $\rho_{calcd} = 2.139$ g cm^{-3}, $\theta = 2.3-26.0°$. Of 8907 reflections collected, 8523 were independent ($R_{int} = 0.0117$), and 7879 with $I > 2\sigma(I)$, 443 parameters, $R_1 = 0.0326$, wR_2 (all data) = 0.0866. **2**: $C_{72}H_{60}I_8N_4P_4$, space group $C2/c$, $a = 1616.0(1)$, $b = 2493.1(2)$, $c = 1792.1(1)$ pm, $\beta = 96.54(1)°$, $Z = 4$, $V = 7173.1(8)$ Å^3, $\rho_{calcd} = 1.963$ g cm^{-3}, $2\theta = 4.6-50.0°$. Of 6674 reflections collected, 6292 were independent ($R_{int} = 0.0202$), and 5231 with $I > 2\sigma(I)$, 399 parameters, $R_1 = 0.0381$, wR_2 (all data) = 0.0963. **3**: $C_{60}H_{45}F_4I_7N_3P_3$, space group $P\bar{1}$, $a = 933.2(2)$, $b = 1406.6(1)$, $c = 2376.7(2)$ pm, $\alpha = 94.19(1)$, $\beta = 101.15(1)$, $\gamma = 96.89(1)°$, $Z = 2$, $V = 3023.9(7)$ Å^3, $\rho_{calcd} = 2.049$ g cm^{-3}, $\theta = 2.4-25.0°$. Of 11262 reflections collected, 10551 were independent ($R_{int} = 0.0162$), and 8827 with $I > 2\sigma(I)$, 695 parameters, $R_1 = 0.0622$, wR_2 (all data) = 0.1721. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410019 (**1**), CSD-410020 (**2**), and CSD-410018 (**3**).

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Oxidations of C–H and O–H Bonds by Isolated Copper(III) Complexes[**]

Mark A. Lockwood, Teresa J. Blubaugh, Andrea M. Collier, Scott Lovell, and James M. Mayer[*]

Metal-mediated abstractions of hydrogen atoms from C–H and O–H bonds are of interest due to their involvement in metalloenzyme and industrial oxidations. We have shown that metal–oxo complexes oxidize hydrocarbons by a hydrogen-atom abstraction mechanism, which is attributed to their thermodynamic affinity for a hydrogen atom ($\equiv H^+ + e^-$) rather than any radical character within the oxidant.[1] We propose that any metal complex with sufficient affinity for an electron and a proton should exhibit such reactivity. Copper(III) complexes are attracting attention as models for intermediates in copper enzymes such as cytochrome c oxidase and dopamine β-hydroxylase.[2] Proposed catalytic cycles for these and other enzymes involve H-atom abstraction from C–H and/or O–H bonds. Here we report apparent examples of such reactions for two known copper(III) complexes, [Cu(Pre)](ClO$_4$) (**1**-ClO$_4$)[3] and [Cu(H$_{-3}$Aib$_3$)] (**2**).[4] Both complexes are reported to undergo aqueous electrochemical reductions with uptake of one proton [Eq. (1)].

$$\mathrm{Cu^{III}(L) + H^+ + e^- \rightleftarrows Cu^{II}(LH)} \qquad (1)$$

[Cu(Pre)]$^+$ (**1**) oxidizes dihydroanthracene (DHA) to anthracene in 60% yield in CH$_2$Cl$_2$. To our knowledge, this is the first report of intermolecular hydrocarbon oxidation by an isolable copper(III) complex (Scheme 1). Other workers have reported intramolecular ligand C–H bond oxidation in copper(III) compounds,[5] and Karlin et al. have very recently observed intermolecular C–H bond oxidations in a copper complex + O$_2$ system.[6] The disappearance of **1** in the presence of excess DHA at 20 °C, as monitored by optical spectroscopy in the absence of air or light, followed simple second-order kinetics over several half lives with no apparent induction period [$k_2 = 2.0(\pm 0.1) \times 10^{-3}\,\mathrm{M^{-1}s^{-1}}$]. At higher temperatures, the kinetics are increasingly complicated by decomposition of **1** and possibly other reactions. A preliminary Eyring plot (based on k_2 values from 287–328 K) gives $\Delta H^{\neq} \approx 15$ kcal mol^{-1} and $\Delta S^{\neq} \approx -23$ cal K^{-1} mol^{-1}, consistent with a bimolecular rate-determining step (1 cal = 4.184 J). A competition experiment at 55 °C using 9,9′,10,10′-[D$_4$]dihydroanthracene showed a primary kinetic isotope effect of 3.3 ± 0.3. The oxidation of xanthene to bixanthenyl by **1** (detected by GC/MS) is about 10 times faster than DHA oxidation, while reaction with fluorene under similar conditions failed to produce any detectable amounts of 9,9′-bifluorenyl. The relative rates are consistent with the C–H bond strengths (in kcal mol^{-1}) of the substrates: k_2(xanthene (75.5)) > k_2(DHA (78)) > k_2(fluorene (80)).[7]

