Synthesis and Characterization of a Novel Class of Dicopper(I) Bis(carboxylate)-Bridged Complexes

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Received March 14, 1997[⊗]

The syntheses, spectroscopic properties, crystal and molecular structures, and bonding of several dicopper(I) bis(carboxylate)-bridged complexes are described in which the bridging dicarboxylate ligand is the dianion of *m*-xylylenediamine bis(Kemp's triacid imide) (H_2XDK, **1**). A sterically demanding benzyl derivative of H_2XDK was prepared, H_2BXDK (**6**). Reaction of these two ligands as well as the propyl analog, H_2PXDK (**2**), with thallium ethoxide provided dithallium salts Tl_2L (L = XDK, **7**; PXDK, **8**; and BXDK, **9**). Reaction of **7**, **8**, or **9** with excess CuBr(Me_2S) in CH_2Cl_2/MeCN afforded dinuclear acetonitrile adducts [Cu_2L(MeCN)] (L = XDK, **10**; PXDK, **11**; and BXDK, **12**) in high yield and multigram quantities. The coordination chemistry of the Cu_2(XDK) platform was explored with a range of ancillary ligands. Treatment of **10**, **11**, or **12** with an excess of the specified neutral donor ligand provided complexes [Cu_2(XDK)(PPh_3)$_2$] (**13**), [Cu_2(XDK)(2,6-$Me_2C_6H_3NC$)$_3$] (**14a**), [Cu_2(XDK)(μ-2,6-$Me_2C_6H_3NC$)(2,6-$Me_2C_6H_3NC$)$_2$] (**14b**), [Cu_2(XDK)(NB)$_2$] (**15**), [Cu_2(XDK)(tmeda)] (**17**), [Cu_2(PXDK)(tmeda)] (**18**), [Cu_2(BXDK)(tmeda)] (**19**), and [Cu(4,4′-Me_2bpy)$_2$][Cu(XDK)] (**20**). Reaction of **10** with an excess of cyclohexene resulted in the loss of the acetonitrile ligand, affording the parent unsubstituted complex [Cu_2(XDK)] (**16**). Attempts to prepare anionic carbon-bridged dicopper(I) complexes with alkyl- or aryllithium compounds or cyanide reagents resulted instead in extraction of one of the Cu(I) ions, affording (Et_4N)[Cu(PXDK)] (**21**) and [CuLi(XDK)(THF)$_2$] (**22**). Crystallographic chemical analysis of the complexes revealed linear two-coordinate, trigonal three-coordinate, and pseudotetrahedral four-coordinate copper(I), depending upon the composition, and variable degrees of Cu−Cu bonding (d_{Cu-Cu} range, 2.5697(8)−3.4211(6) Å).

Introduction

The preparation of multinuclear complexes of transition metal ions in low oxidation states for the reductive activation of small molecules is of fundamental and practical importance in bioinorganic chemistry. Many metalloenzymes utilize this strategy to achieve atom transfer reactions which pose a formidable challenge to the synthetic chemist. For example, soluble methane monooxygenase (sMMO) contains a diiron active site and catalyzes the reaction of dioxygen with methane to produce methanol and water.[1−3] Particulate pMMO carries out the same reaction with a tricopper,[4−7] or possibly a copper−iron,[8] active site. Dopamine β-monooxygenase contains a dicopper active site and catalyzes the O_2-promoted hydroxylation of a benzylic CH bond in phenethylamine derivatives.[9,10] Tyrosinase utilizes a dinuclear copper active site to catalyze the orthohydroxylation of monophenols and the oxidation of catechol derivatives to orthoquinones.[4] Inspired by these natural successes, we seek to prepare functional model complexes of some of the foregoing enzymes to gain a general mechanistic understanding of how two or more metal ions can work in concert to activate dioxygen reductively and harness its oxidizing equivalents for oxygen atom transfer reactions to a suitable substrate molecule. The specific reactions of interest are the hydroxylation of aliphatic, aromatic, and olefinic hydrocarbons where the oxygen atom equivalent is derived from O_2. Because we are primarily concerned with exploring the basic *principles* of multimetal-mediated oxidation reactions, our choice of ancillary ligands is not restricted to mimic the active site residues in any particular enzyme. The target complexes for examining these reactions are required only to have discrete dinuclear units with sufficient kinetic stability toward metal ion rearrangements to avoid thermodynamically viable and catalytically inactive species along an oxidation reaction pathway.

As an initial approach to this objective we have assembled dimetallic complexes with a class of convergent bis(carboxylate) ligands derived from xylylene diamine Kemp's triacid.[11−18] Its attributes include (a) the carboxylate functional group, which forms a host of bridged dinuclear complexes having the desired 2−5 Å metal−metal distance;[19] (b) a pair of preorganized and conformationally rigid carboxylates, which tightly bind two metal ions and resist the formation of higher metal aggregates;[17]

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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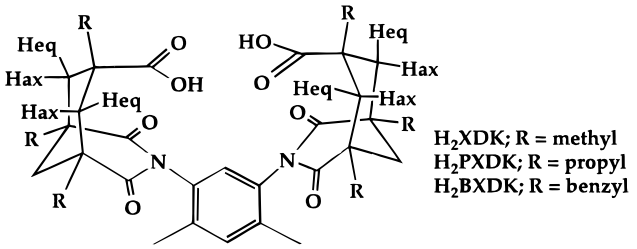
S0020-1669(97)00302-9 CCC: $14.00



and (c) variable substituents (R) peripheral to the metal-binding sites, which provide more steric protection than simple carboxylate ligands.

The reduced metal ion pairs of particular interest to us for exploring O-atom transfer chemistry following reductive activation of dioxygen are homo- and heterodimetallic combinations of Cu(I) and Fe(II). Copper[20−24] and iron[1,11,25−27] oxygenases and hydroxylases have been the subject of an enormous body of structural and functional modeling literature. We are particularly interested in the effects of the basic carboxylate ligand environment for stabilizing oxygen intermediates and for inducing oxo transfer reactivity. A program to investigate the diiron(II) chemistry of this bis(carboxylate) ligand system for the functional modeling of sMMO, in particular, is in progress.[11,12,28]

In the present paper, we report the preparation and characterization of a new class of dicopper(I) bis(carboxylate) complexes carried out as a prelude to an evaluation of their potential to promote hydrocarbon oxidation. The synthesis of a sterically more demanding derivative of H_2XDK,[29] H_2BXDK, is described. Both of these ligands as well as H_2PXDK have been used to prepare complexes with Cu(I). The reactivity of the resulting dicopper(I) XDK species with neutral ancillary ligands has been explored to elucidate fully the electronic nature of this platform and to map out its coordination chemistry. Several unprecedented copper(I) carboxylates were obtained. The dicopper(I) complexes of all three carboxylate ligands have been used in O_2 reactivity studies, affording some stable peroxo intermediates at low temperature. These investigations will be described elsewhere.[30]

Experimental Section

General Considerations. The H_2XDK (**1**)[31] and H_2PXDK (**2**)[11] ligands were prepared according to literature procedures. All reagents were obtained from commercial sources unless otherwise noted. THF, benzene, toluene, pentane, and Et_2O were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane and chlorobenzene were distilled from CaH_2 under nitrogen. Acetonitrile was predistilled from CaH_2 and then from P_2O_5. The NMR solvents $CDCl_3$, CD_2Cl_2, and C_6D_6 were degassed, passed through activated basic alumina, and stored over 3 Å molecular sieves prior to use. All other solvents and reagents are commercially available and were used as received. All air-sensitive manipulations were carried out either in a nitrogen-filled Vacuum Atmospheres drybox or by standard Schlenk line techniques at room temperature unless otherwise noted.

Physical Measurements. NMR spectra were recorded on Bruker AC-250, Varian XL-300, or Varian VXR-500 NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported versus tetramethylsilane and referenced to the residual solvent peak. ^{31}P NMR chemical shifts are reported versus external H_3PO_4 (85%). FTIR spectra were recorded on a BioRad FTS-135 FTIR spectrometer, and mass spectra were determined by using a Finnigan 4000 mass spectrometer with 70-eV impact ionization. UV−vis spectra were recorded on a Cary 1E spectrophotometer. Conductivity measurements were carried out in CH_2Cl_2 at 296 K with a Fisher Scientific conductivity bridge model 9-326 with a platinum black electrode. Elemental analyses were performed by Microlytics, South Deerfield, MA.

Trimethyl *cis,cis*-1,3,5-Tribenzylcyclohexane-1,3,5-tricarboxylate (Benzyl Kemp's Triester, 3). To a mechanically stirred solution of lithium diisopropylamide (1.5 M in THF, 200 mL, 297 mmol) and toluene (400 mL) at 0 °C under N_2 was added trimethyl 1,3,5-cyclohexanetricarboxylate (24.0 g, 92.9 mmol) in toluene (300 mL) dropwise over 1 h. The mixture was stirred for an additional 0.5 h, and then benzyl bromide (35.4 mL, 297 mmol) was added via syringe in one portion. The mixture was warmed to room temperature and then refluxed for 7 h. After this time the reaction mixture was cooled to room temperature and quenched with H_2O (200−300 mL). The organic phase was collected and concentrated in vacuo. The resulting oily residue was taken up in CH_2Cl_2 (200 mL) and extracted with 2 M HCl (2 × 100 mL) and brine (100 mL). The combined organic extracts were dried with $MgSO_4$, and the volatile components were removed in vacuo. The resulting orange-brown solid was suspended in dry Et_2O (200−300 mL) and then isolated by filtration to yield **3** (>95% pure by ^{1}H NMR) as a light yellow solid (31.9 g, 65%). Recrystallization from toluene/pentane provided **3** as colorless blocks. ^{1}H NMR (250 MHz, DMSO, 296 K) δ 7.32−7.20 (9H, m), 7.07 (6H, d, J = 6.6 Hz), 3.43 (9H, s), 2.82 (6H, s), 2.41 (3H, d, J = 14.1 Hz), 1.46 (3H, d, J = 14.1 Hz) ppm; IR (KBr) 3060, 3027, 3000, 2946, 2895, 1738, 1602, 1495, 1451, 1383, 1233, 1206, 1121, 1038, 993, 874, 770, 698, 549 cm^{-1}; high-resolution MS (FAB) calcd for $C_{33}H_{36}O_6$ (M) *m/e* 528.2512, found 528.2505. Anal. Calcd for $C_{33}H_{36}O_6$: C, 74.98; H, 6.86. Found: C, 75.35; H, 6.85.

***cis,cis*-1,3,5-Tribenzylcyclohexane-1,3,5-tricarboxylic Acid (Benzyl Kemp's Triacid, 4).** To a stirred solution of **3** (25.3 g, 47.8 mmol) in EtOH/THF (1:1, 500 mL total volume) was added KOH (63.0 g, 955 mmol) in a minimum amount of H_2O, and the mixture was refluxed for 6 h. The mixture was concentrated in vacuo to a viscous oily solid. It was redissolved in H_2O (300 mL), cooled to 0 °C, and acidified to pH 1 with concentrated HCl. The resulting yellow precipitate was isolated by filtration, washed with H_2O (300−400 mL), and dried in vacuo at 110 °C for 2 h. The powder was then suspended in dry Et_2O and isolated by filtration to yield **4** (>95% pure by ^{1}H NMR) as a white solid (18.4 g, 79%). Recrystallization from acetone/DMSO/Et_2O afforded **4** as colorless blocks: ^{1}H NMR (300 MHz, DMSO, 296 K) δ 12.04 (1H, s), 7.29−7.14 (15H, m), 2.86 (6H, s), 2.39 (3H, d, J = 14.7 Hz), 1.47 (3H, d, J = 13.8 Hz) ppm; IR (KBr) 3010, 2615, 1729, 1698, 1603, 1496, 1457, 1291, 1198, 1127, 1031, 915, 767, 699, 553 cm^{-1}. Anal. Calcd for $C_{34}H_{42}O_8S_2$ (**4**·2DMSO): C, 63.53; H, 6.59. Found: C, 63.44; H, 6.54. The **4**·2DMSO stoichiometry was determined by X-ray crystallography.

***cis,cis*-1,3,5-Tribenzylcyclohexane-1,3,5-tricarboxylic 1,3-Anhydride 5-Acid Chloride (Tribenzyl Kemp's Anhydride Acid Chloride, 5).** This compound was prepared from **4** (22.3 g, 45.8 mmol) and excess $SOCl_2$ (100 mL) by a procedure analogous to one used for the synthesis of the parent trimethyl derivative[31] to yield **5** (>95% pure by ^{1}H NMR) as a white solid (22.3 g, 100%): ^{1}H NMR (250 MHz, $CDCl_3$, 296 K) δ 7.40−7.25 (10H, m), 7.10−7.03 (5H, m), 3.21 (2H, d, J = 13.6 Hz), 2.91−2.84 (4H, m), 2.70 (2H, d, J = 14.4 Hz), 1.87

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(29) Abbreviations used: H_2XDK, *m*-xylylenediamine bis(Kemp's triacid imide); H_2PXDK, *m*-xylylenediamine bis(propyl Kemp's triacid imide); H_2BXDK, *m*-xylylenediamine bis(benzyl Kemp's triacid imide); NB, norbornene; tmeda, N,N,N′,N′-tetramethylethylenediamine; 4,4′-Me_2bpy, 4,4′-dimethyl-2,2′-bipyridine; phen, 1,10-phenanthroline.
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(1H, d, $J = 12.9$ Hz), 1.45 (2H, d, $J = 14.4$ Hz), 1.16 (1H, d, $J = 13.2$ Hz) ppm; IR (KBr) 3062, 3030, 2961, 2928, 1803, 1767, 1604, 1496, 1455, 1445, 1213, 1099, 1057, 1000, 991, 898, 760, 701, 609, 537 cm^{-1}; high-resolution MS (FAB) calcd for $C_{30}H_{27}O_4Cl$ (M) *m/e* 486.1598, found 486.1598.

Benzyl Xylylenediamine Kemp's Triacid (H_2BXDK, 6). This compound was prepared from **5** (22.3 g, 45.8 mmol), 1,3-dimethyl-4,6-diaminobenzene (3.27 g, 24.0 mmol), and 4-(dimethylamino)-pyridine (300 mg, 2.40 mmol) by a procedure analogous to that used to prepare H_2XDK (**1**).[31] Recrystallization from MeOH yielded **6** (>95% pure by ^{1}H NMR) as a white microcrystalline solid (16.6 g, 70%). Recrystallization from $CHCl_3$/pentane provided **6** as colorless blocks which appeared suitable for X-ray crystallography: ^{1}H NMR (300 MHz, $CDCl_3$, 296 K) δ 7.32−7.28 (4H, m), 7.21−6.95 (27 H, m), 6.54 (1H, s), 3.40 (4H, d, $J = 13.2$ Hz), 2.75 (4H, d, $J = 13.8$ Hz), 2.56 (4H, s), 2.31 (4H, d, $J = 13.5$ Hz), 2.02 (2H, d, $J = 13.0$ Hz), 1.18 (6H, s), 1.03 (4H, d, $J = 14.1$ Hz), 0.89 (2H, d, $J = 13.2$ Hz) ppm; ^{13}C{^{1}H} NMR (125 mHz, $CDCl_3$, 296 K) δ 181.6, 173.7, 136.0, 135.4, 135.0, 133.0, 132.9, 131.2, 130.0, 128.4, 128.0, 127.6, 126.8, 126.2, 50.2, 47.3, 45.0, 44.4, 41.8, 36.9, 16.0 ppm; IR (KBr) 3027, 2955, 2924, 2863, 1795, 1707, 1603, 1495, 1461, 1368, 1326, 1231, 1178, 1031, 934, 744, 700, 585, 517 cm^{-1}; high-resolution MS (FAB) calcd for $C_{68}H_{64}N_2O_8$ (M) *m/e* 1036.4663, found 1036.4652. Anal. Calcd for $C_{68}H_{64}N_2O_8$: C, 78.74; H, 6.22; N, 2.70. Found: C, 78.18; H, 6.22; N, 2.67. This sample and others with the BXDK ligand repeatedly analyzed low for carbon, perhaps due to its highly unsaturated composition.

Tl_2(XDK) (7). To a rapidly stirred suspension of **1** (4.00 g, 6.89 mM) in dry THF (100 mL) under N_2 was added TlOEt (1.0 mL, 14 mM) by syringe. The solution initially clarified, and then a white precipitate formed immediately. The mixture was stirred for 4 h, and the volatile components were removed in vacuo, affording **7** (>95% pure by ^{1}H NMR) as a white powder (6.80 g, 100%): ^{1} H NMR (300 MHz, $CDCl_3$, 296 K) δ 7.64 (1H, s), 7.08 (1H, s), 2.72 (4H, *d*, $J = 13.0$ Hz), 2.08 (2H, d, $J = 13.2$ Hz), 1.90 (6H, s), 1.44 (2H, d, $J = 13.2$ Hz), 1.27 (12H, s), 1.16 (6H, s), 1.12 (4H, d, $J = 14.1$ Hz) ppm; IR (KBr) 2958, 2909, 2877, 1728, 1686, 1584, 1459, 1354, 1190, 1086, 958, 884, 761, 632 cm^{-1}; high-resolution MS (FAB) calcd for $C_{32}H_{38}N_2O_8Tl_2$ (M) *m/e* 988.2116, found 989.2195 (MH^+).

Tl_2(PXDK) (8). This compound was prepared from **2** (8.00 g, 10.7 mmol) and TlOEt (1.54 mL, 21.4 mmol) by a procedure analogous to that used to prepare **7**. Compound **8** was obtained (>95% pure by ^{1}H NMR) as a white powder (12.3 g, 100%): ^{1}H NMR (250 MHz, CD_2Cl_2, 296 K) δ 7.38 (1H, s), 7.13 (1H, s), 2.61 (4H, d, $J = 13.0$ Hz), 2.36 (2H, d, $J = 13.0$ Hz), 2.10−1.90 (10 H, m), 1.55−1.10 (26 H, m), 1.00−0.80 (18H, m) ppm; ^{13}C{^{1}H} NMR (75 mHz, $CDCl_3$, 296 K) δ 181.9, 177.0, 134.8, 133.5, 133.2, 128.7, 48.4, 44.3, 43.8, 42.4, 37.7, 25.8, 18.2, 17.9, 17.3, 14.8 ppm; IR (KBr) 2959, 2871, 1734, 1685, 1558, 1499, 1436, 1391, 1361, 1310, 1246, 1185, 1163, 1106, 1035, 930, 861, 760, 629 cm^{-1}; high-resolution MS (FAB) calcd for $C_{44}H_{62}N_2O_8Tl_2$ (M) *m/e* 1156.3994, found 1157.4065 (MH^+).

Tl_2(BXDK) (9). This compound was prepared from crude **6** (3.00 g, 2.89 mmol) and TlOEt (418 μL, 5.78 mmol) by a procedure analogous to that used to prepare **7**, affording **9** (>95% pure by ^{1}H NMR) as a tan powder. Recrystallization from CH_2Cl_2/Et_2O gave **9** as a white microcrystalline solid (3.38 g, 81%): ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ 7.88 (1H, s), 7.30−7.23 (4H, m), 7.21−6.98 (26H, m), 6.51 (1H, s), 3.48 (4H, s, $J = 12.9$ Hz), 2.97 (4H, d, $J = 12.9$ Hz), 2.82 (4H, s), 2.49 (4H, d, $J = 12.9$ Hz), 2.07 (4H, d, $J = 12.9$ Hz), 1.18 (4H, d, $J = 12.9$ Hz), 1.02 (2H, d, $J = 13.2$ Hz), 0.96 (6H, s) ppm; ^{13}C{^{1}H} NMR (75 mHz, $CDCl_3$, 296 K) δ 180.4, 176.2, 138.6, 136.9, 135.6, 133.5, 133.4, 131.8, 131.3, 128.8, 128.6, 128.4, 127.2, 127.1, 51.0, 50.5, 45.9, 45.4, 43.5, 37.9, 16.6 ppm; IR (KBr) 3083, 3027, 2916, 1731, 1681, 1559, 1453, 1357, 1187, 1031, 937, 865, 741, 700, 602, 508 cm^{-1}; high-resolution MS (FAB) calcd for $C_{68}H_{62}N_2O_8Tl_2$ (M) *m/e* 1444.3994, found 1445.4061 (MH^+).

[Cu_2(XDK)(MeCN)] (10). To a stirred solution of **7** (3.67 g, 3.72 mmol) in CH_2Cl_2/MeCN (3:1, 300 mL) under N_2 was added solid CuBr(Me_2S) (2.32 g, 11.1 mmol), and the mixture was rapidly stirred for 3 h. The salts were then removed by filtration through Celite. The filtrate was treated with an additional 3 equiv of CuBr(Me_2S) and stirred for 1 h. The solvent was removed in vacuo, and the solid residue was extracted with CH_2Cl_2 (200 mL) followed by filtration through Celite. The precipitate was extracted with additional CH_2Cl_2 (100 mL) and filtered through Celite. The combined filtrates were concentrated in vacuo to yield a solid residue. The residue was suspended in Et_2O, and the precipitate was recovered by filtration to yield **10** (>95% pure by ^{1}H NMR) as a white solid (2.50 g, 90%). The crude powder was used without further purification for subsequent reactions. Recrystallization from MeCN/CH_2Cl_2/Et_2O afforded **10** as colorless blocks which appeared suitable for X-ray crystallography: ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ 8.47 (1H, s), 6.70 (1H, s), 2.83 (4H, d, $J = 13.1$ Hz), 2.05 (3H, br s), 1.77 (6H, s), 1.71 (2H, d, $J = 15.0$ Hz), 1.20 (12H, s), 0.82 (2H, d, $J = 13.1$ Hz), 0.75 (4H, d, $J = 13.5$Hz), 0.63 (6H, s) ppm; ^{13}C{^{1}H} NMR (75 mHz, CD_2Cl_2, 296 K) δ 186.4, 177.1, 135.7, 134.9, 133.7, 128.5, 117.6, 45.7, 45.2, 43.4, 41.7, 31.5, 26.5, 17.5, 2.6 ppm; IR (KBr) 2963, 2921, 1738, 1704, 1568, 1463, 1403, 1357, 1176, 1086, 957, 891, 849, 759, 734, 622 cm^{-1}. Anal. Calcd for $C_{34}H_{41}N_3O_8Cu_2$: C, 54.68; H, 5.53; N, 5.63. Found: C, 54.39; H, 5.58; N, 5.94.

[Cu_2(PXDK)(MeCN)] (11). This compound was prepared from **8** (500 mg, 0.433 mmol) and CuBr(Me_2S) (241 mg, 130 mmol) by a procedure analogous to that used to synthesize **10**, affording **11** (>95% pure by ^{1}H NMR) as a white powder (360 mg, 91%). The crude powder was used without further purification for subsequent reactions. Recrystallization from CH_2Cl_2/MeCN/Et_2O gave **11** as colorless needles: ^{1}H NMR (500 MHz, CD_2Cl_2, 296 K) δ 8.23 (1H, s), 7.17 (1H, s), 2.69 (4H, d, $J = 13.5$ Hz), 2.39 (2H, d, $J = 12.5$Hz), 2.00−1.92 (13H, m), 1.42−1.18 (26H, m), 0.92 (12H, t, $J = 7.0$ Hz), 0.84 (6H, t, $J = 7.2$ Hz) ppm; ^{13}C{^{1}H} NMR (75 mHz, $CDCl_3$, 296 K) δ 185.4, 176.3, 135.5, 134.9, 133.7, 129.1, 117.8, 48.1, 46.9, 44.7, 42.6, 38.2, 18.0, 17.6, 15.7, 15.0, 14.8, 2.5 ppm (18 of the expected 19 peaks were observed); IR (KBr) 2959, 2872, 1734, 1695, 1566, 1458, 1359, 1247, 1182, 1035, 924, 863, 759, 583 cm^{-1}. Anal. Calcd for $C_{44}H_{62}N_2O_8$-Cu_2Cl_2 (**11** − 1MeCN): C, 60.46; H, 7.15; N, 3.20. Found: C, 60.01; H, 7.32; N, 3.22. This sample was heated at 90 °C for 12 h to remove any residual CH_2Cl_2. The MeCN ligand was removed in the process.