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[*] Prof. J. M. Mayer, M. A. Lockwood, T. J. Blubaugh, A. M. Collier, S. Lovell
Department of Chemistry, University of Washington
Box 351700; Seattle, WA 98195 (USA)
Fax: (+1) 206-685-8665
E-mail: mayer@chem.washington.edu

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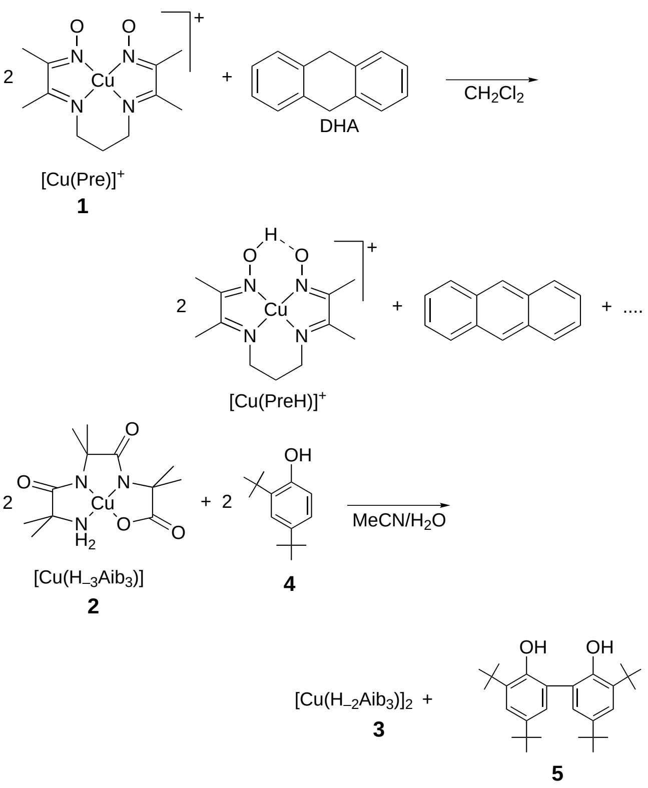

Scheme 1. Oxidations by Cu^{III} complexes. Pre = 3,9-dimethyl-4,8-diazaundecane-2,10-dionedioximate; Aib_3 = tri-α-aminoisobutyric acid.

The protonated ligand of **2**, tri-α-aminoisobutyric acid, was synthesized in about 40 % overall yield by using the recently developed peptide-coupling reagent, HATU.[8] The copper(II) complex was oxidized to $[Cu^{III}(H_{-3}Aib_3)]$ (**2**) by using $IrCl_6^{2-}$.[9] Complex **2** showed no reactivity with DHA or fluorene over several days at room temperature in aqueous acetonitrile. However, **2** readily oxidizes 2,4,6-tri-*tert*-butylphenol under similar conditions to the corresponding phenoxyl radical, which was detected by EPR and UV/Vis spectroscopies.[10] 2,4-Di-*tert*-butylphenol (**4**) reacts with **2** to give an 85 % yield (HPLC, GC) of 2,2′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (**5**), the coupling product from the 2,4-di-*tert*-butylphenoxyl radical (Scheme 1). This reaction also follows a second-order rate law; at 30 °C, $k_2 = 7.4 \times 10^{-3}\,M^{-1}s^{-1}$, $\Delta H^{\neq} = 8.3 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\neq} = -27 \pm 3$ cal K^{-1} mol^{-1} (283 – 313 K). Compound **4** is similarly oxidized by **1** (rapidly forming > 90 % yield of **5**) as well as by copper μ-oxo dimers[2e, 5a] and copper peroxo complexes.[11] Phenol **4** (O–H bond strength: 81 kcal mol^{-1}[12]) is oxidized much faster than DHA (C–H bond strength: 78 kcal mol^{-1}).