[Cu_2(BXDK)(MeCN)] (12). This compound was synthesized from **9** (1.00 g, 0.692 mmol) and CuBr(Me_2S) (435 mg, 2.08 mmol) by a procedure analogous to that used to prepare **10**, to yield **12** (>95% pure by ^{1}H NMR) as a white solid. The crude powder was used without further purification for subsequent reactions. Recrystallization from MeCN/CH_2Cl_2/Et_2O afforded **12** as colorless thin plates (600 mg, 72%): ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ 8.22 (1H, s), 7.25−6.95 (30 H, m), 6.54 (1H, s), 3.51 (4H, d, $J = 13.2$ Hz), 2.85 (4H, d, $J = 13.2$ Hz), 2.59 (4H, s), 2.41 (4H, d, $J = 12.9$ Hz), 2.04 (2H, d, $J = 12.6$ Hz), 1.90 (3H, br s), 1.10 (4H, d, $J = 14.1$ Hz), 0.94 (2H, d, $J = 13.2$ Hz), 0.82 (6H, s) ppm; ^{13}C{^{1}H} NMR (75 mHz, $CDCl_3$, 296 K) δ 182.5, 175.3, 137.6, 136.7, 135.9, 134.3, 134.0, 132.0, 130.9, 128.5, 128.4, 128.3, 127.4, 127.1, 117.5, 50.1, 49.0, 46.2, 45.2, 43.6, 38.1, 15.8, 2.6 ppm; IR (KBr) 3084, 3061, 3028, 2926, 2860, 2251, 1732, 1700, 1565, 1494, 1413, 1359, 1231, 1178, 1031, 928, 844, 749, 698 cm^{-1}. Anal. Calcd for $C_{68}H_{62}N_2O_8Cu_2$ (**12** − 1MeCN): C, 70.27; H, 5.38; N, 2.41. Found: C, 67.67; H, 5.30; N, 2.68. This sample was heated at 90 °C for 12 h to remove any residual CH_2Cl_2. The MeCN ligand was removed in the process.

[Cu_2(XDK)(PPh_3)$_2$] (13). To a stirred suspension of **10** (50 mg, 0.067 mmol) in THF (2 mL) was added PPh_3 (35 mg, 0.13 mmol) in THF (1 mL). The mixture clarified immediately, and after 0.5 h the solvent was removed in vacuo. The solid residue was recrystallized from chlorobenzene/Et_2O to yield **13** as colorless blocks which appeared suitable for X-ray crystallography (45 mg, 55%): ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ 8.05 (1H, s), 7.50−7.43 (10 H, m), 7.04−7.00 (20H, m), 6.80 (1H, s), 2.98 (4H, d, $J = 13.2$ Hz), 1.89 (6H, s), 1.79 (2H, d, $J = 12.5$ Hz), 1.22 (12 H, s), 0.90 (2H, d, $J = 13.2$ Hz), 0.92−0.78 (10H, m) ppm; ^{13}C{^{1}H} NMR (75 mHz, CD_2Cl_2, 296 K) δ 182.5, 176.8, 135.2, 135.1, 134.5 (d, $J_{CP} = 15.8$ Hz), 133.6, 133.1 (d, $J_{CP} = 15.1$ Hz), 130.4, 129.1 (d, $J_{CP} = 9.3$ Hz), 128.8, 45.6, 45.4, 43.5, 41.3, 32.8, 26.5, 17.5 ppm; ^{31}P NMR (121 mHz, CD_2Cl_2, 296 K) δ 5.43 (br s, $\Delta\nu_{1/2} = 45.4$ Hz) ppm; IR (KBr) 3070, 2961, 2926, 1733, 1695, 1571, 1461, 1435, 1400, 1359, 1195, 1097, 958, 851, 745, 694 cm^{-1}. Anal. Calcd for $C_{68}H_{68}N_2O_8P_2Cu_2$: C, 66.38; H, 5.57; N, 2.28. Found: C, 66.07; H, 5.79; N, 2.15.

[Cu_2(XDK)(2,6-$Me_2C_6H_3NC)_3$] (14a) and [Cu_2(XDK)(μ-2,6-$Me_2C_6H_3NC$)(2,6-$Me_2C_6H_3NC)_2$] (14b). This compound was prepared from **10** (100 mg, 0.13 mmol) and 2,6-dimethylphenyl isocyanide (54 mg, 0.40 mmol) by a procedure analogous to that used to make **13**.

Recrystallization from PhCl/Et_2O (vapor diffusion) afforded blocks of colorless **14a** and yellow **14b** in distinct crystal fields, both of which appeared suitable for X-ray crystallography (96 mg, 65%): ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ 8.05 (1H, s), 7.50−7.43 (10H, m), 7.04−7.00 (20H, m), 6.80 (1H, s), 2.98 (4H, d, J = 13.2 Hz), 1.89 (6H, s), 1.79 (2H, d, J = 12.5 Hz), 1.22 (12H, s), 0.90 (2H, d, J = 13.2 Hz), 0.92−0.78 (10H, m) ppm; ^{13}C{^{1}H} NMR (75 mHz, CD_2Cl_2, 296 K) δ 182.9, 176.8, 135.7, 135.1, 134.6, 132.0, 130.2, 129.9, 129.0, 128.4, 127.1, 45.9, 45.8, 43.3, 41.3, 33.0, 26.7, 19.0, 17.6 ppm; IR (KBr) 2957, 2926, 2877, 2134, 1736, 1701, 1592, 1462, 1356, 1197, 1085, 960, 887, 793, 749, 720, 635 cm^{-1}. Anal. Calcd for $C_{59}H_{65}N_5O_8Cu_2$: C, 64.46; H, 5.96; N, 6.37. Found: C, 64.54; H, 5.94; N, 6.04.

[Cu_2(XDK)(NB)$_2$] (15). This compound was prepared from **10** (80 mg, 0.11 mmol) and excess norbornene (650 mg, 6.9 mmol) by a procedure analogous to that used to make **13**. Recrystallization from NB/CH_2Cl_2/Et_2O provided **15** as colorless blocks (69 mg, 72%): ^{1}H NMR (300 MHz, CD_2Cl_2, 296 K) δ 7.24 (1H, s), 7.10 (1H, s), 5.41 (4H, s), 2.85−2.77 (8H, m), 2.06 (2H, d, J = 13.2 MHz), 2.83 (6H, s), 1.58−1.41 (8H, m), 1.32−1.25 (18H, m), 1.20 (4H, d, J = 13.8 Hz), 1.01 (2H, d, J = 8.7 Hz), 0.80 (4H, dd, J = 7.5, 2.4 Hz) ppm; ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 296 K) δ 186.4, 176.8, 135.5, 134.8, 133.6, 127.7, 120.2, 47.4, 45.4, 45.1, 43.7, 42.7, 41.6, 32.4, 26.3, 24.8, 17.5 ppm; IR (KBr) 2957, 2926, 2877, 2134, 1736, 1701, 1592, 1462, 1356, 1197, 1085, 960, 887, 793, 749, 720, 635 cm^{-1}. Prolonged exposure of powdered **15** to high vacuum resulted in removal of 1 equiv of NB, as judged by ^{1}H NMR and elemental analysis. ^{1}H NMR for [Cu_2(XDK)(NB)] (300 MHz, CD_2Cl_2, 296 K): δ 7.58 (1H, s), 7.13 (1H, s), 5.27 (2H, s), 2.85−2.74 (6H, m), 2.08 (2H, d, J = 13.5 Hz), 1.89 (6H, s), 1.59−1.51 (4H, m), 1.47 (2H, d, J = 13.2 Hz), 1.28 (12H, s), 1.25 (6H, s), 1.17 (4H, d, J = 12.6 Hz), 1.00 (2H, d, J = 13.1 Hz), 0.91 (2H, dd, J = 7.4, 2.4 Hz); IR (KBr) 2966, 2928, 1733, 1696, 1592, 1460, 1407, 1356, 1335, 1223, 1136, 957, 851, 760, 684, 638 cm^{-1}. Anal. Calcd for $C_{59}H_{65}N_5O_8Cu_2$ (**15** − 1NB): C, 64.46; H, 5.96; N, 6.37. Found: C, 64.54; H, 5.94; N, 6.04.

Cu_2(XDK) (16). This compound was prepared from **10** (290 mg, 0.38 mmol) and excess cyclohexene (5.0 mL, 49 mmol) by a procedure analogous to that used to prepare **15**. Upon removal of the volatile components in vacuo, all the cyclohexene was driven off to afford **16** as a white solid. Recrystallization from CH_2Cl_2/pentane provided **16** as colorless needles (220 mg, 81%): ^{1}H NMR (300 MHz, CD_2Cl_2, 295 K) δ 8.08 (1H, s), 7.14 (1H, s), 2.77 (4H, d, J = 13.2 Hz), 2.09 (2H, d, J = 13.2 Hz), 1.90 (6H, s), 1.46 (2H, d, J = 13.2 Hz), 1.27 (12H, s), 1.23−1.15 (10H, m) ppm; ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 296 K) δ 187.7, 177.1, 135.8, 134.8, 134.1, 130.4, 45.7, 45.2, 43.6, 41.7, 31.4, 26.4, 17.5 ppm; IR (KBr) 2965, 2924, 1734, 1697, 1559, 1501, 1411, 1341, 1228, 1179, 1087, 956, 848, 761, 700, 623 cm^{-1}. Anal. Calcd for $C_{32}H_{38}N_2O_8Cu_2$: C, 54.46; H, 5.43; N, 3.97. Found: C, 54.67; H, 5.36; N, 3.75.

[Cu_2(XDK)(tmeda)] (17). This compound was prepared by addition of tmeda (23 μL, 0.15 mmol) to **10** (94 mg, 0.13 mmol) in THF (1 mL), followed by recrystallization from THF/pentane at −30 °C, to afford **17** as colorless blocks (81 mg, 78%): ^{1}H NMR (295 K, 300 MHz, C_6D_6) δ 8.45 (1H, s), 6.69 (1H, s), 2.94 (4H, d, J = 13.1 Hz), 2.10 (12 H, s), 1.86 (4H, s), 1.85−1.78 (8H, m), 1.26 (12H, s), 1.05 (6H, s), 0.92 (2H, d, J = 13.1 Hz), 0.84 (4H, d, J = 13.8 Hz); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 296 K) δ 184.2, 176.8, 135.2, 133.5, 129.2, 58.5, 47.3, 45.9, 45.5, 42.9, 41.6, 31.9, 26.6, 17.5 ppm (14 of the expected 15 peaks were observed); IR (KBr) 2984, 2930, 2882, 1735, 1695, 1561, 1461, 1355, 1189, 1086, 957, 850, 697 cm^{-1}. Anal. Calcd for $C_{38}H_{54}N_4O_8Cu_2$: C, 55.53; H, 6.62; N, 6.82. Found: C, 55.39; H, 6.80; N, 6.81.

[Cu_2(PXDK)(tmeda)] (18). This compound was prepared from **11** (57 mg, 0.062 mmol) and tmeda (19 μL, 0.50 mmol) by a procedure analogous to that used to obtain **17**. Recrystallization from THF/pentane provided **18** as colorless needles (39 mg, 72%): ^{1}H NMR (250 MHz, CD_2Cl_2, 295 K) δ 8.02 (1H, s), 7.10 (1H, s), 2.73 (4H, d, J = 12.9 Hz), 2.36 (4H, s), 2.23 (12H, s), 2.00−1.85 (8H, m), 1.50−1.12 (30H, m), 0.91 (12H, d, J = 6.6 Hz), 0.77 (6H, t, J = 6.7 Hz) ppm; ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 296 K) δ 138.2, 176.0, 135.2, 135.1, 133.4, 129.9, 58.6, 48.2, 47.2, 46.4, 44.5, 42.8, 38.5, 18.0, 17.6, 15.1, 14.6 ppm (17 of the expected 19 peaks were observed); IR (KBr) 2958, 2871, 2780, 1733, 1691, 1579, 1459, 1361, 1192, 923, 758, 582 cm^{-1}. Anal. Calcd for $C_{50}H_{78}N_4O_8Cu_2$: C, 60.64; H, 7.94; N, 5.66. Found: C, 59.99; H, 8.32; N, 6.56.

[Cu_2(BXDK)(tmeda)] (19). This compound was prepared from **12** (200 mg, 0.17 mmol) and tmeda (75 μL, 0.50 mmol) by a procedure analogous to that used to synthesize **17**. Recrystallization from THF/pentane provided **19** as colorless needles (138 mg, 65%): ^{1}H NMR (300 MHz, CD_2Cl_2, 295 K) δ 7.91 (1H, s), 7.38−7.22 (6H, m), 7.20−7.05 (24H, m), 6.66 (1H, s), 3.30 (4H, d, J = 12.9 Hz), 2.81 (4H, s), 2.76 (4H, d, J = 13.2 Hz), 2.55−2.45 (8H, m), 2.40 (12 H, s), 1.99 (2H, d, J = 12.6 Hz), 1.36 (4H, d, J = 13.2 Hz), 1.00 (2H, d, J = 12.9 Hz), 0.62 (6H, s) ppm; ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 296 K) δ 183.9, 175.0, 137.0, 136.9, 135.2, 134.5, 133.9, 132.0, 131.9, 129.4, 128.5, 128.2, 127.2, 126.9, 58.5, 48.8, 48.1, 47.7, 45.7, 45.3, 41.5, 38.0, 16.0 ppm; IR (KBr) 3027, 2920, 2828, 1733, 1694, 1577, 1495, 1361, 1184, 1032, 932, 759, 701, 596 cm^{-1}. Anal. Calcd for $C_{74}H_{78}N_4O_8Cu_2$: C, 69.52; H, 6.15; N, 4.38. Found: C, 68.72; H, 6.45; N, 4.42.

[Cu(4,4′-Me_2bpy)$_2$][Cu(XDK)] (20). To a stirred solution of **10** (250 mg, 0.355 mmol) in CH_2Cl_2 (5 mL) was added 4,4′-dimethyl-2,2′-bipyridine (125 mg, 0.670 mmol). The solution immediately turned dark red, and after 0.5 h the volatile components were removed in vacuo. The dried residue was suspended in pentane (10 mL), and the precipitate was recovered by filtration. Recrystallization from THF/CH_2Cl_2/pentane provided **20** as a dark red-brown microcrystalline solid (345 mg, 96%): ^{1}H NMR (250 MHz, CD_2Cl_2, 296 K) δ 8.43 (4H, d, J = 5.1 Hz), 8.02 (4H, s), 7.98 (1H, s), 7.33 (4H, d, J = 5.1 Hz), 7.06 (1H, s), 2.71 (4H, d, J = 13.2 Hz), 2.51 (12 H, s), 2.02 (2H, d, J = 12.8 Hz), 1.81 (6H, s), 1.37 (2H, d, J = 13.0 Hz), 1.21 (12H, s), 1.12−0.90 (10H, m); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 296 K) δ 181.6, 176.9, 152.7, 150.2, 149.0, 135.1, 134.9, 132.5, 130.0, 127.5, 122.8, 46.2, 45.9, 42.5, 41.6, 31.6, 26.8, 21.9, 17.7 ppm; IR (KBr) 2958, 2926, 1734, 1696, 1611, 1460, 1345, 1226, 1193, 1086, 956, 823, 886, 626, 517 cm^{-1}; UV−vis (CH_2Cl_2) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 329 (sh, 2800), 397 (2200), 529 (sh, 630). Anal. Calcd for $C_{56}H_{62}N_6O_8Cu_2$: C, 62.61; H, 5.82; N, 7.82. Found: C, 62.30; H, 5.58; N, 7.69.

(Et_4N)[Cu(PXDK)] (21). To a stirred solution of **11** (1.50 g, 1.64 mmol) in CH_2Cl_2 (25 mL) was added Et_4N(CN) (272 mg, 1.64 mmol) in CH_2Cl_2 (5 mL). The mixture was rapidly stirred for 0.5 h and then filtered through Celite. The colorless filtrate was dried to yield pure **21** (>95% by ^{1}H NMR) as a white powder (1.42 g, 92%). Recrystallization from MeCN/THF/Et_2O afforded **21** as colorless blocks: ^{1}H NMR (250 MHz, CD_2Cl_2, 296 K) δ 7.99 (1H, s), 7.06 (1H, s), 3.26 (8H, m), 2.66 (4H, d, J = 13.0 Hz), 2.32 (2H, d, J = 12.9 Hz), 2.02−1.70 (10H, m), 1.50−1.00 (38 H, m), 0.93−0.70 (18H, m); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 296 K) δ 180.4, 176.6, 135.3, 135.0, 132.4, 130.7, 51.8, 48.2, 46.0, 45.1, 44.7, 43.1, 38.6, 19.4, 18.3, 18.0, 17.7, 15.1, 7.8 ppm; IR (KBr) 2933, 2872, 1731, 1700, 1626, 1498, 1458, 1392, 1346, 1257, 1172, 1107, 1003, 924, 860, 826, 782, 759, 734, 539 cm^{-1}. Anal. Calcd for $C_{52}H_{84}N_3O_8Cu$: C, 66.39; H, 8.79; N, 4.47. Found: C, 66.32; H, 9.02; N, 4.53.

[CuLi(XDK)(THF)$_2$] (22). Method A. To a stirred solution of **10** (50 mg, 0.067 mmol) and 12-crown-4 (43 mL, 0.27 mmol) in THF (3 mL) was added PhLi (37 mL, 1.8 M in cyclohexane/Et_2O). The resulting brown mixture was stirred for 2 h, and then the volatile components were removed in vacuo. The residue was recrystallized from THF/pentane to yield a dark brown precipitate and large colorless blocks. Crystals of **22** separated from the dark residue in Paratone-N (Exxon) and were suitable for X-ray crystallography, but a large-scale purification for spectroscopic and elemental analysis was unsuccessful by this method.

Method B. To a stirred solution of **10** (100 mg, 0.13 mmol) in THF (5 mL) was added LiCN (0.5 M in DMF, 268 μl, 0.13 mmol) via syringe in one portion. An off-white precipitate formed immediately, and after 5 min the mixture was filtered through Celite. The volatile components were removed from the filtrate in vacuo. The resulting tan solid was washed with pentane (5−10 mL) to remove residual DMF. The dried residue was redissolved in CH_2Cl_2 (0.5 mL) and filtered through Celite to remove a fine white precipitate. An equal volume of THF was added, and slow diffusion of pentane into this solution provided **22** as large colorless blocks. When crystalline **22** was isolated from the mother liquor, followed by drying at atmospheric pressure under N_2, one of the THF molecules was lost as judged by ^{1}H NMR and elemental analysis (75 mg, 78%): ^{1}H NMR for [CuLi(XDK)(THF)] (300 MHz, CD_2Cl_2, 296 K): δ 7.64 (1H, s), 7.14 (1H, s), 3.69 (4H, t,

J = 6.3 Hz), 2.72 (4H, d, J = 13.2 Hz), 2.08 (2H, d, J = 13.2 Hz), 1.91 (6H, s), 1.87−1.80 (4H, m), 1.45 (2H, d, J = 12.9 Hz), 1.34−1.05 (22H, m); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 296 K) δ 185.1, 177.5, 135.6, 134.7, 133.2, 128.2, 45.7, 45.2, 43.1, 41.7, 32.3, 31.7, 26.5, 26.1, 17.6 ppm; IR (KBr) 2959, 2868, 1736, 1702, 1402, 1376, 1352, 1227, 1184, 1048, 956, 889, 760, 624 cm^{-1}. Anal. Calcd for $C_{36}H_{46}N_2O_9$-CuLi (**22** − 1THF): C, 59.95; H, 6.43; N, 3.88. Found: C, 59.64; H, 7.10; N, 3.43.

Collection and Reduction of X-ray Data. All crystals were mounted on the tips of quartz fibers with Paratone-N (Exxon), cooled to low temperature (∼−85 °C), and placed on a Siemens CCD X-ray diffraction system controlled by a Pentium-based PC running the SMART software package.[32] The general procedures for data collection and reduction follow those reported previously.[33] All structures were solved by use of the direct methods programs SIR-92[34] or XS, part of the TEXSAN[35] and SHELXTL[36] program packages, respectively. Structure refinements were carried out with XL, part of the SHELXTL program package.[36] All remaining non-hydrogen atoms were located and their positions refined by a series of least-squares cycles and Fourier syntheses. Enantiomorph checks were carried out on **17** and **21** by using the Flack parameter refinement[37] in the XL program. Selection of the correct enantiomer for complex **17** was determined to be unreliable, so it was refined as a racemic twin, resulting in lower R and wR_2 values than were obtained when refining with either of the two enantiomers. Selection of the correct enantiomer for **21** was unambiguous. All hydrogen atoms for **6**, **10**, and **21** were located from difference Fourier maps and refined isotropically. For **15**, the four olefinic hydrogen atoms of the coordinated norbornene molecules were located from difference maps and refined isotropically. The remaining hydrogen atoms of **15**, and all the hydrogen atoms for **13**, **14a**, **14b**, **16**, **17**, and **22**, were assigned idealized positions and given a thermal parameter 1.2 times the thermal parameter of the carbon atom to which each was attached. Empirical absorption corrections were calculated and applied for each structure using SADABS, part of the SHELXTL program package.[36]

The structures of **14a**, **14b**, and **16** contain a disordered chlorobenzene molecule. The chlorine atom in each case is disordered across an inversion center positioned on the centroid of the phenyl ring. Each chlorine atom was refined with a site occupancy of 0.5. The other chlorobenzene in **16** contains two carbon atoms with large thermal parameters. The structure of **17** contains two disordered THF molecules in which the oxygen atoms could not be determined reliably, so both were refined at partial occupancy as cyclopentane molecules. The structure of **21** contains a lattice THF molecule disordered over two positions. It was refined as a cyclopentane molecule with two of the carbon atoms at full occupancy, and the occupancy of the other three carbon atoms was distributed over two positions and refined. One of the propyl groups of **21** is disordered. The carbon atom attached to the cyclohexyl ring was refined at full occupancy, and the occupancy of the other two carbon atoms was distributed over two positions and refined.

Important crystallographic information for each complex including refinement residuals is given in Table 1. Final positional, equivalent isotropic thermal, and anisotropic temperature parameters, as well as all bond distances and angles, are provided as CIF files in the Supporting Information in Tables S1−S50.

Results and Discussion

At the inception of this research, very few well-characterized copper(I) carboxylate complexes had been described. The most notable work came from Floriani's lab, which reported the synthesis of carbon monoxide,[38] isonitrile,[39] and alkyne[40] complexes incorporating Cu(I) benzoate. Copper(I) carboxylate complexes without π-acceptor ligands, except for oligomeric homoleptic complexes, are rare owing to disproportionation to Cu metal and Cu(II) products. In addition, accounts of the reactivity toward dioxygen of any well-defined Cu(I) carboxylate derivatives were nonexistent. Our initial goals were therefore to develop a facile synthesis of a discrete dicopper(I) XDK complex and ascertain its kinetic stability, and to understand the chemical properties of this bis(carboxylate)-bridged "platform" by fully elucidating its coordination chemistry with an array of ancillary ligands, ranging from π-acceptor to σ-only donors. From these studies has emerged a detailed picture of the electronic nature of the dicopper(I) XDK platform and a host of complexes for O_2 reactivity studies.

Ligand Synthesis. Exposure of most dicopper(I) and diiron(II) complexes of XDK and PXDK to dioxygen at low temperature produces transiently stable intermediates at best.[11,41] A possible decomposition pathway in these reactions is the intermolecular reaction between an O_2-derived intermediate and one or more $\{M_2(XDK)\}$ units.[25,26] A more sterically demanding XDK derivative might block this pathway by impeding access to the intermediate or transition state. This strategy presumes that the decomposition pathway does not involve complete dissociation of the metal O_2-derived species from XDK, which may occur in some cases. Nevertheless it represents a reasonable starting point, and we were therefore interested to prepare a sterically more hindered XDK analog.

Derivatization of Kemp's triacid has been achieved by alkylation of trimethyl 1,3,5-cyclohexanetricarboxylate with benzyl chloromethyl ether[42] and allyl bromide,[43] both potent electrophiles. A more sterically demanding and robust substituent than the benzyloxy group was sought which would place a bulky group closer to the metal-binding sites and resist oxidative cleavage. Both neopentyl and benzyl functionalities fulfill these requirements, but efforts to alkylate with neopentyl iodide failed owing to its modest electrophilicity. Reaction of trimethyl 1,3,5-trilithio-1,3,5-cyclohexanetricarboxylate with 3 equiv of benzyl bromide under relatively forcing conditions proceeded in good yield, however, affording multigram quantities of trimethyl *cis*,*cis*-1,3,5-tribenzylcyclohexane-1,3,5-tricarboxylate (benzyl Kemp's triester, **3**, Scheme 1). Deprotection of **3** in refluxing KOH followed by acidification with HCl provided *cis*,*cis*-1,3,5-tribenzylcyclohexane-1,3,5-tricarboxylic acid (benzyl Kemp's triacid, **4**). Under identical conditions but in the absence of THF, only intractable decomposition products were obtained. The tripotassium salt of **4** precipitates out of solution when a 1:1 EtOH/THF solvent mixture is used, and this property may protect it from further degradation. The final ether wash also proved crucial for obtaining pure product, for it removed significant quantities of partially deprotected **3** and other decomposition products. The triacid is soluble in neat DMSO or DMSO solvent mixtures. Synthesis of *cis*,*cis*-1,3,5-tribenzylcyclohexane-1,3,5-tricarboxylic 1,3-anhydride 5-acid chloride (tribenzyl Kemp's anhydride acid chloride, **5**) proceeded by standard procedures[31] in quantitative yield.