Reaction mixtures of **2** and 2,4-di-*tert*-butylphenol slowly deposit dark blue crystals of dimeric $[Cu^{II}(H_{-2}Aib_3)]_2$ (**3**, Figure 1). Whereas the peptide functions as a tetradentate chelate ligand in **2**,[4] in **3** it functions as a tridentate chelate ligand for one copper center, with coordination through the terminal amine group (N(4) and N(3), respectively), the carbonyl oxygen atom of a protonated amide (N(1) and N(6), respectively), and the N atom of the deprotonated amide (N(5) and N(2), respectively), and as a monodentate ligand (through the carboxylate group) for the other copper center.

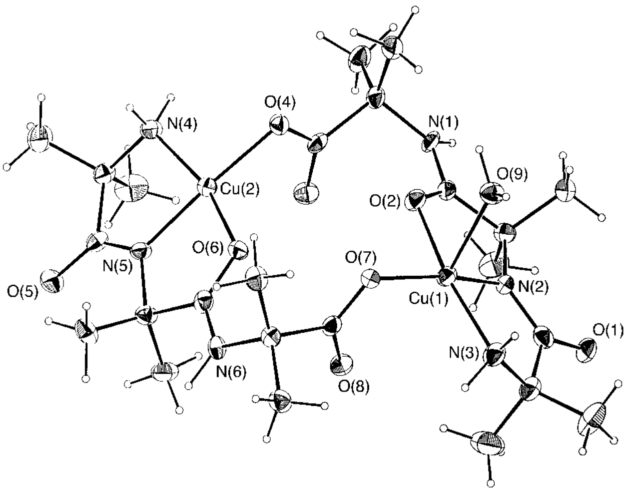

Figure 1. Molecular structure of **3**; solvent molecules have been omitted for clarity. Selected bond lengths [Å]: Cu(1) – O(2) 2.007(4), Cu(1) – N(2) 1.902(4), Cu(1) – N(3) 1.992(4), Cu(1) – O(7) 1.981(4), Cu(1) – O(9) 2.323(4), Cu(2) – N(4) 1.987(4), Cu(2) – N(5) 1.881(4), Cu(2) – O(4) 1.955(4), Cu(2) – O(6) 1.964(4).

Cu(1) also has an axially bound water molecule (2.323(4) Å), and Cu(2) has a weak interaction (3.47 Å) with a carboxylate oxygen atom [O(5)] of an adjacent molecule. Formation of **3** from **2** involves addition of an electron to copper and protonation of an amide nitrogen atom. However, it is possible that hydrogen is initially transferred from the phenol **4** to an amide oxygen atom of **2**. Protonation at this site has been observed in a macrocyclic copper(II) complex.[13]

In summary, the isolated Cu^{III} complex **1** oxidizes hydrocarbon substrates. The reactions are faster for substrates with weaker C–H bonds. Complexes **1** and **2** oxidize substituted phenols to radicals or radical coupling products. The reactivity of **1** and **2** are therefore consistent with their acting as hydrogen-atom abstracting reagents, as predicted based on the ground state thermodynamics. As found for oxyl radicals,[14] H-atom abstraction is much faster from O–H bonds than from C–H bonds of the same strength. Correlation of the rate constants for C–H bond oxidation with enthalpic driving force, as we have done in other systems,[1] is complicated by the coordination of axial ligands on reduction of square-planar d^8 Cu^{III} complexes. The driving force is affected by the nature of the axial ligands and ligand coordination leads to a significant entropic contribution.[15] Addition of $H^{\bullet}$ to **1** gives $[Cu(PreH)]^+$, in which the hydrogen atom bridges the two oxime-oxygen atoms,[16] further complicating the transition state.

Experimental Section

All reactions were performed under an inert atmosphere using dry solvents. Complex **1** was prepared according to the literature method.[3] HATU[8] was used as the coupling reagent in the preparation of tri-α-aminoisobutyric acid (Aib_3) because the reported procedure using carbodiimide coupling[17] did not work in our hands.

2: Instead of the reported flow electrochemical preparation,[4] **2** was prepared as follows: Copper acetate (0.06 g, 0.29 mmol) was added to a solution of the tripeptide (0.10 g, 0.32 mmol) in 0.1 M NaOH (5 mL). Acetate buffer (7 mL, pH 3.5) and Na_2IrCl_6 (0.16 g, 0.29 mmol) were added and the solution was stirred for several hours at room temperature. The resulting brown solution was lyophilized, redissolved in water, eluted through an ion-exchange column (Bio-Rad AG 11A8), and lyophilized a second time. Recrystallization from CH_3CN yielded **2** (62 mg, 50%) as a brown powder.

Complexes **1** and **2** were identified by comparison to the reported spectroscopic data (UV/Vis for both, ^1H NMR for **2**)[3, 4] and by redox titration.