Condensation of **5** with 0.5 equiv of 1,3-dimethyl-4,6-diaminobenzene followed by recrystallization from MeOH

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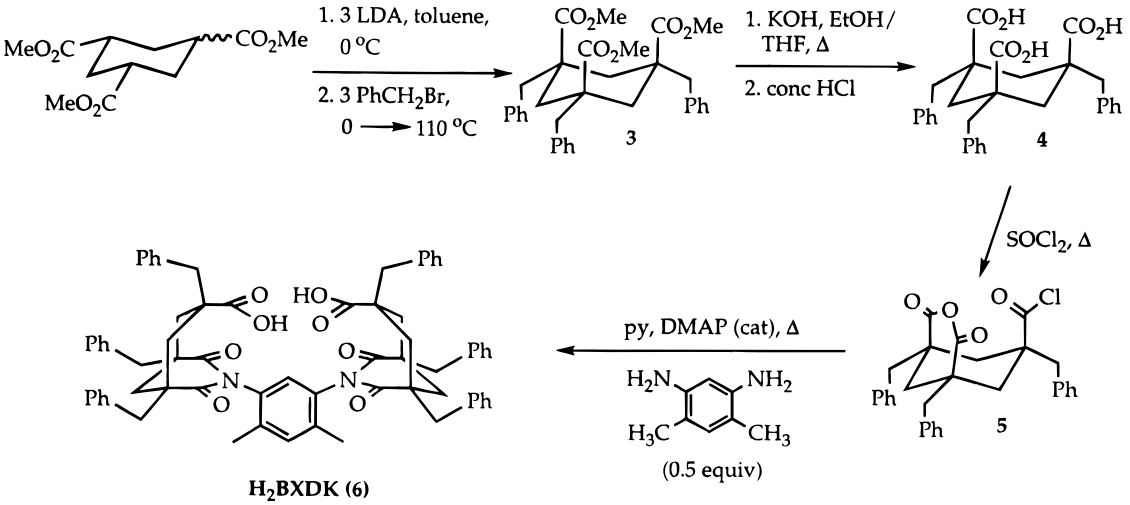
Table 1. Summary of X-ray Crystallographic Data

	H_2BXDK (**6**)	**10**·CH_3CN	**13**·PhCl	**14a**·0.5PhCl	**14b**·0.5PhCl·Et_2O
formula	$C_{62}H_{64}N_2O_8$	$C_{36}H_{44}N_4O_8Cu_2$	$C_{74}H_{73}N_2O_8ClP_2Cu_2$	$C_{62}H_{67.5}N_5O_8Cl_{0.5}Cu_2$	$C_{66}H_{77.5}N_5O_9Cl_{0.5}Cu_2$
fw	965.15	787.83	1342.81	1155.51	1229.64
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/n$
a, Å	11.91550(10)	13.6100(2)	41.7699(6)	11.8747(2)	22.5777(3)
b, Å	28.7491(4)	16.1248(3)	20.07040(10)	13.8800(2)	12.3144(2)
c, Å	17.2033(2)	17.69810(10)	16.2744(2)	18.50390(10)	23.6382(4)
α, deg				97.5001(9)	
β, deg	108.4970(10)	112.2098(7)	102.9530(10)	90.9158(10)	109.96(1)
γ, deg				106.1093(8)	
V, Å^3	5588.72(11)	3595.83(9)	13296.3(3)	2900.64(7)	6190.8(2)
Z	4	4	8	2	4
ρ_{calcd}, g/cm^3	1.147	1.455	1.342	1.323	1.319
T, °C	−85	−85	−85	−85	−85
μ(Mo Kα), mm^{-1}	0.075	1.239	0.785	0.814	0.769
transm coeff	0.854−1.000	0.828−1.000	0.831−1.000	0.857−1.000	0.852−1.000
2θ limits, deg	3−57	3−46	3−57	3−57	3−57
total no. of data	33729	13960	39721	17531	35986
no. of unique data	12738	5089	15154	12211	14149
obsd data[a]	9442	4355	10375	8121	8708
no. of params	959	627	797	703	728
R (%)[b]	5.15	3.41	5.67	4.97	8.00
wR_2 (%)[c]	11.26	7.59	15.25	11.26	21.65
max, min peaks, e/Å^3	0.302, −0.227	0.730, −0.633	1.039, −1.138	0.494, −0.463	1.240, −1.037

	15·Et_2O	**16**·1.5PhCl	**17**·2THF	**21**·0.5CH_3CN	**22**·THF
formula	$C_{50}H_{68}N_2O_9Cu_2$	$C_{73}H_{83.5}N_4O_{16}Cl_{1.5}Cu_4$	$C_{46}H_{70}N_4O_{10}Cu_2$	$C_{53}H_{83.5}N_{3.5}O_8Cu_1$	$C_{44}H_{62}N_2O_{11}Li_1Cu_1$
fw	968.14	1580.27	966.14	961.27	865.44
space group	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P2_1$	$P\bar{1}$
a, Å	12.4880(7)	13.7573(6)	21.3272(4)	10.6886(2)	11.75850(10)
b, Å	13.0087(8)	16.5180(7)	18.0465(3)	16.3952(3)	12.11510(10)
c, Å	15.0250(9)	17.8154(7)	12.4138(2)	30.5770(1)	16.73070(10)
α, deg	93.8052(8)	67.6240(10)			102.1888(2)
β, deg	94.5239(11)	70.5980(10)		96.12(1)	96.4520(6)
γ, deg	98.6628(10)	89.0870(10)			108.5870(2)
V, Å^3	2397.9(2)	3502.5(3)	4777.84(14)	5327.87(14)	2166.22(3)
Z	2	2	4	4	2
ρ_{calcd}, g/cm^3	1.341	1.498	1.343	1.198	1.327
T, °C	−85	−85	−85	−85	−85
μ(Mo Kα), mm^{-1}	0.943	1.326	0.949	0.463	0.565
transm coeff	0.736−1.000	0.795−1.000	0.845−1.000	0.856−1.000	0.900−1.000
2θ limits, deg	3−46	3−57	3−57	3−57	3−57
total no. of data	9589	21334	28775	33173	13402
no. of unique data	6570	14903	9880	22720	9309
obsd data[a]	5445	9646	8203	16140	7405
no. of params	584	862	512	1179	736
R (%)[b]	3.78	6.14	5.01	5.21	5.37
wR_2 (%)[c]	9.58	14.92	12.87	13.99	14.18
max, min peaks, e/Å^3	0.474, −0.378	0.960, −1.016	0.834, −0.399	0.482, −0.331	1.150, −0.573

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR^2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Scheme 1



provided benzyl xylylenediamine Kemp's triacid (H_2BXDK, **6**) in moderate yield and high purity as judged by the ^{1}H NMR spectrum of the bulk product. This spectrum also revealed that the benzyl Kemp's cyclohexyl fragments were in equivalent

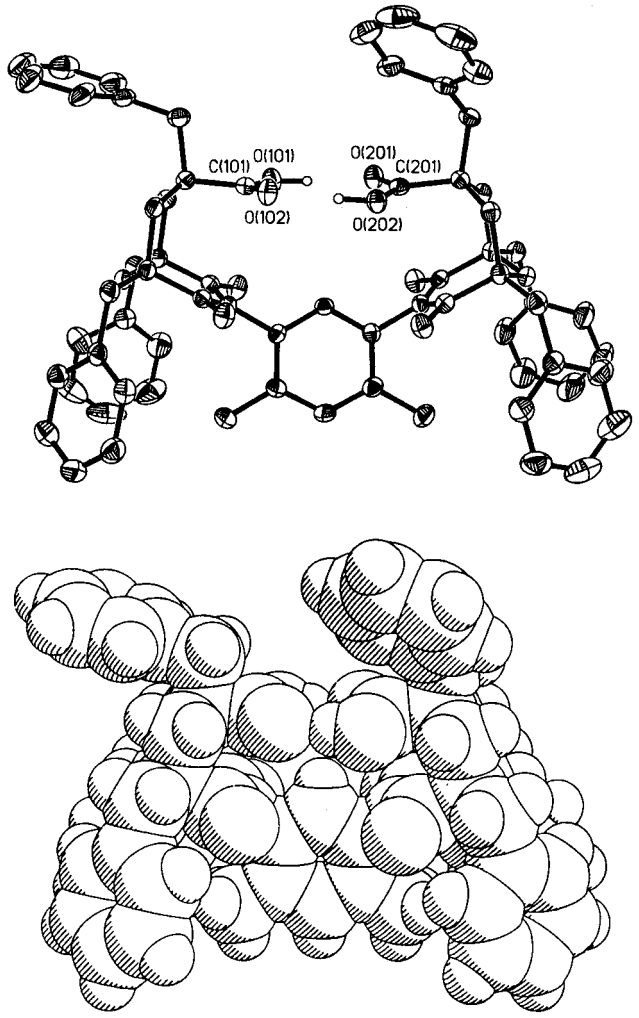


Figure 1. ORTEP (50% thermal ellipsoids) and space-filling diagrams of H_2BXDK (**6**).

magnetic environments, supporting the assignment of C_{2v} symmetry for the product and confirming that the desired U-shaped isomer had been obtained. An X-ray structural determination of **6** confirmed this assignment (Figure 1). The space-filling representation reveals that the peripheral benzyl groups shroud the bis(carboxylate) oxygen plane and the metal-binding sites from above, although rotation toward the outside of the molecule in solution appears facile. This flexibility would preclude steric protection from the sides of a BXDK complex. Nevertheless the benzyl groups are still forced to point up owing to the geometric constraints of the quaternary cyclohexyl carbon atoms, and this property should provide added steric protection at the carboxylate binding sites compared to XDK and PXDK.

Preparation and Reactivity of Dicopper(I) Bis(carboxylate)-Bridged Complexes: Synthesis of [Tl_2L], L = XDK (7), PXDK (8), and BXDK (9); and [Cu_2L(MeCN)], L = XDK (10), PXDK (11), and BXDK (12). Convenient, high-yield procedures were desired for the bis(carboxylate) dicopper(I) starting materials. Other Cu(I) carboxylates have been prepared from their Tl(I) salts and a copper halide,[44] so this approach was adopted (eq 1). Treatment of **1**, **2**, or **6** with 2 equiv of

$$\underset{\text{L = XDK, PXDK, BXDK}}{H_2L + 2TlOEt} \xrightarrow[-2EtOH]{THF,\ rt,\ N_2} [Tl_2(XDK)]\ (\mathbf{7}),\ [Tl_2(PXDK)]\ (\mathbf{8}),\ [Tl_2(BXDK)]\ (\mathbf{9}) \quad (1)$$

TlOEt afforded **7**−**9**, respectively, as white powders in quantitative yields. The ^{1}H NMR spectra of each dithallium(I) complex

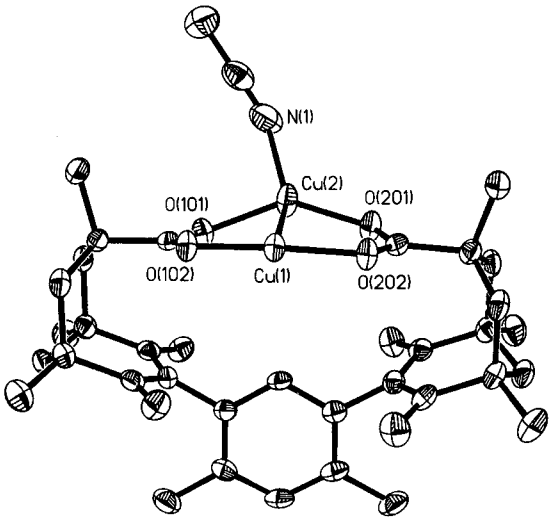


Figure 2. ORTEP diagram of [Cu_2(XDK)(MeCN)] (**10**) with 50% thermal ellipsoids.

showed one set of cleanly shifted resonances and the disappearance of the broad singlet due to the carboxylic acid protons. Complex **7** is only slightly soluble in THF and CH_2Cl_2, whereas **8** and **9** are readily soluble.

Treatment of **7**, **8**, or **9** with excess CuBr(DMS) in CH_2Cl_2/MeCN provided **10**−**12**, respectively, as crude off-white powders in 90% yield (eq 2). The ^{1}H NMR spectrum of each

$$\underset{\text{L = XDK, PXDK, BXDK}}{[Tl_2L]} \xrightarrow[\substack{CH_2Cl_2/MeCN\\ rt,\ N_2\\ -2TlBr}]{\text{excess CuBr(DMS)}} [Cu_2(XDK)(MeCN)]\ (\mathbf{10}),\ [Cu_2(PXDK)(MeCN)]\ (\mathbf{11}),\ [Cu_2(BXDK)(MeCN)]\ (\mathbf{12}) \quad (2)$$

product exhibited a single shifted set of dicarboxylate and MeCN ligand resonances in a 1:1 ratio. A xylene spacer aromatic proton experiences a significant downfield shift, presumably the one ortho to both imide nitrogen atoms, which is in close proximity to the metal-binding sites. Recrystallization from CH_2Cl_2/MeCN/Et_2O afforded colorless blocks or needles. Spectroscopic and analytical data confirm the purity of each complex. Complexes **10**−**12** are all nonelectrolytes in CH_2Cl_2 solution, supporting that the metal ions are strongly coordinated by the carboxylate groups in solution. An X-ray structural determination of **10** confirmed that both Tl ions were displaced in eq 2 to form a dinuclear copper(I) carboxylate-bridged complex. As illustrated in Figure 2, one copper atom is ligated by an acetonitrile and two carboxylate oxygen atoms in a trigonal planar geometry, and the other is coordinated in a nearly linear, two-coordinate fashion to the other two carboxylate oxygen atoms. A linear two-coordinate geometry is not uncommon for Cu(I),[45] which appears to have the ideal ionic radius to be "skewered" by the two rigidly positioned XDK oxygen atoms. The relatively short Cu···Cu distance of 2.6287(5) Å signifies weak metal−metal bonding, a formulation which is supported by molecular orbital calculations on a tetrameric Cu(I) trimethylsilyl complex with similar copper−copper distances.[46]

Reactivity of the Dicopper(I) Acetonitrile Complexes. The reactivity of **10**−**12** with a spectrum of reagents, weak σ donors

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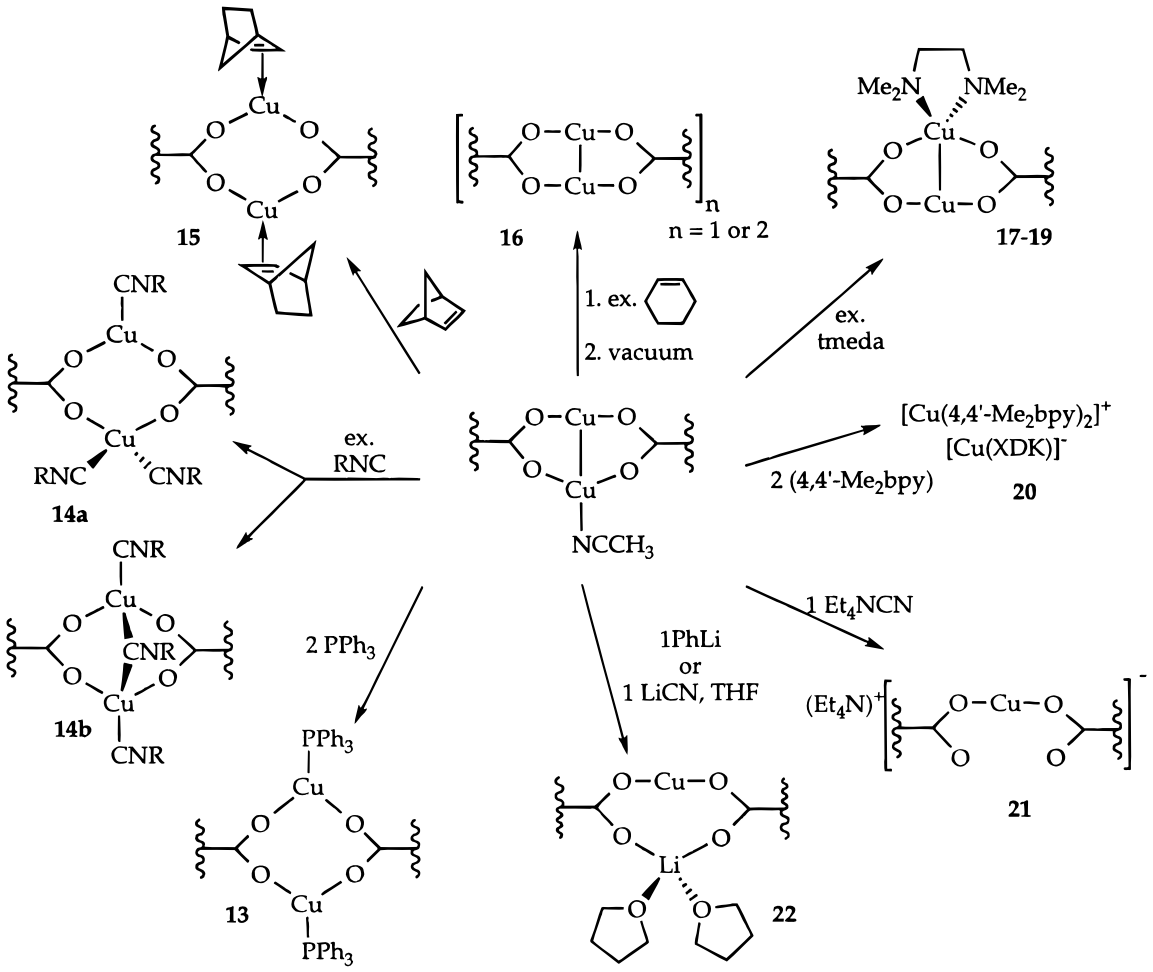
(45) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5, pp 533−774.
(46) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187−2189.

Scheme 2



(π acceptors), basic neutral σ donors, and anionic donors was investigated, and the results are summarized in Scheme 2. ORTEP diagrams of the structurally characterized products are shown in Figures 3 and 4, and selected bond distances and angles are reported in Table 2. The coordination chemistry proved to be essentially identical for all three diacids, so only that for XDK will be described in detail.

Neutral Donor Adducts: Preparation of $[Cu_2(XDK)(PPh_3)_2]$ (13), $[Cu_2(XDK)(2,6\text{-}Me_2C_6H_3NC)_3]$ (14a), $[Cu_2(XDK)(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)(2,6\text{-}Me_2C_6H_3NC)_2]$ (14b), $[Cu_2(XDK)(NB)_2]$ (15), $[Cu_2(XDK)]$ (16), $[Cu_2(XDK)(tmeda)]$ (17), $[Cu_2(PXDK)(tmeda)]$ (18), $[Cu_2(BXDK)(tmeda)]$ (19), and $[Cu(4,4'\text{-}Me_2bpy)_2][Cu(XDK)]$ (20). All of these complexes were prepared by allowing **10** or **11** to react with 2−4 equiv or an excess of the appropriate ancillary ligand, followed by washing with pentane or Et_2O to remove residual free ligand. All were recrystallized to afford analytically pure material.

Treatment of **10** with 2 equiv of triphenylphosphine followed by recrystallization afforded bis(phosphine) adduct **13** as colorless blocks. Conductivity measurements revealed **13** to be a nonelectrolyte in CH_2Cl_2 solution. The ^1H NMR spectrum exhibited one set of XDK resonances and a complicated set of triphenylphosphine resonances in a 2:1 ratio. The proton-decoupled ^{13}C NMR spectrum showed single sets of XDK and triphenylphosphine resonances, and phosphorus coupling to three of the four phenyl ring proton resonances, as is found in free triphenylphosphine in CD_2Cl_2. The ^{31}P NMR spectrum showed one broad singlet at room temperature, shifted slightly downfield from that of free triphenylphosphine (δ 5.1 ppm, $\Delta\nu_{1/2} = 24.7$ Hz, CD_2Cl_2). X-ray structural analysis revealed solid **13** to be composed two inequivalent trigonal planar copper atoms, with one copper displaced laterally from the four-oxygen carboxylate plane and the other lying above the plane (Figure 3). The copper−phosphorus bond lengths are normal for Cu(I) triphenylphosphine complexes having one phosphine ligand per copper atom.[47] Simple Cu(I) carboxylate−triphenylphosphine complexes have been prepared and structurally characterized previously, with $[Cu(OAc)(PPh_3)_2]$ being a representative example.[48] This mononuclear complex consists of a tetrahedrally coordinated copper atom with a chelating acetate and two triphenylphosphine ligands. The dissimilar reactivity of **10** is probably due to steric effects and the convergent nature of the XDK carboxylate ligands.

Exposure of **10** to excess 2,6-dimethylphenyl isocyanide followed by recrystallization provided the tris(isonitrile) adduct **14**. The ^1H NMR spectrum exhibited single sets of cleanly shifted XDK and isonitrile resonances in the expected ratios. The IR spectrum showed one broad isonitrile C≡N stretch at 2134 cm^{-1}. The complex is a nonelectrolyte in CH_2Cl_2 solution. X-ray structural analysis on two different crystals, obtained under identical crystallization conditions, revealed that the tris(isonitrile) complex can exist as two isomers (Figure 3). In all-terminal colorless **14a**, one copper is trigonal and the other tetrahedral, essentially as found in a bis(carboxylate) tris(isonitrile) complex prepared from Cu(I) benzoate and *p*-tolyl isocyanide.[39] The other isomer, yellow **14b**, has the isonitrile

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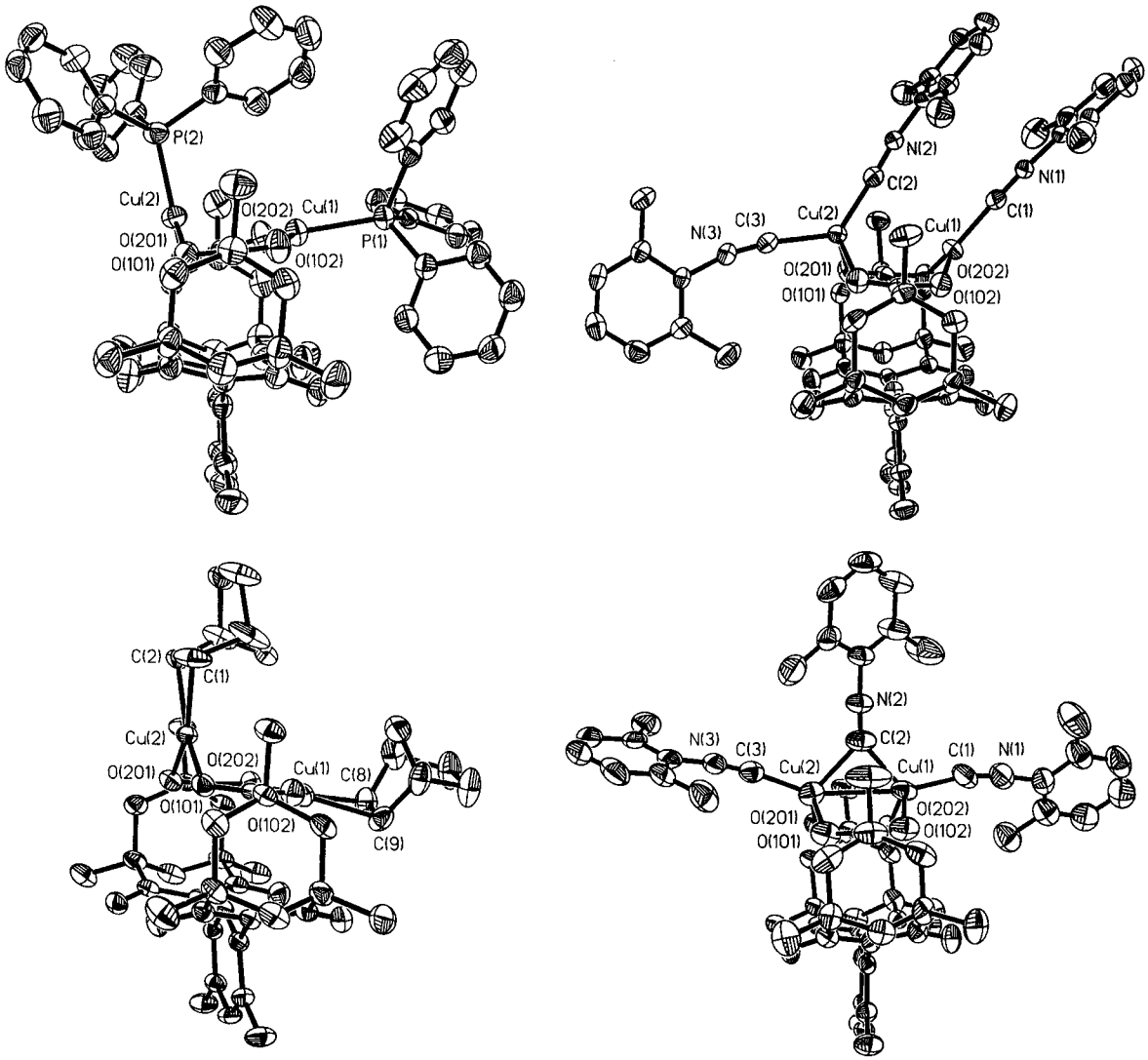