3: Isolated in 50% yield based on **2**. UV/Vis (CH_3OH): $\lambda_{max}(\varepsilon) = 618$ (140). FAB-MS (calcd. for $C_{24}H_{44}N_6O_8Cu_2$): 671 ($[M^+ - H]$). Crystals: $0.33 \times 0.16 \times 0.05$ mm, triclinic $P\bar{1}$, $a = 11.659(1)$, $b = 11.854(1)$, $c = 15.695(1)$ Å, $\alpha = 97.48(1)$, $\beta = 101.75(1)$, $\gamma = 101.87(1)°$, $V = 2044.5(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.389$ g cm^{-3}. Nonius KappaCCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.7107$ Å), 161 K, ω scans, 33764 measured, 7769 independent, 5258 observed reflections [$F > 3\sigma(F)$]. Solved by direct methods (SIR92)[18] and refined using maXus (MacScience, Japan, 1997). $R = 0.057$ [$F > 3\sigma(F)$], $wR = 0.068$ for 460 parameters, $\Delta\rho_{max/min} = 1.49, -0.97$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102174. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Half-Sandwich Alkyl and Hydrido Complexes of Yttrium: Convenient Synthesis and Polymerization Catalysis of Polar Monomers**

Kai C. Hultzsch, Thomas P. Spaniol, and Jun Okuda*

Structurally well characterized organometallic complexes of rare earth metals[1] such as lanthanocene hydrides and alkyls of the type $[\{(\eta^5\text{-}C_5R_5)_2LnX\}_2]$ (X = H, alkyl) have recently attracted considerable interest as cocatalyst-free homogeneous polymerization catalysts for both nonpolar and polar monomers.[2] Catalyst systems based on complexes with only one cyclopentadienyl ligand are anticipated to show greater activity towards sterically more demanding monomers.[3] However, conventional synthesis of mono(cyclopentadienyl) rare earth complexes $[(\eta^5\text{-}C_5R_5)LnX_2(L)_n]$, where at least one ligand X is a hydride or alkyl, is often hampered by ate-complex formation with concomitant alkali metal salt incorporation.[3, 4] Consequently, only a limited number of this type of half-sandwich complexes has been synthesized, and their catalytic performance still remains unexplored.[5] We report here a remarkably facile alkane elimination as a route[6] to yttrium complexes of the type $[(\eta^5\text{-}C_5Me_4SiMe_2X')YX_2(thf)]$, as well as preliminary results on the polymerization of *tert*-butyl acrylate and acrylonitrile with these complexes.

Reaction of $[Y(CH_2SiMe_3)_3(thf)_2]$ (**1**)[7] with $(C_5Me_4H)SiMe_2X'$ (X′ = $NHCMe_3$, Me, Ph, C_6F_5) in pentane at 0 °C for 2 h resulted in the quantitative formation (according to ^1H NMR spectroscopy) of the half-sandwich yttrium complexes $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)Y(CH_2SiMe_3)(thf)]$ (**2**) or $[(\eta^5\text{-}C_5Me_4SiMe_2X')Y(CH_2SiMe_3)_2(thf)]$ (**3**) along with tetramethylsilane (Scheme 1, Table 1). The linked amido-cyclopentadienyl complex **2** was isolated as colorless crystals. Complexes **3a**–**c** are colorless to slightly yellow crystals which melt below room temperature. All complexes are readily soluble in aliphatic and aromatic hydrocarbons. Remarkably, no formation of the metallocene complex could be observed by ^1H NMR spectroscopy: The excess cyclopentadiene was left unchanged even in the presence of two equivalents of $(C_5Me_4H)SiMe_3$. The presence of the silicon substituent on cyclopentadiene is crucial for this complexation reaction to be successful. Mixtures of mono- and bis(cyclopentadienyl) complexes were obtained when silicon-free cyclopentadienes such as C_5Me_5H or $C_5Me_4H_2$ were employed.

When complexes **2** and **3** are in solution at room temperature, the coordinated thf groups are labile on both the chemical and NMR time scale. This is shown by the instantaneous exchange of all coordinated thf molecules upon addition of excess [D$_8$]THF and the substantial high-field

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[*] Prof. Dr. J. Okuda, Dipl.-Chem. K. C. Hultzsch, Dr. T. P. Spaniol
Institut für Anorganische Chemie und
Analytische Chemie der Universität
J.-J.-Becher-Weg 24, D-55099 Mainz (Germany)
Fax: (+49) 6131-39-5605

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