Figure 3. ORTEP diagrams with 50% thermal ellipsoids for (clockwise from top left) $[Cu_2(XDK)(PPh_3)_2]$ (**13**), $[Cu_2(XDK)(2,6\text{-}Me_2C_6H_3NC)_3]$ (**14a**), $[Cu_2(XDK)(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)(2,6\text{-}Me_2C_6H_3NC)_2]$ (**14b**), and $[Cu_2(XDK)(NB)_2]$ (**15**).

ligands coordinated in a symmetrical fashion, with one bridging the two copper atoms and one terminal on each. The bridging isonitrile in **14b** enforces a relatively close Cu···Cu distance of 2.7278(9) Å compared to the value of 3.2560(5) Å for **14a**. A bridging isonitrile derivative similar to **14b** has not been reported for other Cu(I) carboxylates. The isomers appear to be in rapid equilibrium in solution at room temperature since only one set of ^{1}H NMR resonances is observed for the XDK and isonitrile ligands.

Treatment of **10** with excess norbornene followed by recrystallization provided bis(norbornene) adduct **15** as colorless blocks. The X-ray structure was analogous to that determined for bis(triphenylphosphine) adduct **13**, with each trigonal planar copper atom ligated to XDK in a different fashion (Figure 3). Both norbornene ligands are coordinated via the exo face, as has been observed in other Cu(I) norbornene adducts, with characteristic Cu(I)−olefin bond distances.[49] When crystals of **15** are allowed to dry fully under an atmosphere of N_2 at room temperature, one of the norbornene ligands is lost, as judged by ^{1}H NMR spectroscopy and elemental analysis. This complex does not lose the remaining norbornene ligand when exposed to high vacuum. It is probably composed of trigonal planar and linear two-coordinate copper atoms, although an X-ray structure has not been obtained.

Treatment of **10** with excess cyclohexene, followed by evaporation of the volatile components under high vacuum, provided the desolvated parent complex **16**. The ^{1}H and ^{13}C NMR and IR spectra showed no cyclohexene or acetonitrile peaks, and the product is a nonelectrolyte in CH_2Cl_2 solution. X-ray quality crystals of **16** were grown from either CH_2Cl_2/pentane or PhCl/pentane. A low-resolution structure was obtained on crystals grown from CH_2Cl_2/pentane. (X-ray data for **16** from CH_2Cl_2/pentane: $P2_1/n$, $a = 14.0015(3)$ Å, $b = 12.8639(2)$ Å, $c = 22.3936(3)$ Å, $\beta = 106.621(1)°$, $V = 3832.8(1)$ Å^3, $Z = 4$, $T = 188$ K, $R = 0.121$, w$R_2 = 0.355$. This structure was not fully refined due to major disorder of the two lattice CH_2Cl_2 molecules.) This homoleptic dinuclear complex consists of two nearly linear two-coordinate copper ions with no intermolecular bonding to any neighboring $Cu_2(XDK)$ (Scheme 2, $n = 1$). Structural analysis of the crystals grown from PhCl/pentane showed that two $\{Cu_2(XDK)\}$ units in this isomer are linked by a bond between an XDK imide carbonyl oxygen and a neighboring copper atom (Cu2−O504, Figure 4). One of the $\{Cu_2(XDK)\}$ units consists of two linearly coordinated copper atoms with a Cu3···Cu4 distance of 2.6106(9) Å. Each copper atom is pulled laterally out of the four-oxygen carboxylate plane. The other $Cu_2(XDK)$ unit contains two- and three-coordinate copper atoms, with a slightly shorter Cu1···Cu2 distance of 2.5697(8) Å. Instead of being displaced in a lateral direction from the four-oxygen plane, the two-coordinate Cu1

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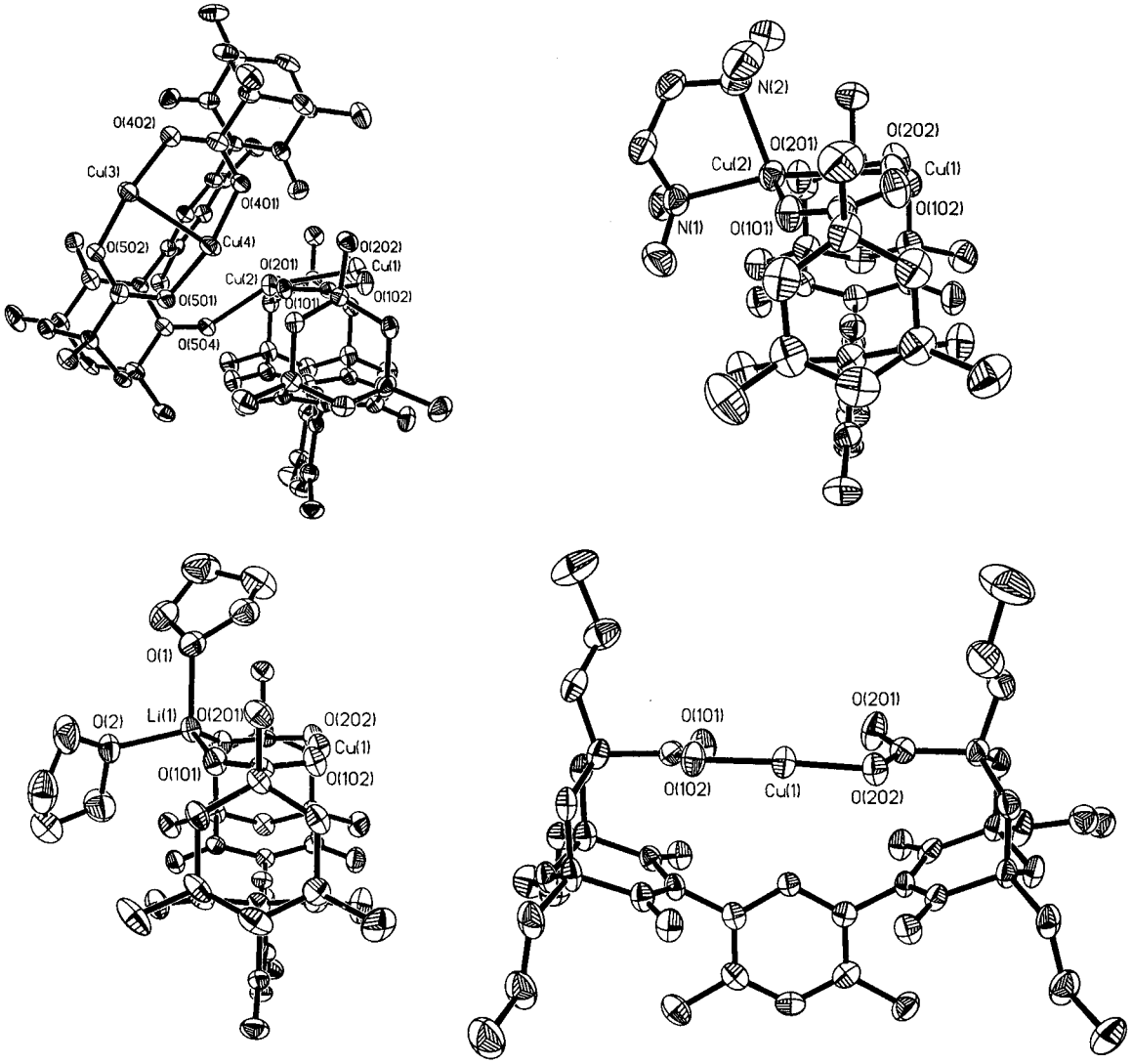

Figure 4. ORTEP diagrams with 50% thermal ellipsoids for (clockwise from top left) $[Cu_2(XDK)]_2$ (**16**), $[Cu_2(XDK)(tmeda)]$ (**17**), $(Et_4N)[Cu(PXDK)]$ (**21**), and $[CuLi(XDK)(THF)_2]$ (**22**).

atom lies slightly above the plane, thus accounting for the slightly shorter Cu···Cu distance in this $\{Cu_2(XDK)\}$ unit. These structures may be contrasted to those of polymeric Cu(I) acetate and tetrameric Cu(I) benzoate,[50] where oligomerization via the bridging carboxylate oxygen atoms occurs, presumably because of the greater conformational flexibility of these ligands. Apparently the convergent nature of the XDK ligand coupled with the chelate effect causes the carboxylate ligands to bind the copper ions more tightly compared to simple Cu(I) carboxylates, thus inhibiting oligomerization.

Exposure of **10** to CO in THF or CH_2Cl_2 solution followed by solvent removal afforded no product, as judged by IR and NMR spectroscopy. These results are in contrast to the stable CO adducts obtained with Cu(I) benzoate and other simple carboxylates.[38,44] Carbon monoxide is a very poor σ donor, and the Cu(I) ions in the $\{Cu_2(XDK\}$ platform must also be unable to engage in π back-bonding with this ligand. Both factors preclude stable adduct formation.

Reaction of **10**, **11**, or **12** with excess tmeda followed by recrystallization from THF/pentane provided mono(tmeda) adducts **17**−**19** as colorless blocks or needles. These reactions do not occur for Cu(I) acetate or benzoate, which upon exposure to excess tmeda under identical conditions immediately disproportionates to Cu metal and uncharacterized Cu(II) products. An X-ray structure was obtained for **17**. This complex is composed of one linear two-coordinate copper, analogous to that observed for acetonitrile complex **10**, and a tetrahedrally ligated copper with a chelating tmeda molecule. The Cu···Cu distances in **10** and **17** are also nearly identical.

Because tmeda adducts **17**−**19** react with dioxygen at low temperature to afford stable peroxo intermediates in some cases,[41] detailed knowledge of their solution properties was desired. Of particular interest was to determine whether the Cu(I) ions remained coordinated to the XDK ligand in solution, and whether the tmeda ligand exhibited fluxional behavior. All of the tmeda adducts are nonelectrolytes in CH_2Cl_2 solution, even in the presence of a 20-fold excess of tmeda, confirming that the Cu(I) ions remain coordinated to the carboxylates in solution. The ^{1}H NMR spectrum of each of the tmeda adducts exhibits a single set of XDK resonances, suggesting that the approximate C_s symmetry of the solid state structure of **17** may not be maintained in solution. If it were, the pair of four-proton doublets assigned to the XDK methylene groups (H_{ax} and H_{eq}, see Introduction) might split into four, two-proton doublets. This phenomenon has been observed for other asymmetrically ligated M_2XDK and heterodimetallic MM′(XDK) complexes, when one of the mirror planes of the C_{2v}-symmetric XDK ligand is lost.[41] The pseudo-C_{2v}-symmetric spectral pattern observed for **17** suggests that the tmeda ligand exchanges between the two

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Table 2. Selected Bond Distances and Angles[a]

	distances (Å)		angles (deg)	
6	O101−C101	1.311(2)	O102−C101−O101	123.2(2)
	O102−C101	1.222(2)	O201−C201−O202	123.09(14)
	O201−C201	1.224(2)		
	O202−C201	1.308(2)		
	O101···O201	2.651(2)		
	O102···O202	2.678(2)		
10	Cu1···Cu2	2.6287(5)	O102−Cu1−O202	172.00(8)
	Cu1−O102	1.857(2)	O101−Cu2−O201	141.37(9)
	Cu1−O202	1.880(2)	O101−Cu2−N1	94.45(11)
	Cu2−O101	2.002(2)	O201−Cu2−N1	123.93(11)
	Cu2−O201	1.919(2)		
	Cu2−N1	1.989(3)		
13	Cu1···Cu2	3.1171(6)	O102−Cu1−O202	138.07(10)
	Cu1−O102	1.963(2)	O101−Cu2−O201	116.93(10)
	Cu1−O202	1.957(2)	O102−Cu1−P1	107.65(8)
	Cu2−O101	1.977(2)	O202−Cu1−P1	113.79(7)
	Cu2−O201	1.998(2)	O101−Cu2−P2	122.21(7)
	Cu1−P1	2.2427(9)	O201−Cu2−P2	120.81(7)
	Cu2−P2	2.1652(9)		
14a	Cu1···Cu2	3.2560(5)	O102−Cu1−O202	117.80(10)
	Cu1−O102	1.972(2)	O101−Cu2−O201	107.41(10)
	Cu1−O202	1.981(2)	O102−Cu1−C1	119.77(12)
	Cu2−O101	2.069(2)	O202−Cu1−C1	121.82(12)
	Cu2−O201	2.084(2)	O101−Cu2−C2	110.96(12)
	Cu1−C1	1.842(3)	O201−Cu2−C2	111.09(12)
	Cu2−C2	1.877(3)	O101−Cu2−C3	98.83(11)
	Cu2−C3	1.930(3)	O201−Cu2−C3	97.12(11)
	C1−N1	1.157(4)	C1−N1−C4	176.1(3)
	C2−N2	1.158(4)	C2−N2−C12	172.9(3)
	C3−N3	1.156(4)	C3−N3−C20	168.0(3)
14b	Cu1···Cu2	2.7278(9)	O102−Cu1−O202	114.05(13)
	Cu1−O102	2.059(3)	O101−Cu2−O201	117.56(13)
	Cu1−O202	2.035(3)	O102−Cu1−C1	109.1(2)
	Cu2−O101	2.071(3)	O102−Cu1−C2	99.3(2)
	Cu2−O201	2.022(3)	O101−Cu2−C2	99.1(2)
	Cu1−C1	1.921(7)	O101−Cu2−C3	98.8(2)
	Cu1−C2	2.001(6)	C1−N1−C4	173.1(6)
	Cu2−C2	2.135(5)	C2−N2−C12	175.3(5)
	Cu2−C3	1.908(6)	C3−N3−C20	172.0(5)
15	Cu1···Cu2	3.4211(6)	O102−Cu1−O202	126.86(10)
	Cu1−O102	1.965(2)	O101−Cu2−O201	105.17(9)
	Cu1−O202	1.963(2)	O102−Cu1−C8	133.95(13)
	Cu2−O101	1.978(2)	O102−Cu1−C9	96.70(13)
	Cu2−O201	1.981(2)	O101−Cu2−C1	108.2(2)
	Cu1−C8	2.070(4)	O101−Cu2−C2	146.6(2)
	Cu1−C9	2.076(4)		
	Cu2−C1	2.023(4)		
	Cu2−C2	2.033(3)		
16	Cu1···Cu2	2.5697(8)	O102−Cu1−O202	168.9(2)
	Cu3···Cu4	2.6106(9)	O101−Cu2−O201	160.85(12)
	Cu1−O102	1.855(3)	O101−Cu2−O504	94.65(11)
	Cu1−O202	1.859(3)	O201−Cu2−O504	98.50(12)
	Cu2−O101	1.970(3)	O402−Cu3−O502	170.87(14)
	Cu2−O201	1.942(3)	O401−Cu4−O501	165.8(2)
	Cu2−O504	2.191(3)		
	Cu3−O402	1.873(3)		
	Cu3−O502	1.871(3)		
	Cu4−O401	1.875(3)		
	Cu4−O501	1.869(3)		
17	Cu1···Cu2	2.6245(7)	O102−Cu1−O202	175.4(2)
	Cu1−O102	1.857(3)	O101−Cu2−O201	143.36(11)
	Cu1−O202	1.859(3)	O101−Cu2−N1	99.50(13)
	Cu2−O101	2.014(3)	O101−Cu2−N2	105.32(13)
	Cu2−O201	1.999(3)	O201−Cu2−N1	101.63(13)
	Cu2−N1	2.165(3)	O201−Cu2−N2	106.25(14)
	Cu2−N2	2.201(4)		
21	Cu1−O102	1.850(3)	O102−Cu1−O202	176.70(14)
	Cu1−O202	1.848(3)		
22	Cu1···Li1	3.023(4)	O102−Cu1−O202	171.63(8)
	Cu1−O102	1.855(2)	O101−Li1−O201	128.3(3)
	Cu1−O202	1.862(2)	O101−Li1−O1	106.0(2)
	Li1−O101	1.901(5)	O101−Li1−O2	107.0(2)
	Li1−O201	1.908(5)	O201−Li1−O1	104.5(2)
	Li−O1	1.986(5)	O201−Li1−O2	103.9(2)
	Li1−O2	1.971(5)		

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figures 1−4.

copper sites in Cu_2(XDK) by an intra- and/or intermolecular fashion, resulting in one set of averaged H_{ax} and H_{eq} resonances.

Additional ^{1}H NMR experiments were carried out to help elucidate the nature of this exchange process. The ^{1}H NMR spectrum of recrystallized **17** in the presence of an additional 1 equiv of tmeda still displayed a single set of tmeda and XDK resonances, slightly shifted from those in **17**, suggesting that free and coordinated tmeda exchange rapidly on the ^{1}H NMR time scale. To determine whether the tmeda ligand in **17** could be exchanging intermolecularly between different {Cu_2(XDK)} units, a ^{1}H NMR spectrum of an equimolar mixture of **17** and parent complex **16** was recorded at room temperature. The spectrum exhibited one set of XDK and tmeda resonances, and the chemical shifts of the XDK resonances were the average of those observed for pure **16** and **17**. A variable temperature (VT) ^{1}H NMR spectroscopic study was carried out on pure **17**. As the temperature was decreased, the two sharp tmeda singlets (methyl and methylene protons) broadened and overlapped one another. The tmeda resonances appeared to coalesce between −70 and −80 °C. Below this temperature one broad singlet was observed for the tmeda methyl groups, and the tmeda methylene resonances appeared to be split into two broad singlets in an approximately 3:1 ratio. One sharp set of XDK resonances was observed down to −85 °C, accompanied by small changes in their chemical shifts. A more detailed interpretation of the VT data was hampered by overlap of the tmeda resonances with each other and with the XDK resonances. Although no detailed mechanistic information could be gleaned from the VT experiments, the broadening and shifting of the tmeda resonances with decreasing temperature does support the occurrence of some fluxional tmeda exchange process(es), perhaps involving copper−nitrogen bond breaking and/or different conformations of the five-membered tmeda chelate ring. Taken together, these additional ^{1}H NMR experiments support the conclusion that the tmeda ligands in complexes **17**−**19** are exchanging rapidly between copper sites, but do not reveal the mechanism.

Treatment of **10** with 2 equiv of 4,4′-dimethylbipyridine afforded **20** as a dark brick-red solid. This color is characteristic of the $[Cu(bpy)_2]^+$ cation[51] and immediately suggested that one of the copper ions had been extracted from the bis(carboxylate) platform. Neutral and ionic species may be in equilibrium, as indicated by eq 3. A similar equilibrium was suggested to

$$[Cu_2(XDK)(4,4'\text{-}Me_2bpy)_2] \rightleftharpoons [Cu(4,4'\text{-}Me_2bpy)_2][Cu(XDK)] \quad (3)$$

explain the solution behavior of $[Cu(phen)_2][Cu(OAc)_2]$, specifically based on its crystal structure and solution conductivity properties.[51,52] Determination of the molar conductivity from a plot of the measured conductivity versus concentration for complex **20** in CH_2Cl_2 solution (Figure S11, Supporting Information) gave approximately the same value as those obtained for Bu_4NPF_6 and $[Cu(MeCN)_4]ClO_4$, consistent with the equilibrium in eq 3 lying completely to the right. Suitable crystals of **20** could not be obtained for X-ray crystallography. On the basis of the similarity of its UV−vis spectral features to those of $[Cu(phen)_2][Cu(OAc)_2]$ and its conductivity properties, **20** is probably composed of a bis(dipyridyl) cation and a linear two-coordinate $[Cu(XDK)]^-$ anion.

Anionic Donors: Preparation of (Et_4N)[Cu(PXDK)] (21) and [CuLi(XDK)$(THF)_2$] (22). We wished to prepare a class

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(52) Darensbourg, D. J.; Longridge, E. M.; Atnip, E. V.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 3951−3955.

of anionic-bridged dicopper(I) XDK complexes in order to explore further the chemistry of this system. Attempts to synthesize thiolate- or cyanide-bridged {Cu_2(XDK)} complexes from Et_4N(SR) (R = Ph, Me) and Et_4N(CN), respectively, were unsuccessful. The former reagents invariably yielded copper(I) sulfide and intractable XDK-containing products. Reaction of acetonitrile adduct **11** with tetraethylammonium cyanide in CH_2Cl_2 immediately resulted in precipitation of Cu(I) cyanide and formation of **21**, as judged by IR and ^{1}H NMR spectroscopic analyses. The solid state structure of **21** is composed of two crystallographically independent clusters which differ only in the orientation of the peripheral propyl groups. Each contains linear two-coordinate copper ligated by *cis*-carboxylate oxygen atoms. This mononuclear complex is unreactive toward additional cyanide, attesting to the effectiveness of the XDK ligand for retaining the remaining copper atom in the "skewered" two-coordinate arrangement.

Alkyl- and aryl-bridged cuprate complexes of XDK were sought for studies of conjugate addition and other R^- transfer reactions. The only structurally characterized Cu(I) carboxylate−alkyl or −aryl complex reported to date is [Cu_3(μ-Mes)(μ-O_2CPh)$_2$], a neutral trinuclear cluster isolated upon exposure of Cu(I) benzoate to pentameric mesitylcopper(I).[53] No well-characterized Cu(I) carboxylate alkyl- or aryl-cuprates have been described. Treatment of **10** with 1 equiv of PhLi in THF afforded heterodimetallic complex **22** as the only XDK-containing product isolated, even when a large excess of 12-crown-4 was added. Much difficulty was experienced in trying to purify **22** from the phenylcopper(I) coproduct and large amounts of an intractable brown material. As in the preparation of mononuclear **21**, this complex was obtained more conveniently from **10** and lithium cyanide. The solid state structure consists of a linear two-coordinate copper atom and a tetrahedrally ligated lithium atom bridged by XDK. Crystals of **22** lose one of the coordinated THF molecules upon isolation and drying, as judged by integration of the ^{1}H NMR spectrum and elemental analysis, presumably to afford [CuLi(XDK)(THF)]. The solid state structure is unknown, but by analogy to other heterodimetallic alkali metal XDK complexes,[54] the lithium ion is probably coordinated to one or more of the XDK imide carbonyl oxygens. Compounds **21** and **22** provided the ideal kinetic stability for the preparation of a host of Cu(I)/Cu(II) mixed-valent and Cu^IM^{II} heterodimetallic bis(carboxylate)-bridged complexes, which are the subject of a separate report.[30]

Conclusions

A more sterically demanding version of XDK and PXDK has been prepared in multigram quantities and high purity. The kinetic stability imparted by the convergent nature of the XDK ligand system provides an excellent template for the synthesis of discrete dinuclear Cu(I) complexes. All three XDK derivatives afford complexes, some heretofore unknown for Cu(I) carboxylates, of π acceptor and σ donor ligands. Disproportionation reactions which occur with the simple Cu(I) carboxylates are not observed with XDK. Attempts to prepare anionic-bridged Cu_2(XDK) complexes resulted instead in extrusion of one Cu(I) ion and formation of monocopper(I) XDK products.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Supporting Information Available: Figures S1−S10, displaying fully labeled ORTEP diagrams for each reported structure, and Figure S11, displaying conductivity plots for **20**, Bu_4NPF_6, and [$Cu(MeCN)_4$]-ClO_4 (11 pages). X-ray crystallographic files, in CIF format, for complexes **6**, **10**, **13**, **14a**,**b**, **15**−**17**, **21**, and **22** are available on the Internet only. Ordering and access information is given on any current masthead page.

IC970302A

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